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KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
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PROCEEDINGS OF THE MEETINGS  
of Saturday May 31 and June 28, 1913.  
VOL XVI.

*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

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**Physiology:** -- "*Investigations into the internal secretion of the pancreas*". By N. WATERMAN M. D. (Communicated by Prof. C. A. PEKELHARING).

(Communicated in the meeting of February 22, 1913).

In the following paper we shall attempt to summarize some series of experiments in connection with the internal secretion of the pancreas, which, though highly probable, is still a matter of conjecture.

1<sup>st</sup> Series (A).

Upon evidence with which we need not here concern ourselves, it has been concluded that the pancreas subserves the carbohydrate metabolism through some product of internal secretion. This being admitted it is quite natural that we should be induced to ascertain whether stimulants that increase the activity of this organ, also exert an action on the carbohydrates of the organism.

Among the agents that considerably promote the function of the pancreas we selected the most potent, viz. secretin, discovered by BAYLISS and STARLING. Our experiments showed results that gave rise to the question whether we could trace any influence of secretin on the amount of sugar in the blood. The fluctuations in this amount were taken as an index of the changes in the carbohydrate metabolism as the latter manifest themselves in the former.

*Experiments.*

1. *Preparation of the secretin.*

Dogs, kindly procured by the "Society for the prevention of cruelty

to animals" were, immediately after being killed, deprived of the duodenum and the proximal part of the jejunum; the mucous membrane of these organs was rubbed up in the ordinary way and mixed with 0.45% HCl, macerated for half an hour, then boiled, neutralised with sodium and finally acidulated with some drops of acetic acid.

#### 2. *The laboratory animal.*

My first experiments were made on rabbits. I used this animal because its amount of blood-sugar both in normal and abnormal condition was pretty well known to me from earlier researches, in which also the technique of the operation (ligature of the carotid), presented hardly any difficulty. According to the size of the animal from 8—15 c.c. of secretin were given intravenously (per auricular vein); at different intervals of time after the injection the amount of sugar in the blood was estimated.

#### 3. *Estimation of blood-sugar.*

The estimation was performed by cautious titration after FEHLING. Beforehand the Fehling-liquid had been accurately tested on invert-sugar. Of the copper test solution 10 c.c. were diluted to 100 c.c. and the reducing power of the blood-sugar solution was repeatedly tested on 5 cc., until the liquid being passed through a wet double filter, gave no longer a red discoloration with an acetic acid solution of potassium ferrocyanid.

#### 4. *Removal of proteins.*

Proteins were separated from the blood after the old method of BERNARD ( $\text{Na}_2\text{SO}_4$ , etc.).

The following table shows the results obtained in this manner:

T A B L E I.

Number	Date	Secretin	Blood-sugar	Remarks
1	Dec. 1911	12 cc	after 45 min. 0.14 %	
2		12 "	" 60 " 0.082 "	
3		14 "	" 90 " 0.077 "	
4		15 "	" 120 " 0.032 "	
5		12 "	" 120 " 0.087 "	
6		8 "	" 115 " 0.071 "	With absolute alcohol substances lowering the bloodpressure were extracted from the mucous membrane.
7		10 "	" 195 " 0.078 "	
8		15 "	" 120 " 0.076 "	

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The following values obtained with normal animals without injection of secretin are given for purposes of comparison:-

T A B L E II.

Number	Date	Secretin	Bloodsugar	Remarks
9	27 Nov. 1911	—	0.14 %	—
10	1 Dec. "	—	0.11 "	—
11	3 Dec. "	—	0.091 "	—

In some other experiments the effect of secretin on the amount of sugar in the blood was determined while the animal was subjected to the action of levo-rotatory suprarenin (HÖCHST).

It is well known, that suprarenin has the property of producing an excessive formation of sugar in the blood by splitting the glycogen in the liver and of exciting glucosuria. By extensive experimentation it has already been pointed out that the rise of the sugar-content in the blood of a rabbit, injected subcutaneously with  $\frac{1}{2}$  mgr. of suprarenin, amounts to about 100 %, i.e. the percentage content of the blood-sugar rises from  $\pm 0.12$  % to 0.25—0.30 % in  $1\frac{1}{2}$  hour.

The following table illustrates the results obtained, after I had given the animal secretin intravenously five minutes before a subcutaneous injection of  $\frac{1}{2}$  mgr. of levorotatory suprarenin.

T A B L E III.

Number	Date	Secretin	Suprarenin	Bloodsugar	Urine in 24 hours
12	Jan. '12	11 cc	0.5 mg.	90 min. after secr. 0.205 %	58 cc ad 0.3%
13	" "	16 "	" "	" " " " 0.151 "	120 " " 0 "
14	" "	13 "	" "	" " " " 0.181 "	60 " " 0.6 "

In the next series I extracted the distal portion of the ileum instead of the duodenum and the proximal portion of the jejunum and tried to detect whether this extract, which should be devoid of secretin, none the less keeps down the percentage of glucose in the blood, as well by itself as when acting concomitantly with suprarenin. The results of four experiments, carried out in this way, implied that this was altogether out of the question.

From the foregoing experiments (18) we arrive at the following conclusions:

Injection of secretin in most cases lowers the amount of sugar in the blood, the average fall being 30 %. This faculty of secretin asserts itself even in counteraction to suprarenin, which of itself produces an increment of 100 % at the end of 1½ hours, but only 50 % under the given circumstances.

However, glucosuria appeared in all cases but one. That the results communicated here are due to the sole action of secretin has been distinctly shown by the experiments, which yielded negative results with injection of other intestinal extracts.

These experimental investigations led me to endeavour to find out whether an internal secretum of the pancreas could actually be elicited and whether injection of secretin excited its activity.

#### *Second series (B).*

It has often struck me, that only few workers have strenuously exerted themselves to obtain in vivo the internal secretum of the pancreas, putting aside of course BIEDL's<sup>1)</sup> and DE MEYER's<sup>2)</sup> experimentation. The former examined the anti-glucosurian action of the lymph from the thoracic duct. The latter the effect of pancreatic extracts or of fluids which had been made to pass through the pancreas artificially, on the glycogenesis of the liver. These researches constitute the best work that has been done in this field, as the other investigations were restricted to biological experiments with blood from the pancreatic vein, especially as regards its fermentative properties.

Our purpose was rather to furnish large quantities of blood from the pancreatic-duodenal vein for further experimentation on carbohydrate metabolism. Let it be stated beforehand, that in large dogs such quantities are not difficult to procure from this vein.

*Method.* In large dogs of 10—15 K.G. an incision is made through the abdominal wall parallel to the arcus costalis to get access to the pancreas, which is drawn out by the hook-shaped finger and immediately wrapped in cloths soaked with a warm physiological common salt solution.

It is then easy to find the pancreatic-duodenal vein, which is ligatured as near the trunk of the portal vein as possible. Subsequently a cannula is inserted, which cannot always be managed. In case of failure the vein is simply cut through. At the same time

<sup>1)</sup> BIEDL. Wiener Kl. Wochensch. 1907.

<sup>2)</sup> DE MEYER. Archiv. Intern. de Phys. 1910.

20—40 cc. of secretin is injected intravenously or subcutaneously. Most times the blood is discharged rapidly, sometimes it issues in a jet, the blood flow can still be accelerated by kneading the pancreas with the full hand and by massage. In this way 80—250 cc. of blood can be collected in about  $\frac{3}{4}$  hour. In some of our experiments the blood was allowed to coagulate and we used the serum separated in the clotting. Most often, however the blood was defibrinated at once.

With this blood or with this serum the following experiments were performed:

Specimens of this blood varying from 5—20 cc. were used upon rabbits<sup>1)</sup> subcutaneously, in which also  $\frac{1}{2}$  mgr. of suprarenin<sup>2)</sup> was injected. After the lapse of  $1\frac{1}{2}$  hours the blood-sugar percentage was determined. The experiments however varied in some details according to the various treatment of the pancreas blood that had been administered. Usually three specimens of dog's blood were given separately to three rabbits of equal weight. The specimens, however, were all different inasmuch as either the blood had flowed from the vein prior to the injection of secretin, or this had occurred concomitantly with the injection, or the blood had been heated for half an hour at  $56^{\circ}$  C., or finally the blood had been liberated from its proteins by addition of three times its volume of alcohol, the alcoholic filtrate having been evaporated down to its original volume.

We subjoin a table illustrating the results of some of our most successful experiments.

By the side of these experiments others were made upon rabbits with homologous serum. It being, however, very difficult to draw an adequate quantity of blood from the rabbit's pancreatic vein, we have to content ourselves with reporting only one satisfactory test. From the pancreatic vein of a rabbit, weighing 3 K.G., 8 cc. of blood was obtained. Four cc. of serum were separated. Subsequently 12 cc. of secretin were injected per vena auricularis; and 15 cc. of blood, furnishing 7 cc. of serum, were drawn from the pancreatic vein.

Next day 2 rabbits, weighing 1300 grms were injected intravenously. The first got the 4 cc. of serum of the first sample and immediately after 1 mgr. of levorotatory suprarenin. The percentage of sugar in the blood was 0.297 after  $1\frac{1}{2}$  hours. The urine passed in 24 hrs. was 15 cc. with 0,6 % of sugar.

<sup>1)</sup> In order to avoid complications the foreign serum was injected only once into each rabbit.

<sup>2)</sup> In this experiment as in all others only fresh suprarenin was used from vials that had just been opened.

T A B E L IV

Weight	Pancreas blood injected	Supra- renin	Blood- sugar	Urine in 24 hours	Details
K.G.	5 cc serum	0.5 m.g.	0.195 %	40 cc à 6½% glucose	Serum from pancreas acted upon by secretin.
"	5 " (blood)	0.5 "	0.183 "	not collected	Blood from pancreas before injection of secretin.
"	4.5 " "	0.5 "	0.156 "	contains much glucose	Blood from pancreas acted upon by secretin.
5 "	10 " "	0.5 "	0.134 "	40 cc à 0.12% glucose	Blood under the influence of secretin.
"	10 " "	0.5 "	0.189 "	presence of glucose	Blood from pancreas before injection of secretin.
"	10 " "	0.5 "	0.177 "	40 cc +	Blood from pancreas acted upon by secretin.
"	10 " serum	0.5 "	0.153 "	> 30 cc à 0.3%	Blood under the influence of secretin.
"	20 " blood	0.5 "	0.185 "	50 cc à 1.8%	Blood under the influence of secretin.
5 "	20 " heated for half an hour at 56° C.	0.5 "	0.145 "	30 cc a 1.68%	Blood under the influence of secretin. Next day hemoglobinuria appears.
"	23 cc. liberated from protein with 3 × its volume of alcohol 96% and evaporated down to its original volume	0.5 "	0.151 "	70 cc à 1.5%	Blood under the influence of secretin. No derangements.

The 2<sup>nd</sup> rabbit got 2 cc. of the serum obtained under the influence of secretin, also intravenously. A few bubbles of air, injected along with the substance were responsible for a slight degree of dyspnoea in the animal, which, however, disappears within a quarter of an hour; 5 minutes after this intravenous injection ½ mgr. of levorotatory suprarenin was administered subcutaneously. At the end of 1½ hrs. the amount of sugar in the blood is 0,178 %. After 24 hrs the quantity of urine is 55 cc. with traces of sugar.

From the experimental evidence above stated it would seem permissible to conclude with a high degree of probability:

1. that together with the blood, a substance is secreted through the pancreatic vein, which, in rabbits, is capable of neutra-

lising to some extent the action of levorotory suprarenin on the sugar-content in the blood, but that, on the other hand, this does not apply to the glucosuria, which, judging from the values above mentioned, has a tendency to be relatively higher with a reduced than with an increased amount of blood sugar.

2. that injection of secretin seems to stimulate the activity of the blood from the pancreatic vein.
3. that, to judge by some experiments, heretofore presented, (others were made which shall be dealt with in a later publication) the substance producing this action is thermostabile and is soluble in 75 % alcohol.

*Third Series (C).*

In connection with the preceding experiments the question suggested itself as to whether the antagonism between suprarenin and the blood from the pancreatic vein was to be looked upon as the outcome of the action of a substance, which exalts the glycogenesis or of one inhibiting the glycogenolysis.

Concerning this point I purpose to publish some data afterwards. For the present I feel called upon to bring forward two experiments demonstrating the action of the blood from the pancreas on the glycogen in the liver. It may be taken for granted that with a dog in nitrogenous equilibrium every derangement in the process of carbohydrate metabolism will also affect the N.metabolism in one way or other. Two successful experiments are available (others were performed, which, however, did not always yield conclusive evidence) actually pointing to a change in the N.metabolism. It was also evident from all these tests that glucosuria is likely to appear, and that in some cases traces of sugar occurred after the injection of blood from the pancreatic vein

We present the data of the tests reported here in the following table: (see table page 9)

N<sup>o</sup>. 36. The urine of a dog in N. equilibrium and weighing 5½ KG. was tested for sugar every day, invariably with a negative result. On the 23<sup>d</sup> of Dec. 30 cc. of blood from the pancreatic vein was injected. Within 24 hrs two portions of urine were collected (80 cc. reduced FEHLING and yielded a positive fermentation test; 60 cc. reduced and yielded a positive fermentation test).

N<sup>o</sup>. 37. 30 cc. of blood from the pancreatic vein, liberated from protein by 96 cc. of alcohol and evaporated down to its original

T A B L E V. (Dog 7 K G.)

Number	Date	Diet	N. per 24 hrs	Urine	Remarks
34	11 June '12	100 gr. horse-flesh 100 " milk 50 " bread	12 a.m. } 1.695	30	
			11 p.m. }		
	11 p.m. } 3.729	75			
	12 a.m. }				
	Total 5.424			105	
	12 " "	150 gr. horse-flesh 100 " milk 50 " bread	12 a.m. } 2.31	33	
			11 p.m. }		
	11 p.m. } 4.22	110	12 a.m. }		
Total 6.53			143		
13 " "	same diet	12 a.m. } 4.068	60		
		11 p.m. }			
11 p.m. } 2.214	49	12 a.m. }			
		Total 6.282			109
14 " "	" "	12 a.m. } 4.013	48	At 8 p.m. a subcutaneous injection of 20 c.c. of blood from the pancreatic vein under the influence of secretin.	
		11 p.m. }			
11 p.m. } 4.208	78	12 a.m. }			
		Total 8.221			126
12 a.m. } 3.706	44	11 p.m. }			
		11 p.m. } 4.407	75		12 a.m. }
Total 8.113					119
12 a.m. } 1.864	20	11 p.m. }			
		11 p.m. } 3.254	50	12 a.m. }	
Total 5.118				70	
12 a.m. } 2.612	34	11 p.m. }		At 11 p.m. the first hour of a new period of 24 hrs 20 c.c. of dog's blood from the jugular vein is used subcutaneously. Two weeks before part of the pancreas had been extirpated without evoking diabetes.	
		11 p.m. } 1.85	21		12 a.m. }
Total 4.462					55
12 a.m. } 3.823	47	11 p.m. }			
		p.m. } 3.084	78		12 a.m. }
Total 6.907					125

T A B L E VI. Dog 11 K.G.

No.	Date	Diet	N. per 24 uur	Urine	Remarks
35	30 Aug.	300 gr. horseflesh 100 » milk 50 » bread	1st portion 4.236 gr.	117	
			2d » 5.92 »	150	
			Total 10.156 gr.	267	
	31 »	same diet	1st portion 4.143 gr.	138	At 9 p. m. an injection of 20 cc. of blood from the jugular vein of a normal dog.
			2d » 7.167 »	210	
			Total 11.31 gr.	348	
4	1 Sept.	»	1st portion 6.7 gr.	204	
			2d » 3.791 »	112	
			Total 10.491 gr.	316	
2	»	»	1st port. } urine 2d » } only once		
				10.27 gr.	
3	»	»	1st port. } urine 2d » } only once		
				Total 7.494 gr.	
4	»	»	1st port. 11.289 gr.	280	At 8 p. m. a subc. inj. of 28 cc. of blood from the pancreatic vein under the influence of secretin. <i>The urine of the 2d port- ion reduces FEHLINGS solution.</i>
			2d » 4.845 »	114	
			Total 16.134 gr.	394	
5	»	»	1st port. }		Outside circumstances are responsible for the fact that the N-determin- ation occurred only once in 24 hrs, so that the average of the two values should be taken.
			2d » } 4.173 gr.	94	
			4.173 gr.	94	
6	»	average = 9.7	1st portion 9.18 gr.	225	
			2d » 6.283 »	154	
			Total 15.463 gr.	379	
7			in 24 hrs 9.395 gr.	238	

volume, was injected into a dog, weighing 11 K.G. Next day the 1<sup>st</sup> portion of urine gave a positive reduction with FEHLING, fermentation test positive. The third day no reduction.

These experiments show, that the blood from the pancreatic vein at first exalts the N. metabolism and then lowers it again. Under these circumstances it would not be proper to dwell any longer on these contrary effects, as we are unable to account for them satisfactorily.

It also appears that the blood favours the permeability of the kidney tubules for sugar.

This experience throws light on the contrary results in our preceding series of experiments in which the glucosuria was disproportionate to the sugar content in the blood. It would seem then that the secretum of the pancreas subserves the function of the kidney as well as the glycogenesis of the liver. Indeed, this has also been admitted by DE MEYER and others, however, on a different basis and just the other way about. DE MEYER held that the internal secretum of the pancreas *prevented* sugar from passing through the kidney. It must be borne in mind, however, that DE MEYER experimented with artificial renal circulations, which readily lead to paradoxical phenomena.

*Summary.*

1. Secretin decreases the amount of sugar in the blood.
2. The blood that has passed through the pancreas, is capable of neutralising the action of levorotatory suprarenin on the sugar content in the blood. In this study no effort has been made to detect whether this action is due to a diminished splitting of the glycogen in the liver or perhaps to an increase in the formation of glycogen. Presumably the activity of this blood (internal secretum) is furthered by the injection of secretin. The secretum is thermostable and is soluble in alcohol. These results are perfectly concordant with DE MEIJER's experience.
3. Our experience that the secretum favours the permeability of the kidney for glucose instead of lessening it, clashes with the results of DE MEIJER's investigations.

*Rotterdam, Dec. 1912.*

**Botany.** — "*On the nucleolus and karyokinesis in Zygnema*". By Prof. C. VAN WISSELINGH. (Communicated by Prof. J. W. MOLL).  
(Communicated in the meeting of April 25, 1913).

Whilst *Spirogyra* has very often been used for the investigation of the nucleus and nuclear division, *Zygnema* has so far as I know, up to the present only been studied for this purpose by two investigators. It should be no cause for surprise that the latter alga has

generally been neglected. The dimensions of the cells and nuclei are so much smaller than those in the larger species of *Spirogyra*, that one would expect to meet with still greater difficulties in a karyokinetic investigation than would arise in the case of *Spirogyra*. Such is indeed the case and in studying karyokinesis I have not been able to trace the details of the process to the same extent as in different species of the genus *Spirogyra*.

MABEL L. MERRIMAN<sup>1)</sup> was the first to study karyokinesis in *Zygnema*. She could not with certainty identify the species studied, because she had no zygosporos at her disposal. The chief results of her inquiry were as follows.

She found in the nucleus of *Zygnema* no body that corresponds to the nucleoli of higher plants. There is in the middle of the nucleus a central body that is composed of the greater portion of the cromatin-granules, whilst the rest of the chromatin-granules is situated in the peripheral network between the central body and the nuclear membrane. During karyokinesis the central body splits into many small ones, whilst the granules in the network increase in size. In this way there are formed 20 or more mostly loose chromosomes. A spirem is not formed. The chromosomes come to lie in a ring round the centre. The nuclear membrane dissolves. Then the chromosomes approach one another, and unite into 4 to 6 tetrads or groups of four, which become arranged in two parallel planes, lying close together. The chromosomes of these two planes separate. No longitudinal splitting takes place. The groups of four now divide into smaller groups, which form two rings. Thereupon the central body is formed, composed usually of the greater number of the chromosomes. A nuclear membrane also appears again. Daughter nuclei with many tetrahedral granules, with several masses and with a single mass are observable.

EUD. ESCOYEZ<sup>2)</sup> investigated the nucleus and karyokinesis in a species of *Zygnema*, which he believes to have been different from that studied by Miss MERRIMAN, but which he could not identify.

His results are entirely different from those of Miss MERRIMAN. He states that in the resting nucleus, there can be distinguished a network, an ordinary nucleolus and a nuclear membrane. Rarely there are two nucleoli in the nucleus. The nucleolus, according to ESCOYEZ, lies in a cavity (cavité périnucléolaire) which is surrounded by a

<sup>1)</sup> MABEL L. MERRIMAN, Nuclear division in *Zygnema*, Reprinted from The Botanical Gazette, 41, Jan. 1906, p. 43—53.

<sup>2)</sup> EUD. ESCOYEZ, Le Noyau et la Caryocinèse chez le *Zygnema*, Extrait de la Revue "La Cellule", t. XXIV, 2<sup>d</sup> fasc. 1907, p. 355—367.

very thin membrane. He thinks it possible, however, that this cavity is formed in the fixing. He describes the nucleolus as mostly spherical and homogeneous; in some cases it shows an irregular, very aberrant form.

ESCOYEZ states that during the prophase of karyokinesis thicker parts arise in the network which shows a looser structure. Finally 30 to 40 chromosomes are formed which resemble rodlets.

The chromosomes arise directly from the network which does not first form a spirem. The nucleolus plays no morphological part in the formation of chromosomes. Its shape undergoes modification and finally it completely dissolves. ESCOYEZ states that the nuclear spindle penetrates into the nuclear-cavity and that the chromosomes subsequently form an equatorial ring. Then longitudinal splitting takes place, the chromosome halves take up a position near the two poles of the nuclear spindle, which are found near the chromatophores. They crowd together into plate-shaped bodies. Later they again become visible to the number of 30 to 40. Gradually a network forms which corresponds with that of the resting nucleus. ESCOYEZ says that the nucleolus is first a small body which gradually increases in size. Its formation is independent of the chromosomes.

The object of ESCOYEZ's investigation was not only to control Miss MERRIMAN's results, which diverge greatly from those generally obtained in karyokinetic inquiry, but he wished also to answer the question whether *Zygnema* so far as the nucleolus and karyokinesis are concerned, agrees with *Spirogyra* where according to ESCOYEZ J. BERGHS<sup>1)</sup> has established that the twelve chromosomes arise exclusively derived from the nucleolus. As is already evident from the above, ESCOYEZ's investigation yielded negative results on both points. His results differ widely from those of Miss MERRIMAN and also from those of BERGHS obtained with *Spirogyra*.

With regard to the latter, I remark, that the opinions of investigators on the nucleolus and karyokinesis of *Spirogyra* are very divergent and that weighty objections can be advanced against the conclusions of BERGHS in particular<sup>2)</sup>.

The object of my own inquiry was to answer the question concerning the agreement of the two genera in respect of the nucleoli and karyokinesis, of which I had already made a complete study in five species of *Spirogyra*. The results obtained with three thick

<sup>1)</sup> J. BERGHS, Le Noyau et la Cinèse chez le *Spirogyra*, Extrait de la Revue "La Cellule", t. XXIII, 1<sup>er</sup> fasc. 1906, p. 55--85.

<sup>2)</sup> C. VAN WISSELINGH, Ueber die Karyokinese bei *Oedogonium*, Beihefte zum Botan. Centralblatt. Bd. XXIII (1907), Abt. I. pag. 152 and foll.

species have been already described<sup>1)</sup>, those with two thinner ones are still to be published.

The species of *Zygnema* which I examined and of which I also had the zygospores, I identified as *Zygnema cruciatum*.

The method of investigation was mainly the same as that which I had previously used with good results in the case of *Spirogyra* and other plants, namely, fixing with FLEMMING's mixture and treating with chromic acid. I modified the method slightly so as to facilitate the investigation of *Zygnema*. The many globules of fat in the cytoplasm sometimes greatly hinder the investigation of the nuclei. For this reason I fixed with absolute alcohol, then left the material for some days in ether, transferred it again to absolute alcohol and replaced this by distilled water. Finally the material was placed in FLEMMING's mixture, in which it remained some days, until the treatment with chromic acid yielded the desired result, namely, slow solution of the cytoplasm and chromatophores and isolation of the nucleus. The latter afterwards gradually dissolves, during which process some of the more resistant parts become very clearly visible. No contraction or coalescence of the protoplast should occur. Should this happen as the result of a faulty application of the method, the material is useless. The strength of the chromic acid solution, which I applied was 10 or 25%. Sometimes the chromic acid, when it had acted sufficiently was washed out with distilled water and the preparations were stained blue by means of "Brilliantblau extra grunlich".

The preliminary treatment with alcohol and ether was advantageous and unaccompanied by any drawback. The troublesome fat was got rid of and it seemed to me that the fixation of the nuclei in *Zygnema* was even better than by the direct action of FLEMMING's mixture. I did not see the cavity round the nucleolus, which ESCOYEZ named cavité périnucléolaire, and regarding the existence of which in the living object there are also differences of opinion in other cases. Therefore I assume that no such cavity occurs in the living material and this agrees with the results I obtained previously with other plants.

*Resting nucleus.* The nucleus is situated in the middle of the cell between the two chromatophores and is stretched longitudinally. The following parts can be distinguished in the resting nucleus: the nuclear membrane, the network composed of small granular bodies

<sup>1)</sup> C. VAN WISSELINGH, Ueber den Nucleolus von Spirogyra, Bot. Zeitung 1898, Heft XI/XII, p. 195. — Ueber Kernteilung bei Spirogyra, Flora, 1900, 87. Bd. 4. Heft, p. 355. — Untersuchungen über Spirogyra, Bot. Zeitung, 1902, Heft VI, p. 115. — Ueber abnormale Kernteilung, Bot. Zeitung, 1903, Heft X/XII p. 201.

united by fine threads, and the nucleolus. I never saw a resting nucleus with two nucleoli. There is nothing special to say about the nuclear membrane and the nuclear network. With regard to the latter there is here as little reason as in other cases for assuming that the granules and the connecting threads are chemically different.

The nucleolus calls for special attention. Superficial observation would lead to the assumption that it is an almost spherical body, about which nothing special can be said. More exact observation, even before the action of chromic acid, shows that sometimes two small points on the nucleolus can be distinguished. During the action of chromic acid they become much more visible and are seen to be small bodies which sometimes resemble rodlets. They are situated on the periphery of the nucleolus, usually opposite one another and seem often half immersed in the principal mass. According as a more concentrated or weaker solution of chromic acid is used, the nuclear network or the main mass of the nucleolus dissolves first. In either case, however, the two small bodies show a longer resistance. During the process of dissolution it can be seen that the two small bodies are united by a thread which generally runs across the nucleolus and is straight or slightly bent, but which may also be much curved. When the nuclear network has dissolved and the chromic acid has also had a strong solvent action on the main mass of the nucleolus, the thread which unites the two small bodies can be distinguished, and when the preparations are further stained with "Brilliantblau extra grünlich", all is still more clearly and more easily visible. The two corpuscles are stained dark-blue, the thread, which unites them, is paler and the rest of the nucleolus is light blue. After more prolonged action of the chromic acid the thread with the two corpuscles alone is still present; after a still longer action, only the latter are found and finally these also are seen to have dissolved. This can all be seen with special clearness after staining with "Brilliantblau extra grünlich."

In every preparation that I made, the above observations were confirmed dozens of times, so that I am in no doubt that the nucleolus in *Zygnema* differs in type from that of the higher plants, and resembles the nucleolus of *Spirogyra* in having a peculiar structure. In *Spirogyra* there are two convoluted threads or a threadwork or network, in *Zygnema cruciatum* there are two short corpuscles united by a thread or indeed a thread with two thickened ends.

I consider the main mass of the nucleolus in *Zygnema* as identical with the substance which occurs in *Spirogyra* together with the threads or the thread- or network in the nucleolus. I have not been

able to answer the question whether the nucleolus in *Zygnema*, like that of *Spirogyra*, possesses a membrane.

A few nucleoli did not seem to correspond to the above description, although I cannot definitely state, that these were aberrant. I have never met with very abnormal nucleoli such as ESCOYER observed in the resting nucleus so that the question occurs to me whether such nucleoli do not arise in fixing, like the perinucleolar cavity or whether perhaps they may be of a pathological nature.

*Karyokinesis.* In investigating karyokinesis in *Zygnema* the first question concerned the behaviour of the thread with thickened ends in the nucleolus, for in *Spirogyra crassa* I was able to determine without interruption the karyokinetic changes in the two nucleolar threads. In *Zygnema* I have not succeeded in doing this. Observation in this case must necessarily be so much more minute and is accompanied by so many more difficulties, that after a few futile attempts I was obliged to abandon the study of the changes in the nucleolar thread. I am unable therefore to give any further information about this important point.

At the beginning of karyokinesis the nuclear network has a somewhat coarser and looser structure; everywhere there arise by aggregation portions which are much thickened, whilst the meshes become wider. The nucleolus acquires an irregular shape and seems to dissolve completely. By further aggregation of the nuclear network threads are formed, resembling strings of pearls. The nuclear-wall is then still visible. In later stages it is dissolved and the network has formed a number of short, thick corpuscles, which are connected together by thin filaments. Meanwhile there arises from the cytoplasm gathered round the nucleus a well developed nuclear spindle, whose pointed poles extend to the chromatophores. The nuclear network now moves back more and more into the equatorial plane, so that finally there is in the centre of the nuclear spindle a flat round disc surrounded by the spindle-fibres. This is the nuclear-plate. It is composed of a number of small bodies resembling short thick pieces of thread or lumps which are joined to each other by fine threads, or they may be intimately connected or completely united. Their number cannot be determined. Clearly visible and well-formed chromosomes, such as occur in some *Spirogyra* species to the number of 12 or 6, are not found in *Zygnema*, but there is no great objection to calling the small, short bodies of the nuclear plate chromosomes, in agreement with the usual nomenclature. The mass out of which the nuclear plate is composed appears noticeably smaller than that of the network of the resting nucleus.

The nuclear plate of *Zygnema cruciatum* is not ring-shaped. Miss MERRIMAN and ESCOYEZ believe that they have seen annular nuclear-plates in *Zygnema*, but I think this in a visual delusion. When a nuclear-plate is seen edge-ways it may appear as if it were a ring, but if looked at afterwards from the side, as is possible in using the chromic acid method, all doubt immediately vanishes. I came to the same conclusion with *Closterium*<sup>1)</sup>, in which LAUTERBORN<sup>2)</sup> had described a ring-shaped nuclear-plate.

The nuclear-plate divides by longitudinal splitting into two halves which separate. At first their structure becomes more dense. When, by the use of chromic acid, they have been isolated and fall over, they somewhat resemble round discs which appear spotted in consequence of local differences in density. These halves of the nuclear-plate develop into daughter-nuclei which acquire a membrane and consequently show a sharp outline. It is difficult to say when the nuclear membrane reappears. The dense structure of the halves of the nuclear plate again gives place to a looser one and finally there is again spread out within the nuclear-membrane a fine network, which resembles that of the resting nucleus. During the entire process of karyokinesis the nuclear network forms a coherent whole. When the structure becomes looser again, the nucleoli also quickly appear. At first there can be distinguished in the network many small masses more or less globular and irregular, which gradually unite into several larger masses and finally form one single spherical mass in the centre of the nucleus. This representation of the origin of the nucleolus differs very much from that given by ESCOYEZ, but it agrees with what has been observed in *Spirogyra* where also many nucleoli flow together into a single one.

There is a further point to be noted concerning the development and position of the daughter nuclei in *Zygnema cruciatum*. In *Spirogyra* and other cases the halves of the nuclear plate take up a position near the poles of the spindle where they develop into daughter-nuclei. In *Zygnema cruciatum* the development takes place earlier. Before the poles have been reached, the daughter-nuclei have already a membrane and consequently show a sharp outline, whilst the nucleoli have already united into several larger masses. The spindle-fibres lie immediately against the daughter-nuclei. Between the halves of the nuclear plate, the spindle greatly increases in

<sup>1)</sup> C. VAN WISSELINGH, Ueber Kernstruktur und Kernteilung bei *Closterium*, Beih. zum Bot. Centralbl., Bd. XXIV (1912), Abt. I. p. 429.

<sup>2)</sup> R. LAUTERBORN, Untersuchungen über Bau, Kernteilung und Bewegung der Diatomeen, 1896. Fig. 68.

circumference through its fibres becoming longer and bending outwards. At the end of karyokinesis the spindle moves away and often turns so that its longitudinal axis makes an angle with that of the cell. The daughter-nuclei move against the chromatophores which divide into two. They take up a position between the new chromatophores of the daughter-cells. The transverse wall develops in the same way as in *Spirogyra*. It arises at the longitudinal wall and grows inwards until the cell is divided into two. The division of the chromatophores generally occurs after cellular division, but it is not limited to the latter, for cells with 3 or 4 chromatophores are sometimes met with.

*Summary of results.*

1. In *Zygnema cruciatum* as in *Spirogyra* the nucleolus has a peculiar structure. It contains a thread with two thickened ends or indeed two corpuscles, which are united by a thinner thread.

2. The nucleolus dissolves when karyokinesis begins. I cannot say with certainty whether, as in *Spirogyra*, there remain behind morphological elements, which play a part in karyokinesis, but I consider this probable.

3. There is no perinucleolar cavity (cavité périnucléolaire of ESCOYEZ) in living specimens of *Zygnema cruciatum*.

4. In *Zygnema* the chromosomes, short threadlike pieces or lumps, arise from the nuclear network, as ESCOYEZ also assumes and not from the nucleolus, as Miss MERRIMAN imagines.

5. During karyokinesis the chromosomes remain continually united.

6. In *Zygnema cruciatum* the chromosomes do not form tetrads as Miss MERRIMAN claims to have established in this genus.

7. The nuclear membrane dissolves, but this is not accompanied by a penetration of the spindle-fibres into the nucleus or nuclear cavity.

8. The halves of the nuclear-plate arise, as ESCOYEZ also assumes, through longitudinal splitting of the nuclear-plate, and not through the grouping of the chromosomes in two parallel planes without splitting, as Miss MERRIMAN maintains.

9. In *Zygnema cruciatum* the nuclear plate is disc-shaped and not annular as Miss MERRIMAN and ESCOYEZ believe they have seen in *Zygnema*.

10. The network of the daughter-nuclei develops from the halves of the nuclear plate.

11. The nucleolus is formed by the coalescence of many smaller ones to a single body.

12. In *Zygnema cruciatum* the halves of the nuclear plate develop already to daughter-nuclei within the nuclear spindle, and before they reach the poles. That part of the spindle which lies between the daughter-nuclei increases in circumference, so that the spindle becomes peculiar in shape.

The results obtained by Miss MERRIMAN, ESCOYEZ and myself differ very greatly. This may partly be ascribed to the circumstance that different species of *Zygnema* were investigated. To a much greater extent the differences must be assigned to other causes, in particular to a different interpretation of observations. The observations themselves however, are also sometimes different and perhaps not always complete. Also the fixing agent and the method of investigation may contribute to the divergence between the results of different investigators. ESCOYEZ, for example, observed a perinucleolar cavity, whilst I, using an other method of fixation observed no such cavity. Miss MERRIMAN and ESCOYEZ both believe they have seen ring-shaped nuclear-plates, whilst I came to a different conclusion, using a method by which the nuclear-plates could be observed edgewise as well as sideways.

It seems to me desirable that the various investigators should endeavour to complete their observations on *Zygnema*, and extend them to more species and also should apply different methods of investigation. Exchange of material might also be very useful. Some such action would be conducive to agreement, which will not be readily obtained by other means.

**Physiology.** — “*On the change in the permeability of the red blood corpuscles (also in man)*”. (*A contribution to the knowledge of chlorine-retention in fever*<sup>1</sup>). By I. SNAPPER. (Communicated by Prof. HAMBURGER).

(Communicated in the meeting of April 25, 1912).

It has been known for a long time that in a number of febrile diseases an important change in the excretion of chlorine is to be observed. Under normal circumstances, all the chlorine which is taken up with the food leaves the body within 24 hours, not so, however, in the above mentioned diseases; though the patients take daily 5 or 6 grammes of NaCl, only some hundreds of milligrammes

<sup>1</sup>) A detailed account of these researches will be published in the *Biochemische Zeitschrift*, and in the *Zeitschrift für Klinische Medizin*.

are excreted. This means an almost absolute retention of chlorine.

Many theories have been suggested to account for this retention, without a satisfactory explanation being arrived at. Our investigations have shown that the chlorine percentage in blood and blood-serum has fallen so much, that the kidneys can no longer withdraw chlorine from the blood<sup>1)</sup>. The lower chlorine percentage of the blood can only be explained by the supposition that chlorine is retained by the tissues, and that it does not, as in normal circumstances, pass from the tissues into the blood. The question: "what causes chlorine retention in febrile diseases" is, therefore, turned into another question: "why does not chlorine pass, in these circumstances, from the tissues into the blood?"

*Is it because the permeability of the tissue-cells for chlorine has been modified?*

It is difficult to investigate the permeability of human tissue-cells, even for anorganic substances. The only cells which admit of such researches are the red blood-corpuscles. Hence we have made use of these cells. But before experimenting on this valuable material, it was found desirable to investigate various questions relating to permeability, on the blood-corpuscles of animals.

If the composition of the medium in which the red blood-corpuscles are suspended is altered, interchanges between red blood-corpuscles and their medium take place. Until now it has been found possible to explain these interchanges, as an osmotic phenomenon<sup>2)</sup>; there was no need to assume that a change in the nature of the surface of the red blood-corpuscles had taken place. It was even found that an intentional modification of this surface did not modify the osmotic interchanges.

HAMBURGER, namely, found that an addition of chloroform to red blood-corpuscles did not in the least affect their resistance to diluted salt-solutions<sup>3)</sup>. This result had not been expected by him. Indeed there were grounds for assuming, that the lipoid substances, which form at least part of the surface of the red blood-corpuscles, are softened by chloroform. After this process this outer layer will offer less resistance to the swelling caused by hypotonic solutions. Still nothing of this decreased resistance was observed. And we too could show, in accordance with this fact, that the interchange of

<sup>1)</sup> I. SNAPPER, Dissertatie, Groningen 1913.

<sup>2)</sup> HAMBURGER, Osmotischer Druck und Ionenlehre.

<sup>3)</sup> HAMBURGER. Biologie der Phagozyten. 1913, p. 199.

This resistance of the red blood-corpuscles is a good criterion as regards their permeability.

substances between blood-corpuscles and medium remains absolutely unaffected by the addition of chloroform (see p. 1469).

Yet we found that there are cases when a modification in the nature of the surface, and consequently a modified permeability *must* be assumed.

From considerations which cannot be detailed here, but which are connected with the varying results obtained by HAMBURGER with intravenous injections of salt mixed with acid, on horse and calf, the following experiments were made.

I. *Experimental modification of the chlorine-interchange under the influence of acids.*

The experiments were carried out with horse's, cow's, and dog's blood. In order to find a criterion for the normal permeability of the blood-corpuscles, it was first investigated how chlorine behaved if part of the serum was replaced by a  $\text{Na}_2\text{SO}_4$ -solution. It was known that if all the serum of the blood was replaced by an isotonic  $\text{Na}_2\text{SO}_4$ -solution, chlorine passed from the blood-corpuscles into this sulphate-solution: this is an osmotic process, dependent on the normal permeability of the blood-cells. In order not to deviate too far from physiological conditions, only part of the serum was replaced by  $\text{Na}_2\text{SO}_4$ -solution; then it was investigated if the chlorine-percentage of the serum had been changed, owing to chlorine having entered into the blood-corpuscles or having left them.

In all the experiments, of 15 cm<sup>3</sup> of blood 1 cm<sup>3</sup> of serum was replaced by 1 cm<sup>3</sup> of isotonic or 2 × hypertonic  $\text{Na}_2\text{SO}_4$ -solution. Since part of the serum is replaced by a solution containing no chlorine, the chlorine in the serum must decrease. This decrease, however, can be calculated beforehand from the amount of serum contained in 15 cm<sup>3</sup> of blood. Supposing for instance, 15 cm<sup>3</sup> of blood contain 9 cm<sup>3</sup> of serum, replacing 1 cm<sup>3</sup> of serum by the sulphate-solution must, therefore, cause the chlorine of the serum to fall to  $\frac{8}{9}$  of the original amount. *It appears now that in the above-mentioned kinds of blood, after ± 12% of the serum has been replaced by  $\text{Na}_2\text{SO}_4$ -solution, the chlorine in the serum falls just as much as could be calculated beforehand from the dilution of the serum with a solution containing no chlorine.*

It may not be concluded from this that under these circumstances no chlorine leaves the blood-corpuscles. The addition of the 2 × hypertonic  $\text{Na}_2\text{SO}_4$ -solution causes the blood-corpuscle to shrink, because water passes from the blood-corpuscles into the serum

Thereby the serum would be more diluted than could be calculated from the addition of the solution which contained no chlorine. That in spite of this the chlorine of the serum agrees with the value calculated beforehand, proves that, with the water, chlorine has passed from the blood-corpuses into the serum.

The following experiment may serve as an example :

EXAMPLE.

Change in the amount of chlorine of the serum of horse's, cow's, and dog's blood, if 12% of the serum has been replaced by sulphate-solution.

Of 15 cc. of blood 1 cc. serum is replaced by 1 cc. of 2 × hypertonic Na <sub>2</sub> SO <sub>4</sub> -solution The chlorine of 4 cc. of serum corresponds with:	Of 15 cc. of blood 1 cc. serum is replaced by 1 cc. of isotonic Na <sub>2</sub> SO <sub>4</sub> -solution. The chlorine of 4 cc. of serum corresponds with:	The chlorine of 4 cc. of normal serum corresponds with:	15 cc. of blood contain:	If no transfer of chlorine took place, the chlorine of 4 cc. of serum, after 1 cc. of serum had been replaced by a solution containing no chlorine, would correspond with:
3.95 cc. AgNO <sub>3</sub>	3.96 cc AgNO <sub>3</sub>	4.44 cc. AgNO <sub>3</sub>	66% = 9.9 cc. AgNO <sub>3</sub>	$\frac{9.9 - 1}{9.9} \times 4.44 = 3.99 \text{ cc. AgNO}_3$

It was, therefore, certain that blood-corpuses with a normal permeability always react in the same way if part of the serum is replaced by a Na<sub>2</sub>SO<sub>4</sub>-solution.

When chloroform was added to the blood — so much even that slight, but distinctly visible haemolysis set in — the same rules were found to hold good: the transfer of chlorine under the influence of Na<sub>2</sub>SO<sub>4</sub> is the same in normal and in chloroform-blood.

EXAMPLE.

The permeability of the blood-corpuses is determined before and after 1.2% of chloroform has been added to the blood.

Of 15 cc. of blood 1 cc. of serum is replaced every time by:					
1 cc. of H <sub>2</sub> O. The chlorine of 5 cc. of serum corresponds with:		1 cc. of 2 × hypertonic Na <sub>2</sub> SO <sub>4</sub> -solution. The chlorine of 5 cc. of serum corresponds with:		1 cc. of isotonic Na <sub>2</sub> SO <sub>4</sub> -solution. The chlorine of 5 cc. of serum corresponds with:	
normal blood	chloroform-blood	normal blood	chloroform-blood	normal blood	chloroform-blood
5.13 cc. AgNO <sub>3</sub>	5.12 cc. AgNO <sub>3</sub>	4.93 cc. AgNO <sub>3</sub>	4.96 cc. AgNO <sub>3</sub>	4.94 cc. AgNO <sub>3</sub>	4.96 cc. AgNO <sub>3</sub>

*Hence the conclusion was confirmed that an addition of chloroform does not affect the permeability of the red blood-corpuses.*

Does the fact that lipolytics do not affect the permeability of the red blood-corpuses, prove that their permeability cannot be modified?

Others have proved from analyses that the view that the stroma of the red blood-corpuses consists exclusively of lipoids, is incorrect. Only a third part of the stromata are formed by lipoids, the other two thirds are albuminous substances<sup>1)</sup>.

For the permeability for anorganic substances, however, the subject under consideration, the albuminous part of the stroma of the blood-corpuses will be the most important: lipid membranes are impermeable for anorganic substances, albuminous membranes are permeable. A priori it is, therefore, probable that lipolytic substances will not affect the permeability for anorganic matter, as they leave the albuminous part of the stroma intact.

In order to settle the question about a change in the permeability, another substance than chloroform had to be added to the blood. An acid was taken, because acids act upon albumin.

It was known that acid, added to blood, causes the blood-corpuses to swell and effects a transfer of chlorine from the serum to the blood-corpuses. This also takes place when acid is added to a suspension of other cells in serum<sup>2)</sup>.

This transfer of water and chlorine was observed again when these experiments were repeated. It was, however, also observed that after an acid had been added, the permeability of the red blood-corpuses had changed. The latter conclusion was based on the following observations:

1. Of 15 cc. of blood 1 cc. of serum was replaced by 1 cc. of an isotonic  $\text{Na}_2\text{SO}_4$ -solution, to which a trace of  $\text{H}_2\text{SO}_4$  had been added. The transfer of chlorine, taking place now, is considerably greater than that effected by  $\text{H}_2\text{SO}_4$  only. In normal blood an addition of the same volume of  $\text{Na}_2\text{SO}_4$  causes no transfer of chlorine. If, however, an acid has been added to the blood, the  $\text{Na}_2\text{SO}_4$  increases the transfer of chlorine, under the influence of the acid.

*Hence  $\text{Na}_2\text{SO}_4$  acts in different manners upon normal blood and upon blood to which an acid has been added: the permeability of the red blood-corpuses has been affected by the acid.*

<sup>1)</sup> PASCUCCI, HOFMEISTER's Beiträge. Bd. VI. 1905.

<sup>2)</sup> HAMBURGER l.c.

## EXAMPLE.

In normal blood hardly any transfer of chlorine if  $\pm 12\%$  of the serum is replaced by  $2\times$  hyperton.  $\text{Na}_2\text{SO}_4$  solution.

In blood to which an acid has been added, a considerable transfer of chlorine, under the same circumstances.

Of 15 cc. of blood 1 cc. of serum is replaced every time by:	
1 c.m <sup>3</sup> . $\frac{1}{20}$ n . $\text{H}_2\text{SO}_4$	1 cc. of a $\frac{1}{20}$ n . $\text{H}_2\text{SO}_4$ -solution, which at the same time contained so much $\text{Na}_2\text{SO}_4$ that it was $2\times$ hypertonic:
chlorine of 4 c.m <sup>3</sup> . serum 4.23 c.m <sup>3</sup> . $\text{AgNO}_3$	chlorine of 4 cc. of serum 3.96 c.M <sup>3</sup> . $\text{AgNO}_3$

2. As we said before, in normal blood it makes no difference if of 15 cc. of blood 1 cc, of serum is replaced by 1 cc. of isotonic or 1 cc. of  $2\times$  hypertonic  $\text{Na}_2\text{SO}_4$ -solution. In blood to which a trace of an acid has been added, these values are different. An addition of 1 cc. of  $2\times$  hypertonic  $\text{Na}_2\text{SO}_4$ -solution causes much more chlorine to enter the blood-corpuseles than an addition of 1 cc. of isotonic  $\text{Na}_2\text{SO}_4$ -solution.

This furnishes another proof of the changed permeability of the blood-corpuseles.

## EXAMPLE.

In normal blood no difference between the transfer of chlorine, caused by an isotonic  $\text{Na}_2\text{SO}_4$ -solution, and that, caused by a  $2\times$  hypertonic  $\text{Na}_2\text{SO}_4$ -solution.

In blood to which at the same time an acid has been added, a difference is found.

Of 15 cc. of blood 1 cc. of serum is replaced every time by :			
1 cc. of $2\times$ hyper- tonic $\text{Na}_2\text{SO}_4$ - solution (7.4%)	1 cc. isotonic $\text{Na}_2\text{SO}_4$ -solution (3.7%)	1 cc. of a $\frac{1}{20}$ n. $\text{H}_2\text{SO}_4$ -solution containing also 7.4% $\text{Na}_2\text{SO}_4$	1 cc. of a $\frac{1}{20}$ n. $\text{H}_2\text{SO}_4$ -solution containing also 3.7% $\text{Na}_2\text{SO}_4$
4.15 cc. of $\text{AgNO}_3$	4.18 cc. of $\text{AgNO}_3$	3.96 cc. of $\text{AgNO}_3$	4.08 cc. of $\text{AgNO}_3$

chlorine of 4 cc. serum.

This proved that it was possible to modify the permeability of the blood-corpuseles by the addition of acids.

II. *Interchange of chlorine between blood-corpuses and medium in human blood.*

It had to be investigated now to what extent these facts could contribute towards an explanation of the chlorine-retention in febrile diseases.

For this purpose the permeability of blood-corpuses, of persons with a normal chlorine excretion was first examined. The results were as follows :

1. If in 10 cc. of human blood 0.6 cc. of serum is replaced by 0.6 cc. of an isotonic  $\text{Na}_2\text{SO}_4$  solution, the amount of chlorine in the serum is greater than the dilution with the solution containing no chlorine, would lead us to expect.

Under these circumstances, therefore, chlorine passes from the blood-corpuses into the serum. Evidently human blood-corpuses behave in a manner different from horse's, cow's, or dog's blood-corpuses if the medium in which they are suspended, is modified.

2. If to 10 cc of human blood 25 mgr. of crystallized  $\text{Na}_2\text{SO}_4$  is added, chlorine passes from the blood-corpuses into the serum.

EXAMPLE.

Transfer of chlorine in human blood if  $\pm 12\%$  serum is replaced by isotonic  $\text{Na}_2\text{SO}_4$  solution, or if crystallized  $\text{Na}_2\text{SO}_4$  is added to the blood.

Chlorine in 4 cc of normal serum corresponds with :	10 cc of blood contain:	After 25 mgr. of $\text{Na}_2\text{SO}_4$ have been added to 10 cc of blood the chlorine in 4 cc of serum corresponds with :	Of 10 cc of blood 0.6 cc of serum is replaced by 0.6 of isotonic $\text{Na}_2\text{SO}_4$ solution. The chlorine in 4 cc of serum corresponds with :	If no transposition of chlorine had taken place, the chlorine in 4 cc of serum would in the latter case have corresponded with:
4.24 cc of $\text{AgNO}_3$	6.8 cc of serum	4.44 cc of $\text{AgNO}_3$	4.05 cc of $\text{AgNO}_3$	$\frac{6.8-0.6}{6.8} \times 4.24 = 3.85$ cc of $\text{AgNO}_3$ .

In a series of cases, in which the blood was examined of people in good health and of patients, of people whose food contained much and of others whose food contained little chlorine, of people with and without fever, these two results were invariably arrived at. In all these cases, however, the metabolism of chlorine was normal.

The same experiments were now carried out with the blood of fever patients showing marked retention of chlorine. The results were as follows :

1. If of 10 cc of blood 0.6 cc of serum is replaced by 0.6 cc of an isotonic  $\text{Na}_2\text{SO}_4$  solution, the amount of chlorine in the serum is exactly the same as that which can be calculated beforehand from the serum being diluted with a solution without chlorine.

*The transfer of chlorine from the blood corpuscles to the serum, found in people with a normal chlorine-excretion, is, therefore not met with in patients with chlorine-retention.*

2. If to 10 cc of blood 25 mgr. of crystallized  $\text{Na}_2\text{SO}_4$  are added, the chlorine in the serum decreases.

*Hence the chlorine now moves in an opposite direction, if this result is compared with the chlorine transfer, found in people with a normal metabolism of chlorine.*

#### EXAMPLE.

Chlorine-transfer in the blood of patients with chlorine-retention, if  $\pm 12\%$  of the serum is replaced by isotonic  $\text{Na}_2\text{SO}_4$ -solution, or if solid  $\text{Na}_2\text{SO}_4$  is added to the blood.

Chlorine in 4 cc of normal serum corresponds with :	10 cc of blood contain:	25 mgr. of $\text{Na}_2\text{SO}_4$ having been added to 10 cc of blood the chlorine of 4 cc of serum corresponds with :	Of 10 cc of blood 0.6 cc of serum is replaced by 0.6 of isotonic $\text{Na}_2\text{SO}_4$ solution. The chlorine of 4 cc of serum corresponds with :	If no chlorine-transfer took place, the chlorine of 4 cc of serum would in the latter case correspond with :
4.87 cc of $\text{AgNO}_3$	5.5 cc of serum	4.59 cc of $\text{AgNO}_3$	4.34 cc of $\text{AgNO}_3$	$\frac{5.5-0.6}{5.5} \times 4.87 = 4.33$ cc of $\text{AgNO}_3$

It seems that from the result of these experiments no other conclusion can be drawn, except that in patients with chlorine retention a modified permeability of the red blood-corpuscles is to be observed. The question suggests itself if the permeability for the other body-cells has not also undergone a change.

For the permeability of the red blood-corpuscles is very constant if the chlorine-metabolism is normal. However ill the patient may be, the permeability of the red blood-corpuscles is normal if the chlorine-metabolism is normal. Now the patients with chlorine-retention show a different permeability. This points to the fact that in this diseased organism, influences have been active which have had a powerful effect upon the permeability of the red blood-corpuscles. Since these noxious influences have been able to change the otherwise so constant permeability of the red blood-corpuscles, perhaps the supposition that the permeability of the other body-cells has also been affected, is

not too hazardous. As we know the permeability of red blood-corpuscles agrees, in many respects, with that of the other body cells. We also know that acids affect the permeability of blood-corpuscles and other body-cells. Then we are not so far removed from the conclusion that, if in vivo this stable permeability of the red blood-corpuscles has been affected, the permeability of the other body-cells might also have been modified.

#### *Conclusions.*

*On the ground of these facts we might form the following conception. As in vitro the permeability of cells can be changed by an addition of acid, this can be done in vivo by other influences, in the case of some febrile diseases. In the latter case chlorine enters the cells under the same circumstances under which it leaves the cells in the normal individual. The consequence of this may be that with these patients chlorine cannot pass from the tissues into the blood.*

*The fact that the chlorine-transfer is constant in normal people and in patients with a normal chlorine-excretion, that the chlorine-transfer is constant in an opposite direction, in people with chlorine-retention, suggests the possibility that a modified permeability of the cells will have to be reckoned among the causes of chlorine-retention in febrile diseases.*

*Groningen, March 1913.*

**Chemistry.** — “*The systems phosphorus and cyane.*” By Prof. A. SMITS. (Communicated by Prof. J. D. VAN DER WAALS).

As was already stated before<sup>1)</sup> it has been ascertained that the vapour tension curve of liquid white phosphorus cannot be the metastable prolongation of the vapour tension line of molten red phosphorus. This fact is in perfect harmony with the circumstance that it can be calculated from the determinations of ASTON and RAMSAY<sup>2)</sup> on the surface tension that the liquid white phosphorus must become critical at  $\pm 422^\circ$ .

In consequence of the existence of this critical point the particularly interesting case presents itself that the *P, T*-figure for white

<sup>1)</sup> These Proc.

<sup>2)</sup> Journ. Chem. Soc. 65, 173 (1894).

phosphorus lacks any connection with that of the violet and the red modification. Precisely the same holds for cyane and paracyane, and what is most remarkable about it, is that what follows only indirectly from experiment for phosphorus, may be easily realised for the system cyane and vice versa. The critical point of liquid white phosphorus below the melting point of the red modification is not to be realised, but follows from the vapour tension curve and from the surface tension; the critical point of cyane on the other hand is easy to observe, and lies at  $126.5^\circ$  and under a pressure of 58.2 atmospheres.

On the other hand the melting-point under the vapour pressure of the red phosphorus can be determined, though not easily, at  $588.5^\circ$  and 42 atmospheres, whereas the melting-point of paracyane, which represents the stable modification and is therefore comparable to the red phosphorus above  $460^\circ$ , cannot be realised, because paracyane is decomposed before this temperature is reached. It follows from this that the systems phosphorus and cyane supplement each other in the most convenient way. As I suspected this, I charged Mr. TERWEN with the examination of the system cyane hoping to come to a decision in this way as to whether we have to do with internal equilibria for the system cyane, just as for phosphorus.

The first thing required was to have cyane of great purity at our disposal, and it was particularly this part of the investigation that presented difficulties which were difficult to surmount. In the preparation of cyane a part is always decomposed, and in consequence of this the product always contains nitrogen. The removal of this nitrogen presented great difficulties, and only after a long laborious process, in which the solid cyane was subjected to repeated fractionated sublimation did we finally succeed in obtaining cyane of so great purity that the investigation about the complexity of cyane could be undertaken. The result rewarded the pains.

Just as for phosphorus the complexity was examined by the determination of curves of solidification under *perfectly* the same circumstances during the solidification. The difference in the successive experiments consisted only in this that in one case the liquid had been previously slowly cooled down, in the other case rapidly from higher temperature.

As was expected the result was that in case of slow previous cooling a line of solidification with perfectly horizontal intermediate portion was found, and that this was wanting when the cooling took place rapidly. The initial point of solidification could be raised  $0.5^\circ$  in the latter case. So the result was qualitatively the same as

for phosphorus, and shows clearly that pure liquid cyane is built up of different kinds of molecules, which get into equilibrium when the process goes slowly. Though in consequence of its small conductivity of heat solid cyane did not furnish reliable results in the determination of curves of heating, we may accept without any doubt that what holds for the liquid phase, will also hold for the solid phase, though it can only be shown in a less clear way.

It is for the rest clear that it is sufficient for our purpose to show the complexity of one of the phases, so that it does not matter that paracyane is altogether inaccessible to an investigation as to its internal constitution.

We may therefore conclude in virtue of the obtained result that phosphorus and cyane are really quite comparable systems.

Before we proceed to a discussion of the pseudo-systems among which the unary systems phosphorus resp. cyane must be classed, it is worth while mentioning what BAKHUIS ROOZEBOOM<sup>1)</sup> has stated about the points of agreement between the two said systems.

“Das Cyan unterscheidet sich weiter vom Phosphor darin, dass kein Schmelzpunkt der polymeren Form (Paracyan) bekannt ist. Praktisch ist es unmöglich, einen solchen zu erreichen, weil das Paracyan sich oberhalb 600° stark zersetzt.”

“Es erhebt sich gleichwohl die interessante Frage, ob — falls diese Zersetzung ausgeblieben wäre — ein Schmelzpunkt hätte erreicht werden können.”

Eine Umwandlung des Paracyans in die gewöhnliche Flüssigkeit ist natürlich unmöglich, weil ihr kritischer Punkt bei 124° liegt. Wohl aber wäre eine Umwandlung oberhalb 640°, also unter grösserem Druck als 1 Atm., in eine polymere Flüssigkeit denkbar.”

“In solchen Fällen besteht also kein kontinuierlicher Uebergang zwischen den beiden Flüssigkeiten. Dadurch stehen die verschiedenen festen Phasen eigentlich nicht mehr im Verhältnis der Monotropie zu einander, sondern die polymere Form verhält sich als ein besonderer Körper.” And in a footnote on the same page he writes: “Es ist sogar fraglich, ob nicht auch der Phosphor noch zu dieser Kategorie gehört, denn ein kontinuierlicher Uebergang zwischen dem gewöhnlichen flüssigen Phosphor, und der Schmelze des roten, ist noch nicht konstatiert.”

We see from this that BAKHUIS ROOZEBOOM took a lively interest in the problem in question, and that he indicated already clearly what is peculiar about it.

BAKHUIS ROOZEBOOM pointed out that there is no connection at all

<sup>1)</sup> Lehrbuch Heterog. Gleichgewichte, 176.

between the two modifications of the substance cyane, and that therefore strictly speaking it is not correct to speak of monotropy here. Now, however, we come to another conclusion. It is true the lines for the internal equilibrium in the different phases of cyane and paracyane lack any connection, and yet we know that all kinds of phenomena are known which very certainly do point to a connection between cyane and paracyane; thus e.g. the vapour of paracyane yields cyane on cooling, and from the vapour of liquid or solid cyane, paracyane may be obtained when it is heated to a high temperature. So there is, indeed, a connection, but this connection could not be demonstrated formerly, and this was also the case with phosphorus. The theory of allotropy guides us here again. The systems *phosphorus* and *cyane* are, as experiment has shown, pseudo-systems, and for the present it is sufficient to assume that each of these systems is built up of two kinds of molecules. Now it has been pointed out before that the pseudo-system phosphorus may be expected to belong to the type ether-anthraquinone, and the same thing applies to the pseudo-system cyane.

If we first discuss the system phosphorus it is easy to show that the existence of two critical endpoints in the pseudo-system  $\alpha P-\beta P$  enables us to explain the peculiar behaviour of phosphorus in an exceedingly simple way. In Fig. 1 in the first place the  $P,T$ -projection

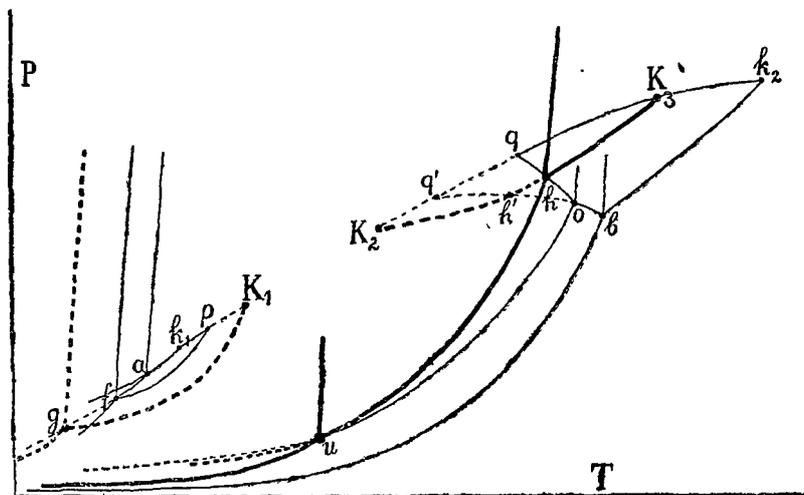


Fig. 1.

of the pseudo-binary system  $\alpha P-\beta P$  is indicated. The points  $p$  and  $q$  denote the critical endpoints and the only thing that makes this  $P,T$ -figure somewhat less simple than that of ether-anthraquinone is this that the three-phase line  $go$ , which refers to the equilibrium between red mixed crystals, liquid, and vapour, at  $o$  passes into

the three-phase line  $ob$ , which holds for the coexistence between violet mixed crystals, liquid, and vapour.

If these latter three-phase lines are prolonged towards lower temperatures, this line must terminate in a metastable critical endpoint  $q'$ . From the triple point  $O$  two more three-phase lines start, of which  $OU$  relates to the equilibrium between violet mixed crystals, red mixed crystals, and vapour. We have now discussed what is peculiar in the  $P,T$ -figure of the pseudo-system. If in this figure we now draw the  $P,T$ -lines of the unary system, we get what follows. The vapour-tension line of the liquid white phosphorus, which must be considered as a supersaturated solution, lies under the three-phase line  $fp$ , and meets the metastable part of the plaitpoint curve at  $K_1$ . If the critical temperature calculated from the surface tension is accepted as correct, this point lies at  $422^\circ$  and 18 atmospheres. At the triple point of the red phosphorus, which was found at  $588^\circ,5$  and 42 atmospheres by Mr. BOKHORST <sup>1)</sup>, liquid is formed again, and it is now clear that the vapour tension line for liquid phosphorus starting from this point, has nothing to do with the vapour tension line of molten white phosphorus.

Now it is interesting to question how the metastable part of the vapour tension line of liquid red phosphorus prolonged towards lower temperatures will run. In fig. 1 one of the possibilities is drawn. In this it is assumed that the said vapour tension line meets the metastable intermediate part of the plaitpoint curve in  $K_2$ , and will therefore end in a *lower*-critical endpoint. As was stated before unmixing can also occur in the metastable region, and in this case when the plait is closed the point  $K_2$  can occur at much lower temperature and pressure than  $K_1$ , and then the line  $hK_2$  will lie under  $gK_1$ . This line cannot extend far towards low temperature, however, for then there would have to exist two different kinds of liquid white phosphorus, of which nothing has appeared. If the plait was open, the metastable part of the vapour tension line of the liquid red phosphorus would also proceed to lower temperatures under  $gK_1$ , but the objection advanced just now, is then of force, so that the most probable assumption by far is that the said vapour tension line terminates in a metastable lower-critical endpoint  $K_2$ . We shall get perfect certainty when the prolongations of the two vapour tension lines  $gK_1$  and  $hK_2$  intersect. Investigations specially undertaken for this purpose may soon decide this. It must further be noted that the vapour tension line of red phosphorus,

<sup>1)</sup> The former determinations were made with an apparatus which appeared to yield inaccurate results at high temperatures.

which starts from  $h$  at about  $460^\circ$  must meet the line  $OU$ , as the transition point between red and violet phosphorus lies at this temperature. So a triple point occurs again in  $U$ , and the only stable unary equilibrium below this point is that between violet phosphorus and vapour.

A similar  $PT$ -figure holds for cyane, as Fig. 2 shows. Here it is remarkable that it was not necessary to find the critical point  $K_1$  by calculation as for white phosphorus, but that it could be easily observed. On the other hand, the triple point of the red modification of phosphorus could be determined by experiment; the triple point of paracyane, on the contrary, is not to be realised because the substance decomposes before that time. As we know only one kind of liquid cyane below the temperature of the critical

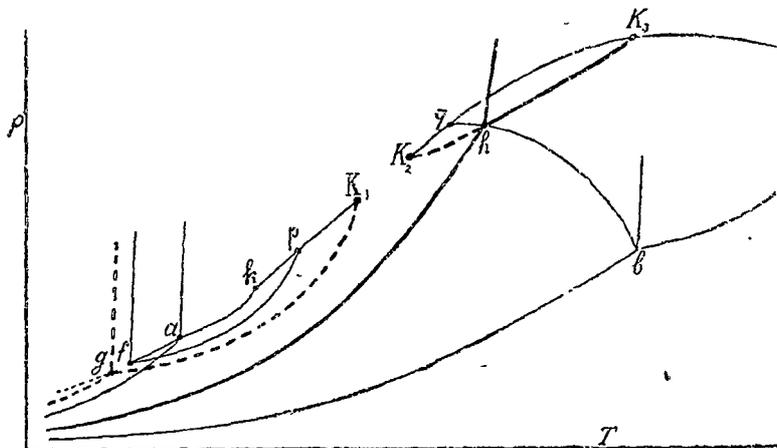


Fig. 2.

point  $K_1$ , it is assumed here too that the metastable prolongation of the vapour tension line of molten paracyane must end in a lower critical endpoint  $K_2$ .

We see therefore that according to the earlier view not a single connection could be indicated between the different phases of the white phosphorus on one side and the violet and the red phosphorus on the other side; nor could any be given between cyane and paracyane, though some connection *must* exist, because the different forms of the phosphorus resp. cyane can be converted into each other by some means or other.

The theory of allotropy demonstrates this connection in a very simple way, as Figs. 1 and 2 show.

A deeper insight is obtained when the projection of the three-phase regions of the pseudo-binary and that of the two-phase regions of the unary system on the  $T$ - $X$ -surface are drawn. These projec-

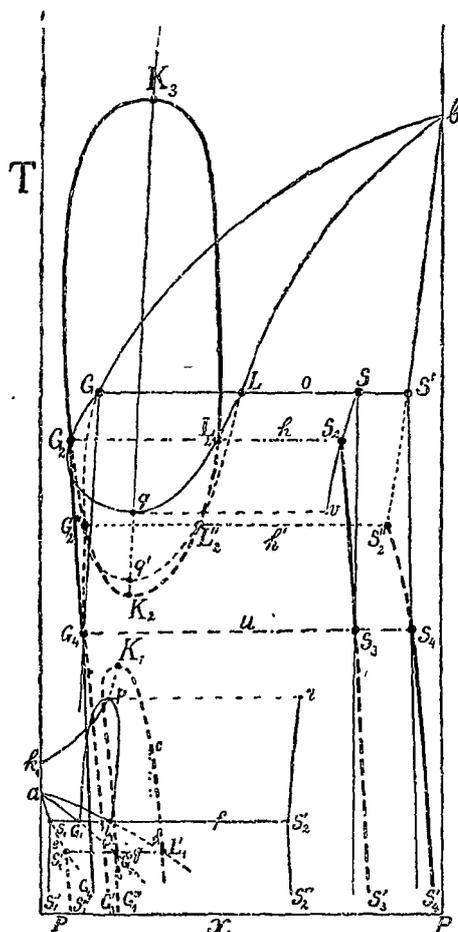


Fig. 3.

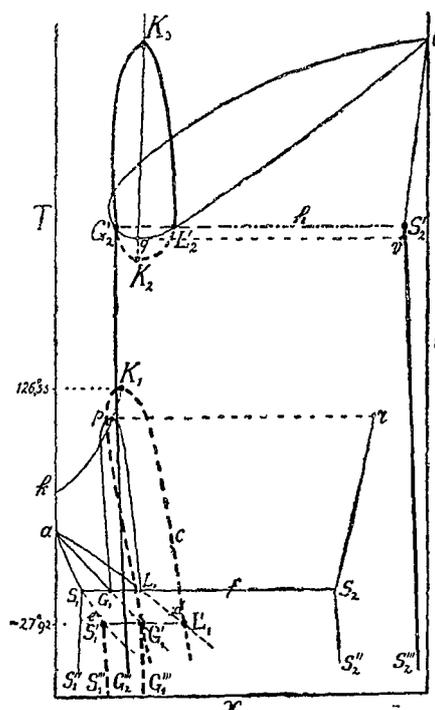


Fig. 4.

tions are given in the figures 3 and 4, and they are easy to understand if we compare what was published before about the system ether-anthraquinone and the system phosphorus.

*Anorg. Chem. Laboratory of the University.*

*Amsterdam, May 30, 1913.*

**Chemistry.** — “*On the pseudo system Methylrhodanide — Methyl-mustard oil.*” By Prof. A. SMITS and H. VIXSEBOXSE. (Communicated by Prof. A. F. HOLLEMAN).

In 1906<sup>1)</sup> WALDEN stated the fact that different salts dissolved in methylrhodanide  $\text{CH}_3\text{SCN}$  do not bring about a rise of the boiling point, but a lowering of the boiling point.

It appears from the following table that this phenomenon is brought about by the salts  $\text{N}(\text{C}_3\text{H}_7)_4\text{I}$ ,  $\text{N}(\text{C}_2\text{H}_5)_4\text{I}$ ,  $\text{CdI}_2$ , and  $\text{NH}_4\text{CNS}$ .

<sup>1)</sup> Zeitschr. f. phys. Chem. 55, 297 (1906).



naturally led to expect the same for methylrhodanide, and it was now naturally supposed that the methylrhodanide, as it is obtained in the preparation, is not yet in internal equilibrium, and that the lowering of the boiling point or the increase of the vapour tension which occur, are a consequence of the setting in of the internal equilibrium which is possibly reached with appreciable velocity under the influence of the said salts. These salts would therefore be catalysts.

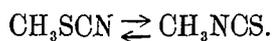
Now it is known that in sealed tubes heated to 180° methylrhodanide is partly converted to the isomer methyl mustard oil<sup>1)</sup>.

We have here an intramolecular atomic shifting



As methylrhodanide boils at 130,5° and the isomer, the mustard oil at 119°, this conversion when accelerated by the said salts, might give rise to a lowering of the boiling point resp. increase of vapour tension.

This consideration led us to the supposition that the internal equilibrium which was mentioned just now, might be an equilibrium between the isomer molecules  $\text{CH}_3\text{SCN}$  and  $\text{CH}_3\text{NCS}$



Before we now proceeded to test this supposition, the difference of vapour tension between pure methylrhodanide and a saturate solution of  $\text{CdI}_2$  in methylrhodanide was examined at different temperatures in a small tensimeter, in which mercury was used as the liquid measuring the tensions.

It was remarkable to see that in the first moments the saturate  $\text{CdI}_2$ -solution possessed a smaller vapour-tension, but soon the difference of vapour tension passed through zero, and then obtained the opposite sign. At 25° the position of the mercury manometer appeared not to change any more after a fortnight, and the increase of vapour tension amounted to 11,2 mm. Hg. The same experiments were also made at higher temperatures, and, as was expected, they gave a greater difference of vapour tension as result. These were, however, less reliable quantitatively, because mercury seems to have analysing power at higher temperatures. Accordingly glass-spring manometers will be used to obtain more accurate results when the investigation is continued.

After it had thus appeared that by the addition of  $\text{CdI}_2$  after a transient decrease of vapour tension actually an *increase of vapour*

<sup>1)</sup> For allylrhodanide conversion to mustard oil already takes place after distillation under atmospheric pressure.

*tension* takes place, the following experiment was undertaken. A glass vessel filled with methylrhodanide and an excess of  $\text{CdI}_2$  was exhausted, and then kept for 6 weeks in a thermostat of  $20^\circ$ . Then the vessel was opened and the liquid investigated, in the first place as to its boiling point, and in the second place as to the formation of mustard oil.

Before we proceeded to the determination of the boiling point of this liquid the boiling-point of the pure methylrhodanide used by

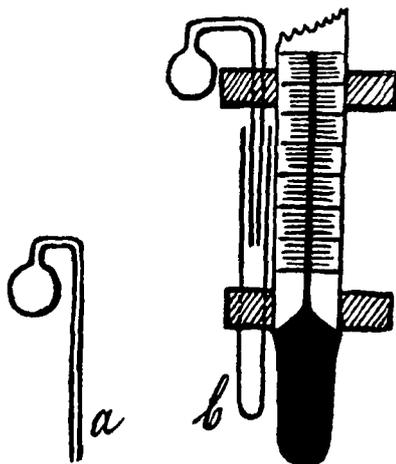


Fig. 1.

Fig. 2.

us, was examined, by the exceedingly convenient method of SMITH<sup>1)</sup>, which enables us to investigate extremely small quantities of substance. A tube of the shape indicated in fig. 1, is filled with the liquid which is to be examined, then fastened to a thermometer (fig. 2), and placed in a suitable liquid bath, which is slowly heated, and vigorously stirred. At the boiling-point a continuous stream of vapour bubbles escapes from the open end. If then the temperature is again slowly lowered, the escaping of the vapour bubbles will suddenly cease as soon as the temperature has fallen somewhat below the boiling-point. This point can be sharply observed, and the experiment may be so often repeated till all the substance has evaporated.

As we used an oil-bath, and  $\text{CH}_3\text{SCN}$  easily dissolves in oil at  $130^\circ$ , we made the narrow tube *a* of the boiling bulb open into a tube *b* which was  $\pm 2$  mm. wider. In this way we succeeded in making the escaping vapour bubbles very clearly visible and prevented that they immediately dissolved in the rapidly moving oil.

When the experiment was repeated till almost all the liquid was evaporated, the pure methylrhodanide gave the following result:

1st bulb	2nd bulb
130.9°	130.9°
131.4	131.1
131.5	131.3
131.5	131.4 almost all the liquid has disappeared

<sup>1)</sup> Americ Chem. Soc. 32, 897 (1910).

from which appears that it was *not* perfectly pure, but that it contained a trace of a more volatile component which pretty quickly disappears when the liquid is boiled, so that after  $\pm \frac{1}{4}$  has evaporated a boiling-point is found which is constant within the errors of observation, viz.  $\pm 131.3^\circ$ .

After these determinations the liquid was examined which at  $20^\circ$  had been in contact with  $\text{CdI}_2$  for six weeks. In the determination of the boiling-point in the way described just now the following result was obtained, the experiment being repeated 18, resp. 19 times with the same filling.

1 <sup>ste</sup> bulb	2 <sup>nd</sup> bulb
123.6°	124.8°
124.5	125.9
125.4	127.0
127.4	128.0
129.3	128.8
130.2	129.6
131.1	130.1
131.7	130.5
131.8	130.9
131.8	131.3
131.9	131.7
132.0	131.8
132.3	131.9
132.6	132.2
132.9	132.6
133.2	133.4
134.0	134.3
almost empty 136.5	135.8
	136.4 almost empty

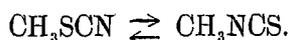
From these experiments it appears with the greatest clearness that by the contact with  $\text{CdI}_2$  at  $20^\circ$  the boiling-point of the methylrhodanide is lowered by an amount of at least  $7^\circ.7$  (1<sup>st</sup> bulb), but at the same time the course of the boiling point shows that on conti-

nued evaporation the lowering of the boiling-point becomes smaller and smaller, soon passes through zero, and then becomes a rise of the boiling-point. This phenomenon shows that a more volatile component with lower boiling-point is formed in the methylrhodanide, and that the vapour is much richer in this component than the coexisting liquid, so that this new component can easily be expelled on prolonged evaporation.

That under these circumstances the lowering of the boiling-point of the substance under investigation is finally replaced by a rise of the boiling-point is easy to understand, as the liquid contained dissolved  $\text{CdI}_2$ .

That the *first* experiment with the first bulb yielded  $123^{\circ}6$ , and that with the second bulb  $124^{\circ}8$  is owing to this that more vapour escaped from the second bulb than from the first bulb before the first determination was made.

Finally we undertook the chemical investigation of another part of the same liquid. This chemical investigation consisted in this that we examined whether mustard oil had formed in this liquid. In order to do this we boiled the liquid with dilute sulphuric acid in a flask which was closed by means of a pierced cork with a long glass tube. It is known that in the presence of mustard oil  $\text{H}_2\text{S}$  is formed under these circumstances, which can be immediately demonstrated by means of a lead-acetate paper laid on the mouth of the long glass tube. The result was a very clear hydrogen sulphide reaction, which quite failed to appear in the investigation of the "pure" methylrhodanide <sup>1)</sup>, which was a conclusive proof that the lowering of the boiling point is accompanied with the formation of mustard oil, so that it is all but certain that the peculiar phenomenon which was observed for the first time by WALDEN must be ascribed to the formation of this substance, and that when the substance behaves as a unary one we shall have to do with the following internal equilibrium.



It is clear that if on continued investigation the above equilibrium really appears to exist, we have again a very interesting system here, which urgently calls for further investigation. This will certainly be taken in hand; first of all the pseudo-system methylrhodanide-methyl mustard oil will be examined, and then by means of catalysers the situation of the unary system will be determined in

<sup>1)</sup> Probably this contains also a trace of mustard oil, which in the experiment escapes the action of the  $\text{H}_2\text{SO}_4$ .

this pseudo-system, as well with regard to the gaseous as to the liquid and the solid phase.

The phenomenon, observed here with great probability, of internal equilibrium between structure isomers will be of pretty general occurrence without any doubt, so that it will not be difficult to discover many more interesting examples, which are accessible to experiment.

*Anorg. Chem. Lab. of the University.*

*Amsterdam, May 27, 1913.*

**Physics.** — “*On the point in which the solid state disappears as an answer to the question in how far this point can be compared to the critical point of a liquid. The easiest way to do this is by means of the  $\psi$ -curve*”. By Prof. J. D. VAN DER WAALS.

(Communicated in the meeting of February 22, 1913).

If the  $\psi$ -curve is drawn at the triple point, the same straight line is touched by: 1. the  $\psi$ -curve liquid-vapour, 2. the  $\psi$ -curve for the solid substance. Let us put the case that occurs most frequently, in which  $v_s < v_l < v_g$ . On rise of the temperature the  $\psi$ -curves descend, but not in an equal degree. The liquid-vapour curve descends more than the curve for the solid substance. Relatively  $\psi_s$  ascends therefore. And accordingly the tangent for the coexisting states liquid-vapour, and that for the coexisting states liquid-solid are separated. The pressure has increased, but that for the coexistence solid-liquid far more than for the coexistence liquid-vapour. When the temperature continues to rise the  $\psi$ -curve for the liquid will more and more approach the  $\psi$ -curve for the solid substance, and it will reach it at the temperature at which the solid state disappears at infinite pressure. At the critical point liquid-vapour these two states are identical; the solid state on the other hand has been expelled by the liquid state. This, however, takes place at a pressure equal to infinity and so a volume equal to  $v_0$ . Above this temperature the solid state no longer exists, but the liquid state does. I have shown elsewhere, however, that then, when the pressure again approaches infinity, and hence the volume to  $v_0$ , the viscous-solid state will probably appear.

If we now consider the case, in which, as for water and ice  $v_s > v_l$ , the  $p, T$ -line for the coexisting phases runs from the triple point to lower temperatures. Now two cases are possible, viz. that

this line continues to proceed to lower temperatures, and  $p$  continues to rise to infinitely great; or that after having reached certain minimum of temperature, it proceeds to higher temperatures, again before  $p$  has become infinitely great. If the latter should be the case there is in the  $p, T$ -line of the coexistence a point in which  $\frac{dp}{dT} = \frac{\eta_l - \eta_s}{v_l - v_s} = \infty$ , or  $v_l = v_s$ . And for the points of the line of coexistence which lie higher,  $v_l$  has then become  $> v_s$ , and the above described case occurs again. Nor is there a difference of significance when  $v$  always remains greater than  $v_l$ . At the temperature of the disappearance of the solid state, which is then lower than the temperature of the triple point, this disappearance takes place at a pressure equal to infinity. Since, however,  $v_s$  is always greater than  $v_l$ , we can hardly continue to speak of "expelled". The volumes  $v_s$  and  $v_l$  have now however both become equal to  $v_0$ , and on rise of the temperature it is again only the liquid which can exist.

Assuming here again that liquids under a very high pressure, and so in a very small volume, almost equal to  $v_0$ , assume the viscous state, we might point out the following difference. If  $v_s < v_l$  these substances have the solid state in volumes which are little greater than  $v_0$  at temperatures somewhat below that of the disappearance of the solid state; they have the viscous state on increase of volume, and on further increase of the volume they have the liquid state. If on the other hand  $v_s > v_l$ , the succession of the 2 solid states is reversed.

At the highest temperature for the existence of the solid state the difference between solid and viscous has probably disappeared under infinite pressure.

**Physics.** — "*On a system of curves occurring in EINSTEIN'S theory of gravitation*". By Ch. H. VAN OS. (Communicated by Prof. H. A. LORENTZ).

In Prof. P. EHRENFEST'S communication on EINSTEIN'S gravitation theory (Vol. XV, p. 1187) a system of  $\infty^2$  curves occurs which is determined by the condition that a hyperboloid :

$$H \equiv A(x^2 + y^2 - z^2) + Bx + Cy + Dz + E = 0, \quad \dots (1)$$

a so-called "light hyperboloid" can always be brought through two of these curves. This system will be examined more closely here.

The curves are intersections of the hyperboloids  $H$ . As they must also have a conic  $K_\infty$

$$x^2 + y^2 - z^2 = 0, w = 0 \quad . \quad . \quad . \quad . \quad . \quad (2)$$

at infinity in common, so that their intersections must degenerate, the considered curves are either straight lines or conics.

A. All the curves are straight lines. Then they must either all pass through one point, so that the  $H$ 's degenerate into planes, or (at most with the exception of one) as generatrices of the  $H$ 's, form angles of  $45^\circ$  with the  $z$ -axis, hence be so-called "light lines".

B. Not all the curves are straight lines. Through one conic pass  $\infty^1$   $H$ 's, because these  $H$ 's have also  $K\infty$ , so a biquadratic spacial curve in common. Hence they form a sheaf:

$$H_1 + \lambda H_2 = 0. \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Let us take  $\frac{B}{A} = \xi, \frac{C}{A} = \eta, \frac{D}{A} = \zeta, \frac{E}{A} = \tau$  as coord. of a point in an

$R_4$ , the image point of the corresponding  $H$ . The image point of an  $H$  of the sheaf (3) then becomes:

$$\frac{\xi_1 + \lambda \xi_2}{1 + \lambda}, \quad \frac{\eta_1 + \lambda \eta_2}{1 + \lambda}, \quad \frac{\zeta_1 + \lambda \zeta_2}{1 + \lambda}, \quad \frac{\tau_1 + \lambda \tau_2}{1 + \lambda}.$$

The image points of the  $H$ 's of this sheaf therefore form a straight line, the image line of this sheaf.

Two arbitrary sheaves of the system have always an  $H$  in common, viz that passing through the base curves of these sheaves. Hence the homologous straight lines intersect each other in the image point of this  $H$ . The image lines of the considered sheaves form a system of  $\infty^2$  straight lines in  $R_4$  such that two of these straight lines always intersect. Now two cases may be distinguished:

a. All the straight lines pass through one point. Then all the sheaves have the  $H$  whose image point this is, in common, and accordingly their base curves all lie on one hyperboloid. This case is trivial.

b. Not all the straight lines pass through one point. If a plane is brought through two of them, every other will have the points in which it intersects the two first, in common with this plane, and therefore lie entirely in this plane. Then all the image lines and image points lie in one plane. If  $(\xi_1, \eta_1, \zeta_1, \tau_1), (\xi_2, \eta_2, \zeta_2, \tau_2), (\xi_3, \eta_3, \zeta_3, \tau_3)$  are three of these image points, the coordinates of the others are:

$$\xi = \frac{\lambda_1 \xi_1 + \lambda_2 \xi_2 + \lambda_3 \xi_3}{\lambda_1 + \lambda_2 + \lambda_3}, \quad \eta = \frac{\lambda_1 \eta_1 + \lambda_2 \eta_2 + \lambda_3 \eta_3}{\lambda_1 + \lambda_2 + \lambda_3} \text{ etc.};$$

if this is substituted in (1), we find for the general equation of the  $H$ 's of the system:

$$\lambda_1 H_1 + \lambda_2 H_2 + \lambda_3 H_3 = 0.$$

So these form a net. If we put  $z = it$ , this is changed into a net of spheres. So all the  $H$ 's, just as all the spheres of a net, pass through two points  $\Omega_1$  and  $\Omega_2$ . Hence the curves which are their intersections also pass all through these points.

Through the joining line  $\Gamma$  of  $\Omega_1$  and  $\Omega_2$  pass  $\infty^1$  planes. As there are  $\infty^2$  curves,  $\infty^1$  curves lie in each of them.

All of these pass through  $\Omega_1$  and  $\Omega_2$ , and through the points of intersection of their plane with  $K\infty$ , and so they form a sheaf. Now the general shape of the system is determined.

The following cases may now be distinguished.

I.  $\Gamma$  lies at infinity.

a.  $\Omega_1$  and  $\Omega_2$  do not lie both on  $K\infty$ . Then the plane at infinity has a conic and another point in common with each of the  $H$ 's, and so it constitutes part of it. So the  $H$ 's degenerate into planes, the curves into straight lines.

b.  $\Omega_1$  and  $\Omega_2$  both lie on  $K\infty$ . The curves in each plane have two pairs of coinciding points at infinity in common, and so they are concentric, similar, and similarly placed. The centres in the successive planes are the centres of parallel sections of one of the  $H$ 's and lie therefore on one straight line.

II.  $\Gamma$  does not lie at infinity. Now the following cases are possible:

1. The angle of  $\Gamma$  with the  $z$ -axis is  $> 45^\circ$
2. „ „ „  $\Gamma$  „ „  $z$ -axis „  $= 45^\circ$
3. „ „ „  $\Gamma$  „ „  $z$ -axis „  $< 45^\circ$

- |                                        |                                  |
|----------------------------------------|----------------------------------|
| a. $\Omega_1$ and $\Omega_2$ are real. | b. They coincide.                |
| c. They are conjugate imaginary.       | d. One of them lies at infinity. |
| e. Both lie at infinity.               |                                  |

In the cases 1d, 1e, 3d, and 3e the plane at infinity has besides  $K\infty$  another point in common with each of the  $H$ 's, so that the  $H$ 's degenerate into planes.

In the cases 2a, 2b, and 2c  $\Gamma$  intersects  $K\infty$ , and has therefore 3 points, viz. this point of intersection,  $\Omega_1$  and  $\Omega_2$  in common with each of the  $H$ 's; so  $\Gamma$  is a common generatrix of it. As the  $H$ 's have moreover  $K\infty$  in common, their further sections, i.e. the considered curves, are straight lines.

At 2d the curves in every plane have a twopoint contact, at 2e a three-point contact at infinity.

In the cases 1b and 1c the tangents of all the curves form angles  $> 45^\circ$  with the  $z$ -axis. If they are considered as world lines, the

corresponding velocities are  $>$  the light-velocity, which is physically excluded.

#### REMARK.

It is easy to extend the problem raised by Prof. EHRENFEST to an  $n$ -dimensional laboratory, or to an  $(n + 1)$ -dimensional "world".

It must again be possible to bring through two of the world-lines a ruled surface, on which two systems of light-lines lie in such a way that every straight line of the 1st system intersects every line of the 2nd system. If through two straight lines of the first system an  $R_3$  is brought, every straight line of the 2nd system has 2 points in common with this  $R_3$ , and is therefore entirely contained in it; the whole surface lies then in an  $R_3$ , and is a hyperboloid  $H$ .

The curves do not all lie in the same  $R_n$ ; therefore the hyperboloids do not do so either. Now two  $H$ 's lying in different  $R_3$ 's have at most a conic in common in the plane of intersection of these  $R_3$ 's; so the curves are straight lines or conics.

A. The curves are in general straight lines.

B. " " " " " conics. We will only consider this case.

An  $H$  can always be brought through two curves, hence an  $R_3$  can be brought through their planes; these planes therefore always intersect each other along a straight line.

a. All the planes do not pass through one straight line. If an  $R_3$  is brought through two of them, every other plane has two straight lines in common with this  $R_3$ , and so it lies entirely in it. Then all the curves would lie in one and the same  $R_3$ , which is contradictory to what was put.

b. So all the planes pass through one straight line  $\Gamma$ . Now the curves will all cut  $\Gamma$  in the same two points.

For, if an  $H$  is brought through 2 of the curves, their points of intersection with  $\Gamma$  are also the points of intersection of this  $H$  with  $\Gamma$ . If there were more than two,  $\Gamma$  would be a generatrix of  $H$ , but then a plane through  $\Gamma$  could further only have a straight line in common with  $H$ , and so the two curves would be straight lines.

In this way it is proved that the world lines are either straight lines or hyperbolae, which all pass through 2 same points of a straight line  $\Gamma$ . In each of the  $\infty^{n-1}$  planes through  $\Gamma$  lie again  $\infty^1$  curves, forming a sheaf. The number of fields of gravitation arising in this way in an  $n$ -dimensional laboratory therefore amounts to  $\infty^{2n+2}$ .

**Physics.** — “Some difficulties and contradictions met with in the drawing up of the equation of state.” By J. J. VAN LAAR. (Communicated by Prof. H. A. LORENTZ).

(Communicated in the meeting of April 25, 1913).

1. The latest papers by VAN DER WAALS on the equation of state<sup>1)</sup> — also in connection with my own recent investigations<sup>2)</sup> — induce me to publish the following remarks, which may not be entirely devoid of interest at the present stage of the question.

When we start from VAN DER WAALS'S fundamental equation, viz.

$$p = \frac{RT}{v-b} - \frac{a}{v^2}, \dots \dots \dots (1)$$

and for the present disregard association or quasi-association, there are — the chosen form of the equation of state being retained — only two possibilities for the explanation of the found deviations from the above equation:

The quantity  $b$  is still a function of  $v$  (and possibly of  $T$ ).

“ ” “  $a$  ” “ ” “ ” “  $v$ , or of  $T$ .

If at first we still disregard the variability with the temperature, we shall in the first place ascertain the consequences of the variability of  $b$  with  $v$ .

If  $b = f(v)$ , the above equation of state gives at the critical point:

$$\left. \begin{aligned} \left(\frac{dp}{dv}\right)_t &= -\frac{RT}{(v-b)^2}(1-b') + \frac{2a}{v^3} = 0 \\ \left(\frac{d^2p}{dv^2}\right)_t &= \frac{2RT}{(v-b)^3}(1-b')^2 + \frac{RT}{(v-b)^2}b'' - \frac{6a}{v^4} = 0 \end{aligned} \right\}$$

where  $b'$  is written for  $\frac{db}{dv}$ , and  $b''$  for  $\frac{d^2b}{dv^2}$ .

Hence it follows from this that

$$\left. \begin{aligned} RT_k(1-b'_k) &= \frac{2a(v_k-b_k)^2}{v_k^3} \\ RT_k \left[ 2(1-b'_k)^2 + (v_k-b_k)b''_k \right] &= \frac{6a(v_k-b_k)^3}{v_k^4} \end{aligned} \right\}$$

<sup>1)</sup> These Proc. Vol. XV, 903—910; XV, p. 971—981; XV, p. 1131—1145. (To be cited as v. d. W I, II, and III).

<sup>2)</sup> These Proc. Vol. XIV, p. 278—298; XIV, p. 428—442; XIV, p. 563—579; XIV, p. 711—724. (To be cited as v. L. I, II, III and IV). Further XIV, p. 771—781; XIV, p. 1091—1107. (To be cited as v. L. A and B.)

Division gives:

$$3 \frac{v_k - b_k}{v_k} = 2(1 - b'_k) + (v_k - b_k) \frac{b''_k}{1 - b'_k},$$

hence, putting  $v_k b''_k : (1 - b'_k) = \beta''_k$ :

$$\frac{v_k - b_k}{v_k} = \frac{2(1 - b'_k)}{3 - \beta''_k}.$$

With  $\frac{v_k}{b_k} = r$ , we get finally:

$$\frac{r-1}{r} = \frac{2}{3} \frac{1 - b'_k}{1 - \beta''_k / r} \dots \dots \dots (2)$$

Further follows from the first of the above equations for  $RT_k$ :

$$RT_k = \frac{a}{b_k} \cdot \frac{2b_k(v_k - b_k)^2}{v_k^3(1 - b'_k)},$$

hence:

$$RT_k = \frac{a}{b_k} \cdot \frac{1}{r} \left( \frac{r-1}{r} \right)^2 \frac{2}{1 - b'_k} = \frac{8}{27} \lambda_1 \frac{a}{b_k} \dots \dots (3)$$

We find finally for  $p_k$  from the equation of state by substitution of the value of  $RT_k$ :

$$p_k = \frac{a}{v_k^3} \frac{2(v_k - b_k)}{1 - b'_k} - \frac{a}{v_k^2} = \frac{a}{v_k^2} \left[ \frac{v_k - b_k}{v_k} \frac{2}{1 - b'_k} - 1 \right],$$

i.e.

$$p_k = \frac{a}{b_k^2} \cdot \frac{1}{r^2} \left[ \frac{r-1}{r} \frac{2}{1 - b'_k} - 1 \right] = \frac{1}{27} \lambda_2 \frac{a}{b_k^2} \dots \dots (4)$$

Then ( $v_k = r b_k$ ):

$$s = \frac{\left( \frac{r-1}{r} \right)^2 \frac{2}{1 - b'_k}}{\frac{r-1}{r} \frac{2}{1 - b'_k} - 1} = \frac{8 \lambda_1}{r \lambda_2} \dots \dots \dots (5)$$

is found for the quantity  $s = \frac{RT_k}{p_k v_k}$ .

If therefore  $b'_k$  and  $b''_k$  are known,  $r$  is given by (2), and further  $RT_k$ ,  $p_k$ , and  $s$  by (3), (4), and (5). Reversely  $b'_k$  and  $b''_k$  can be calculated when  $r$  and  $s$  are known.

Thus e.g. with  $s = 3,774$  ( $1 : s = 0,265$ ) and  $r = 2,11$  from (5) -- as then  $(r - 1) : r = 0,526$  and  $(r - 1)^2 : r^2 = 0,277$  -- for  $2 : (1 - b'_k)$  we find the value 2,21, hence  $b'_k = 0,094$ . From (2) we then calculate further  $\beta''_k = -0,44$ , i.e.  $v_k b''_k = -0,40$ .

For  $\lambda_1$  and  $\lambda_2$  we then find from (3) and (4)  $\lambda_1 = 0,98$ , and also  $\lambda_2 = 0,98$ .

*Remark.* The values of  $\lambda_1$  and  $\lambda_2$  found, change only very little when association or quasi association is assumed. Then the expressions for  $r = v_k : b_k$ ,  $RT_k$ ,  $p_k$  and  $s$ , indeed, become more intricate (cf. Van L. I and II), and we shall among others find — according as partial (very slight) association to *double* molecules is assumed, or association to *triple* ones — in which the quantity  $b$  changes in consequence of this association (loc. cit. I, p. 295—297; II, p. 428—431):

$r$	$b'_k$	$-v_k b''_k$	$\lambda_1$	$\lambda_2$	$\alpha_k$
2.114	0.0534	0.295	1.004	1.007	0.977
2.102	0.0319	0.196	1.010	1.019	0.972

out the values of  $\lambda_1$  and  $\lambda_2$  remain in the immediate neighbourhood of unity; that of  $\lambda_1$  on an average 1,007, and that of  $\lambda_2$  on an average 1,013; i.e. they are about 1% above unity, whereas when the association is disregarded, they remain about 2% below it.

For  $b'_k$  and  $-v_k b''_k$  lower values, viz. the mean values 0,043 and 0,25 are found when association is assumed; whereas 0,094 and 0,40 are found, when association is left out of account.

As appears from the above values of the factor  $\alpha_k$  of  $RT_k$  (resp.  $= (1 + \beta_k : 2$  or  $(1 + 2\beta_k) : 3$ ), the association at the critical point is still exceedingly slight<sup>1)</sup>; the mean value of  $\alpha_k$  being  $= 0,975$ , on an average only  $2\frac{1}{2}\%$  of the simple molecules have aggregated to multiple ones.

<sup>1)</sup> In their interesting and thorough paper on the equation of state in the Encyklopädie der Math. Wiss. (12 Sept. 1912, p 615—945) KAMERLINGH ONNES and KEESOM make the very true remark on p. 177 (paging of the reprint in the "Comm."), that it is going too far to ascribe every deviation from the ideal equation of state to association. Also my statement in the TEYLER-paper cited there, is too sweeping in this respect. It appears sufficiently from the above remarks that the simple assumption of the variability of  $b$  with  $v$  can also satisfactorily account for these deviations (see also § 2). It remains of course to be seen to what this variability of  $b$  is due: in a quasi or in a real diminution of the volume of the molecules (v. D. WAALS) — or in a variation of  $b$  also in consequence of the association (v. L. I and II).

On this occasion, in connection with the footnote on p. 178 in the cited paper by KAMERLINGH ONNES and KEESOM, we may remind of the fact that according to my considerations there would indeed be double and triple molecules in the neighbourhood of the critical temperature — but only to an exceedingly slight amount, viz. about  $2\frac{1}{2}\%$  (see above).

Also the value of  $r$ , viz. 2,11 on an average, remains in the neighbourhood of 2,1, the value found for it experimentally.

I calculated all these values then not from those of  $s$  and  $r$ , but from those of  $s$  and  $f$ , viz.  $s = 3,774$ ,  $f = 7$ .

It is seen that the assumption of possible *association* does not bring a *real change* in the values of the *critical* quantities (determined by  $r$ ,  $\lambda_1$ , and  $\lambda_2$ ) — and may therefore be left out of account in their determination.

Another *Remark*. We put  $v_k : b_k = r$  in the above, and *not*  $v_k : b_g$  (v. D. W. l. c.). In the expressions for the critical quantities namely  $b_k$  occurs, and *not*  $b_g$  — and therefore to get more certainty in the formulae, and to remain independent of the theoretically and experimentally somewhat unwieldy relation  $b_g : b_k$ , I have thought I ought to introduce  $b_k$  and not  $b_g$  into the formulae (cf. v. L. A., p. 772). [According to the association theory, see v. L. II, p. 422 and 431,  $b_g : b_k$  is resp.  $= 1,03$  or  $= 1,015$  according as partial association (to an amount of on an average only about  $2\frac{1}{2}\%$ , see above) to double or to triple molecules is assumed].

There is another advantage in putting  $v_k : b_k = r$ , namely this that now the factors  $\lambda_1$  and  $\lambda_2$  in the formulae (3) and (4) for  $RT_k$  and  $p_k$  are much nearer unity than when  $b_g$  is introduced. For both for  $RT_k$  and for  $p_k$  (leaving the factor  $r-1$  out of account)  $r = v_k : b_k$  occurs to the *third* power, so that the deviation of the ratio  $b_g : b_k$  from unity will be found in  $\lambda_1$  and  $\lambda_2$  at least *three times enlarged*. If therefore according to VAN DER WAALS  $b_g : b_k = 1,04$  à  $1,05$ , or according to the above  $1,015$  à  $1,03$  <sup>1)</sup>, hence on an average about 1,03,  $\lambda_1$  and  $\lambda_2$  can differ about **10%** from unity when  $r = v_k : b_g$  is assumed instead of  $r = v_k : b_k$ , and the relations drawn up by VAN DER WAALS between  $r$ ,  $s$ , and  $f$  will be valid *only by approximation*, whereas they may be considered as *almost entirely accurate* when  $r = v_k : b_k$  is introduced.

<sup>1)</sup> As  $rs = 8 \frac{\lambda_1}{\lambda_2}$ ,  $b_g : b_k$  may be determined from:

$$\frac{b_g}{b_k} = \frac{r}{r'} = \frac{rs}{r's} = 8 \frac{\lambda_1}{\lambda_2} : r's,$$

when  $r' = v_k : b_g$  is known from experiment.

As  $\frac{r-1}{r} = \frac{s}{f}$  or  $r \left(1 - \frac{s}{f}\right) = 1$  follows from (6) — see § 2 — also

$r' \left(1 - \frac{s}{f}\right) = \frac{r'}{r} = \frac{b_k}{b_g}$ , from which the relation  $b_g : b_k$  may also be determined.

[When association is taken into account, the factor  $\alpha_k$  is added to  $s$ ].

2. The quantity  $f$ . Relations between  $f$ ,  $r$ , and  $s$ .

When neither  $a$  nor  $b$  is a function of  $T$ , it follows from (1) that

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b}, \text{ or } = \frac{1}{T} \left(p + \frac{a}{v^2}\right),$$

and so also :

$$\frac{T}{p} \left(\frac{dp}{dT}\right)_v = \frac{RT}{p(v-b)}, \text{ or } = 1 + \frac{a}{pv^2}.$$

At the critical point  $\left(\frac{dp}{dT}\right)_v = \left(\frac{dp}{dT}\right)_{\text{coex.}} = \frac{dp}{dT}$ , so that there

$$f = \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = \frac{RT'_k}{p_k(v_k-b_k)} = s \frac{v_k}{v_k-b_k}, \text{ or } = 1 + \frac{a}{p_k v_k^2}.$$

After substitution of the value  $s$  from (5),  $p_k$  from (4), and  $v_k = r b_k$ , we get :

$$f = s \frac{r}{r-1} = \frac{8}{r-1} \frac{\lambda_1}{\lambda_2}, \text{ or } f-1 = \frac{27}{r^2} \frac{1}{\lambda_2} \dots \dots (6)$$

If in the second relation according to (5) we substitute  $\frac{s^2}{64} \left(\frac{\lambda_2}{\lambda_1}\right)^2$  for  $\frac{1}{r^2}$ , then

$$\frac{f-1}{s^2} = \frac{27}{64} \frac{\lambda_2}{\lambda_1^2} \dots \dots (7)$$

As  $r$  no longer occurs in this, VAN DER WAALS was justified in saying that this equation derived by him, viz.  $\frac{f-1}{s^2} = \frac{27}{64}$ , would be almost entirely exact, whereas the two others, viz, (5) and (6) with  $r' = v_k : b_g$ , would only be true by approximation. But as we already observed above, when not  $r'$  but  $r = v_k : b_k$  is taken, these latter equations too will hold with the same degree of accuracy as (7).

As, when association is disregarded,  $\lambda_1 = 0,977$  and  $\lambda_2 = 0,980$ ; whereas, when it is taken into account, on an average  $\lambda_1 = 1,007$ ,  $\lambda_2 = 1,013$ , the ratio  $\lambda_1 : \lambda_2$  will be  $= 1 - 0,003$  or  $= 1 - 0,006$  in (5) and (6), i.e. it may be put equal to unity. For  $\lambda_2 : \lambda_1^2$  we find 1,026 or 1,001, so that this ratio approaches unity still more closely than  $\lambda_1 : \lambda_2$  on assumption of association, but with disregard of it will not differ more from unity than 2 or 3 %. Finally  $1 : \lambda_2$  in the second equation (6) will remain either 2% above, or about 1% below unity.

The value 2,11 is found for  $r$  from (5) with  $s = 3,774$ , while the second equation (6) with  $f = 7$  also yields the value 2,11. Further  $s^2 : (f-1) = 14,24 : 6 = 2,37$ , and also  $64 : 27 = 2,37$ ; so

that equation (7) is accurately satisfied with these values of  $s$  and  $f$ .

With regard to the first equation (6) it should be borne in mind that when association is taken into account, a factor  $\alpha_k$  appears in the second member. (because then  $f$  becomes  $= \alpha_k RT_k : p_k (v_k - b_k)$ ). Thus :

$$f = \alpha_k s \frac{r}{r-1} = \frac{8}{r-1} \alpha_k \frac{\lambda_1}{\lambda_2},$$

in which according to the table in §1  $\alpha_k$  has the mean value of 0,975. (cf. also v. L. A., p. 772). From

$$f-1 = \frac{27}{r^2} \frac{1}{\lambda_2} ; \quad \frac{f-1}{s^2} = \frac{27}{64} \frac{\lambda_2}{\lambda_1^2}$$

$r$  and  $s$  may be expressed in  $f-1$ , and we find then :

$$r = \frac{3}{\sqrt{\frac{f-1}{3} \lambda_2}} ; \quad s = \frac{8}{3} \sqrt{\frac{f-1}{3} \frac{\lambda_1^2}{\lambda_2}}, \quad \dots \quad (8)$$

two relations also derived by VAN DER WAALS, — but now, the factors  $\lambda_1$  and  $\lambda_2$  having been taken into account, *quite accurate*.

Putting  $\lambda_1$  and  $\lambda_2 = 1$ , we find from this approximately, when  $f = 7$ :

$$r = \frac{3}{\sqrt{2}} = 2,12 ; \quad s = \frac{8}{3} \sqrt{2} = 3,77.$$

That the factor  $\sqrt{2}$  plays a part, I had already surmised before, without knowing the cause. See inter alia the Vorlesungen über theoretische und physik Chemie by VAN 'T HOFF, 3<sup>es</sup> Heft, p. 14, and the Vorwort p. VI (1900). Besides already in 1905 (Arch. TEYLER) I expressed some critical quantities in experimentally determinable quantities in a perfectly analogous way as later VAN DER WAALS — however with the exclusion of the quantity  $f$ , as the possibility that  $b$  and particularly  $a$  could be functions of the temperature, was not excluded by me. (Cf. also v. L. A., p. 773).

### 3. Difficulties and objections.

So far there is not a single objection, and if there were no other characteristic critical quantities than  $r$ ,  $s$ , and  $f$ , it would suffice to consider  $b$  as function of  $v$ , and to seek the cause of this variability. The association (or quasi-association) might then be accepted or left as a gratuitous addition. It would not be necessary.

But unfortunately, matters are different. There is namely one more characteristic quantity, i.e. the quantity  $\varphi$ , given by

$$\varphi = \frac{F-1}{F_k-1} \frac{\varepsilon}{d_1 d_2},$$



$$\left. \begin{aligned} \left(\frac{dp}{dT}\right)_v &= -\frac{RT}{(v-b)^2} (1-b') - a_k \left(-\frac{2\theta}{v^3} + \frac{\theta'}{v_k v^2}\right) = 0 \\ \left(\frac{d^2p}{dT^2}\right)_v &= \frac{2RT}{(v-b)^3} (1-b')^2 + \frac{RT}{(v-b)^2} b'' - a_k \left(\frac{6\theta}{v^4} - \frac{4\theta'}{v_k v^3} + \frac{\theta''}{v_k^2 v^2}\right) = 0 \end{aligned} \right\}$$

when  $\theta' = \frac{d\theta}{dn}$  and  $\theta'' = \frac{d^2\theta}{dn^2}$  .- ( $n = v : v_k$ ).

Hence:

$$\left. \begin{aligned} RT_k (1-b'_k) &= \frac{2a_k(v_k-b_k)^2}{v_k^3} (\theta_k - {}^1/2\theta'_k) \\ RT_k \left[ 2(1-b'_k)^2 + (v_k-b_k)b''_k \right] &= \frac{6a_k(v_k-b_k)^3}{v_k^4} \left( \theta_k - {}^2/3\theta'_k + {}^1/6\theta''_k \right) \end{aligned} \right\}$$

yielding by division:

$$3 \frac{v_k-b_k}{v_k} = \frac{2(1-b'_k) + (v_k-b_k) \frac{b''_k}{1-b'_k}}{(1-{}^2/3\theta'_k + {}^1/6\theta''_k) : (1-{}^1/2\theta'_k)}$$

as  $\theta_k$  apparently = 1.

With  $v_k : b_k = r, v_k b''_k : (1-b'_k = \beta''_k, (1-{}^2/3\theta'_k + {}^1/6\theta''_k) : (1-{}^1/2\theta'_k) = \omega$  we get:

$$\frac{r-1}{r} (3\omega - \beta''_k) = 2(1-b'_k),$$

or

$$\frac{r-1}{r} = \frac{2}{3} \frac{1-b'_k}{\omega - {}^1/3\beta''_k}, \dots \dots \dots (2a)$$

so that (2a) differs from (2) only in this, that now  $\omega - {}^1/3\beta''_k$  occurs in the denominator instead of  $1 - {}^1/3\beta''_k$ .

We now find for  $RT_k$  and  $p_k$ :

$$RT_k = \frac{a_k}{b_k} \cdot \frac{1}{r} \left(\frac{r-1}{r}\right)^2 \frac{2(1-{}^1/2\theta'_k)}{1-b'_k} \dots \dots \dots (3a)$$

$$p_k = \frac{a_k}{b_k^2} \cdot \frac{1}{r^2} \left[ \frac{r-1}{r} \frac{2(1-{}^1/2\theta'_k)}{1-b'_k} - 1 \right], \dots \dots \dots (4a)$$

s becoming:

$$s = \frac{\left(\frac{r-1}{r}\right)^2 \frac{2(1-{}^1/2\theta'_k)}{1-b'_k}}{\frac{r-1}{r} \frac{2(1-{}^1/2\theta'_k)}{1-b'_k} - 1} \dots \dots \dots (5a)$$

In this the factor  $1 - {}^1/2\theta'_k$  always occurs as a multiplier of  $2 : (1-b'_k)$ .

So with  $s = 3,774$  and  $r = 2,11$  we now find the value 2,21 for  $2(1 - \frac{1}{2}\theta'_k) : (1 - b'_k)$ , i. e.  $(1 - \frac{1}{2}\theta'_k) : (1 - b'_k) = 1,105$ . And as  $b'_k$  has a very small positive value,  $\theta'_k$  will necessarily have a very small (probably negative) value. But then  $\theta''_k$  must possess a very great positive value, viz. about 2,7, if  $(\frac{d\varphi}{dm})_k$  is to become  $= -7$  (see above), as we shall show now.

We namely derived before (v. L. B, p. 1098, formulae (4) and (5)):

$$\varphi = \frac{F'-1}{F'_k-1} \frac{\varepsilon_{coex.}}{d_1 d_2} = 1 + \lambda(1-m) + \dots,$$

in which

$$\lambda = (\alpha^2 - 2\beta) - \frac{F'_k}{F'_k-1} \dots \dots \dots (9)$$

In this  $F'_k$  represents  $(\frac{d^3 \varepsilon_{coex.}}{dm^2})_k$ , while  $\alpha$  and  $\beta$  are the first coefficients of the expansion into series

$$\left. \begin{aligned} d_1 &= 1 + \alpha \sqrt{1-m} + \beta(1-m) + \dots \\ d_2 &= 1 - \alpha \sqrt{1-m} + \beta(1-m) - \dots \end{aligned} \right\}$$

given by (see p. 1094 and 1096 loc. cit.)

$$\alpha = \sqrt{\frac{6\varepsilon''_{v,t}}{\varepsilon''_{v^3}}}; \quad \beta = \alpha^2 - \frac{\varepsilon'''_{v^2,t} - \frac{1}{10}\alpha^2 \varepsilon''''_{v^4}}{\varepsilon''_{v^3}}$$

In this  $\varepsilon''_{v,t}$  stands for  $(\frac{d^2 \varepsilon}{dn \cdot dm})_k$ ,  $\varepsilon'''_{v^2,t}$  for  $(\frac{d^3 \varepsilon}{dn^2 \cdot dm})_k$ ,  $\varepsilon''_{v^3}$  for  $(\frac{d^2 \varepsilon}{dn^2})_k$ , and  $\varepsilon''''_{v^4}$  for  $(\frac{d^4 \varepsilon}{dn^4})_k$ . The quantities  $\varepsilon$ ,  $m$ , and  $n$  are resp. the reduced pressure, temperature, and volume.

Now taking the value of  $F'_k$ , viz. (see p. 1098 and 1104 loc. cit.)  $F'_k = \varepsilon''_{v^2} - (\alpha^2 - \beta) \varepsilon''_{v,t} - \frac{1}{6} \alpha^2 \varepsilon'''_{v^2,t}$  into account, we may also write for :

$$\lambda = \frac{-\varepsilon''_{v^2} + \alpha^2 [(f-1) + \varepsilon''_{v,t} + \frac{1}{6} \varepsilon'''_{v^2,t}] - \beta [2(f-1) + \varepsilon''_{v,t}]}{f-1}, \dots (9a)$$

in which  $\varepsilon''_{v^2} = (\frac{d^2 \varepsilon}{dm^2})_k$ , i. e. for  $n(v)$  constant. (so  $\varepsilon$  not the reduced pressure of coëxistence). For  $F'_k$  we haven written  $f$  (see § 2).

We now find — as  $\lambda = -(\frac{d\varphi}{dm})_k$  — the value 7 (at the least 6,8 loc. cit. p. 1101) for this quantity  $\lambda$ .

Let us now calculate the different differential quotients of  $\varepsilon$  with respect to  $m$  and  $n$  with the aid of (1a). We find :

$$\begin{aligned} \left(\frac{dp}{dT}\right)_v &= \frac{R}{v-b} = \frac{1}{T} \left(p + \frac{a_k \theta}{v^2}\right); & \left(\frac{d^2p}{dT^2}\right)_v &= 0 \\ \frac{d^2p}{dvdT} &= \frac{1}{T} \left[\frac{dp}{dv} + a_k \left(-\frac{2\theta}{v^3} + \frac{\theta'}{vkv^2}\right)\right] \\ \frac{d^3p}{dv^2dT} &= \frac{1}{T} \left[\frac{d^2p}{dv^2} + a_k \left(\frac{6\theta}{v^4} - \frac{4\theta'}{vkv^3} + \frac{\theta''}{v^2kv^2}\right)\right]. \end{aligned}$$

Hence for  $T_k$  ( $\theta_k = 1$ ,  $\frac{dp}{dv} = 0$ ,  $\frac{d^2p}{dv^2} = 0$ ):

$$\begin{aligned} f &= \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = 1 + \frac{a_k}{p_k v_k^2}; & \varepsilon''_{v^2} &= 0 \\ \varepsilon''_{v,t} &= \frac{v_k T_k}{p_k} \left(\frac{d^2p}{dvdT}\right)_k = \frac{a_k}{p_k v_k^2} (-2 + \theta'_k) \\ \varepsilon'''_{v^2,t} &= \frac{v_k^2 T_k}{p_k} \left(\frac{d^3p}{dv^2dT}\right)_k = \frac{a_k}{p_k v_k^2} (6 - 4\theta'_k + \theta''_k). \end{aligned}$$

So we find for  $\lambda$  :

$$\lambda = \alpha^2 \left[1 + (-2 + \theta'_k) + \frac{1}{6} (6 - 4\theta'_k + \theta''_k)\right] - \beta \left[2 + (-2 + \theta'_k)\right],$$

i. e.

$$\lambda = \alpha^2 \left(\frac{1}{6} \theta'_k + \frac{1}{6} \theta''_k\right) - \beta \theta'_k.$$

As experimentally about (see also v. L. B, p. 1101):

$$\alpha^2 = 15; \quad \beta = 0,9; \quad \lambda = 6,8$$

has been found, we get:

$$4,1 \theta'_k + 2,5 \theta''_k = 6,8.$$

Hence if  $\theta'_k$  is very small — which is inevitable according to (5a) (see above) —  $\theta''_k$  will necessarily have to lie in the neighbourhood of 2,7 (with  $\theta'_k = -0,1$ ,  $\theta''_k$  would be found even 2,9). We may therefore consider the value 2,7 as the *lowest* required to make  $\lambda = 6,8$ , as no doubt  $\theta'_k$  will always have a *negative* value, even though it be a very small one (see above).

Granting this to be true — and it is hardly possible to deny the above, when for the equation of state the form (1a) is assumed with  $b$  and  $a$  as functions of  $v$  — it is easy to see that the result found leads to a *perfectly impossible* result for  $b''_k$ , if the critical volume etc. must also have the desired experimental value.

For from (2a), viz.

$$\frac{r-1}{r} = \frac{2}{3} \frac{1 - b'_k}{\omega - \frac{1}{2} b''_k},$$

with  $r = 2,1$  and  $b'_k$  small, e.g.  $= 0,04$  — since the value of

$$\omega = (1 - \frac{2}{3} \theta'_k + \frac{1}{6} \theta''_k) : (1 - \frac{1}{2} \theta'_k)$$

will amount to about  $= 1 + \frac{1}{6} \times 2,7 = 1,45$  — will follow :

$$\beta''_k = 0,69, \text{ i. e. } v_k b''_k = 0,66.$$

So instead of finding a *negative* value, which varies according to the different assumptions from  $-0,40$  to  $-0,20$  ( $-0,40$  when association is not assumed), we now find an impossibly large positive value for  $v_k b''_k$ .

And as nobody will think possible the fantastical course of the quantity  $b$  following from this, *any* attempt to account for the course of the characteristic quantity  $\varphi$  in the neighbourhood of  $T_k$ , where  $\frac{d\varphi}{dm} = -7$ , — while *at the same time* the ordinary quantities must

retain their known experimental values — by the addition of a factor  $\theta = f(v)$  by the side of  $a/v^2$  — hence also of VAN DER WAALS'S factor  $(1 - \frac{1}{2} x)^2$ , in which  $x$  is a function of  $v$  — should be rejected.

In this state of affairs there is nothing left but to assume *direct* dependence of the quantities  $a$  or  $b$  on the *temperature*.

4. *The quantities  $a$  or  $b$  are functions of the temperature.* When  $a$  or  $b$  are temperature-functions, all the relations derived in § 1 remain unchanged at the critical point, because in their derivation we only differentiated with respect to  $v$  with  $T$  constant.

But the value of  $f$ , derived in § 2, will in general undergo a change.

a. When  $a$  is a temperature-function, we may put  $a = a_k \tau$ , in which  $\tau = f\left(\frac{T}{T_k}\right)$ . From

$$p = \frac{RT}{v-b} - \frac{a_k \tau}{v^2} \dots \dots \dots (1b)$$

follows, when  $\frac{d\tau}{dm}$  ( $m = T : T_k$ ) is represented by  $\tau'$ :

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} - \frac{a_k \tau'}{T_k v^2}, \text{ or } = \frac{1}{T} \left(p + \frac{a_k \tau}{v^2}\right) - \frac{a_k \tau'}{T_k v^2}.$$

Hence also :

$$\frac{T}{p} \left(\frac{dp}{dT}\right)_v = \frac{RT}{p(v-b)} - \frac{T a_k \tau'}{p T_k v^2}, \text{ or } = 1 + \frac{a_k (\tau - m \tau')}{p v^2},$$

or because evidently  $\tau_k = 1$  :

$$f = \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = \frac{RT_k}{p_k (v_k - b_k)} - \frac{a_k \tau'_k}{p_k v_k^2}, \text{ or } = 1 + \frac{a_k (1 - \tau'_k)}{p_k v_k^2}.$$

After substitution of the values of  $s$  from (5),  $p_k$  from (4) and  $v_k : b_k = r$ , this becomes :

$$f = s \frac{r}{r-1} - \frac{27}{r^2} \frac{1}{\lambda_2} \tau'_k, \text{ or } = 1 + \frac{27}{r^2} \frac{1}{\lambda_2} (1 - \tau'_k), \dots (6a)$$

in which also  $\frac{8}{r-1} \frac{\lambda_1}{\lambda_2}$  can be written for  $s \frac{r}{r-1}$  according to (5).

As with  $s = 2,77$ ,  $r = 2,1$  the value of  $s \frac{r}{r-1}$  or  $\frac{8}{r-1} \frac{\lambda_1}{\lambda_2}$  amounts already to 7, and also  $1 + \frac{27}{r^2} \frac{1}{\lambda_2} = 7$  — it follows necessarily that

the value of  $\tau'_k$  must either be (almost) = 0 or *exceedingly small*<sup>1)</sup>.

In consequence of this the formulæ (6), (7), and (8) can also be kept unchanged.

Let us now calculate the value of the characteristic function  $\varphi$ , or rather of the quantity  $\lambda = - \left( \frac{d\varphi}{dm} \right)_k$ .

Now we proved in a preceding Paper (see v. L. B, p. 1104–1105), that when only  $\alpha$  is a function of  $T$ , the coefficients of  $\alpha^2$  and  $\beta$  in the expression (9a) for  $\lambda$  both become = 0, and that therefore only :

$$\lambda = - \frac{\varepsilon''_{t^2}}{f-1} \dots \dots \dots (9b)$$

is left.

In this experimentally the value — 40,8 is found for  $\varepsilon''_{t^2}$ <sup>2)</sup>, so

1) We will just remind here of the fact, that some thirty years ago, when  $r$  was still = 3, the value — 1 had to be assumed from  $f = 1 + \frac{27}{r^2} (1 - \tau'_k) = 1 + 3(1 - \tau'_k)$  for  $\tau'_k$  to make  $f = 7$ . CLAUSIUS' function  $\tau = 1 : m$  satisfied this condition, but also the better function  $\tau = e^{1-m}$  of VAN DER WAALS.

2) The mere fact that so high a (negative) value is found for  $\varepsilon''_{t^2}$ , i.e.  $\left( \frac{d^2\varepsilon}{dm^2} \right)_k$  for  $v$  constant, is a proof that  $\alpha$  (or  $b$ ) *must* be a temperature-function. If one substitutes in the above given expression for  $F'_k$ , viz.  $F'_k = \left( \frac{d^2\varepsilon_{\text{coex.}}}{dm^2} \right) = \varepsilon''_{t^2} - (\alpha^2 - \beta) \varepsilon''_{v,t} - \frac{1}{6} \alpha^2 \varepsilon'''_{v^2,t}$  for  $F'_k$ ,  $\varepsilon''_{v,t}$  and  $\varepsilon'''_{v^2,t}$  resp. the values 39,6, — 11,4 and 29,6 experimentally found (loc. cit. p. 1101–1103), one finds namely with  $\alpha^2 = 15$ ,  $\beta = 0,9$  for  $\varepsilon''_{t^2}$  the value  $39,6 + 14,1 \cdot (-11,4) + 2,5 \cdot 29,6 = 39,6 - 160,7 + 74,0 = -47$ . If the values — 11,4 and 29,6 are raised resp. to — 12 and 36 for the reasons given on p. 1103–1105, one finds for  $\varepsilon''_{t^2}$  the above given value — 40,8. At any rate this value differs much from 0, and  $\alpha$  (or  $b$ ) is therefore *certainly* a temperature-function.

that  $\lambda$  with  $f = 7$  assumes the value  $40,8 : 6 = 6,8$ . [The original equation (9) gives 39,6 for  $F'_k$  with the experimental value, and of course also  $\lambda = 13,4 - 6,6 = 6,8$  with  $\alpha^2 = 15,2$ ,  $\beta = 0,9$ ]. This value is in perfect agreement with the course of the value of  $\varphi$  in the immediate neighbourhood of  $T_k$  (loc. cit. p. 1100—1102), from which even a somewhat higher value would follow.

Let us now calculate the value of  $\varepsilon''_p$  on the supposition that  $a$  is a function of  $T$ . From the value found above for  $\left(\frac{dp}{dT}\right)_v$ , viz.

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b} - \frac{a_k \tau'}{T_k v^2}, \text{ follows immediately } \left(\tau'' = \frac{d^2\tau}{dm^2} = \frac{d\tau'}{dm}\right):$$

$$\left(\frac{d^2p}{dT^2}\right)_v = -\frac{a_k \tau''}{T_k^2 v^2},$$

hence

$$\varepsilon''_p = \left(\frac{d^2\varepsilon}{dm^2}\right)_k = \frac{T_k^2}{p_k} \left(\frac{d^2p}{dT^2}\right)_k = -\frac{a_k \tau''_k}{p_k v_k^2},$$

so that we find;

$$\lambda = \frac{a_k \tau''_k}{p_k v_k^2}; \quad \frac{a_k(1-\tau'_k)}{v_k v_k^2} = \frac{\tau''_k}{1-\tau'_k}, \quad \dots \dots \dots (9c)$$

when we substitute the value found above for  $f-1$ .

Now  $\tau'_k = 0$  may be put (see above), so that with  $\lambda = 6,8$  we shall have (see also p. 1106 loc. cit.):

$$\tau''_k = 6,8.$$

So when — as an explanation of the course of  $\varphi$  at  $T_k$  —  $a = a_k \tau$  is put, in which  $\tau = f(m)$ ,  $\tau$  must satisfy the two conditions:  $\tau'_k = 0 (\pm)$  and  $\tau''_k = 7$ .

$\beta$ ). If  $b$  is supposed to be a function of the temperature, then from

$$p = \frac{RT}{v-b_k \tau} - \frac{a}{v^2}, \quad \dots \dots \dots (1c)$$

in which  $\tau$  is therefore both a function of  $v$  and of  $T$ , follows:

$$\left(\frac{dp}{dT}\right)_v = \frac{R}{v-b_k \tau} + \frac{RT}{(v-b_k \tau)^2} \frac{b_k \tau'}{T_k} = \frac{R}{v-b_k \tau} \left[1 + \frac{m b_k \tau'}{v-b_k \tau}\right],$$

when  $\tau' = \frac{d\tau}{dm}$  at  $v$  constant.

Hence:

$$f = \frac{T_k}{p_k} \left(\frac{dp}{dT}\right)_k = \frac{RT_k}{p_k(v_k-b_k)} \left(1 + \frac{b_k \tau'_k}{v_k-b_k}\right), \quad \dots \dots \dots (6b)$$

because at  $T_k$  the value of  $\tau$  is evidently again  $= 1$ . And since

again the factor  $RT_k: p_k(v_k - b_k) = s \frac{r}{r-1}$  yields already  $f=7$ , now too  $\tau'_k$  must be either (about) 0<sup>1)</sup>, or *exceedingly small*, so that also in this case the formulae (6), (7), and (8) can remain intact.

And as for  $\tau'_k=0$  again formula (9b) holds, viz.  $\lambda = -\varepsilon''_{\rho} : (f-1)$ , because the coefficients of  $\alpha^2$  and  $\beta$  in (9a) will be  $=0$  (see above at  $\alpha$ ), we again determine only  $\varepsilon''_{\rho}$ .

We find:

$$\left(\frac{d^2p}{dT^2}\right)_v = \frac{2R}{(v-b_k\tau)^2} \frac{b_k\tau'}{T_k} + \frac{2RT}{(v-b_k\tau)^2} \left(\frac{b_k\tau'}{T_k}\right)^2 + \frac{RT}{(v-b_k\tau)^2} \frac{b_k\tau''}{T_k^2},$$

hence, when  $\tau'_k=0$  is put:

$$\varepsilon''_{\rho} = \frac{T_k^2}{p_k} \left(\frac{d^2p}{dT^2}\right)_k = \frac{RT_k}{p_k(v_k-b_k)^2} b_k\tau''_k = f \cdot \frac{b_k}{v_k-b_k} \tau''_k,$$

taking the value of  $f$  into account according to (6b) — when  $\tau'_k$  is put there  $=0$ .

So we find for  $\lambda$ :

$$\lambda = -\frac{f}{f-1} \frac{\tau''_k}{r-1}, \dots \dots \dots (9d)$$

in which  $\tau'' = \frac{d^2\tau}{dm^2}$  for  $v$  constant. We draw attention to this, that  $\lambda = \tau''_k$  was found on the assumption of  $a = a_k\tau$  (formula 9c).

Now  $f: (f-1)(r-1) = 7:6 \times 1,11 = 1,05$ , so that we must now get:

$$\tau''_k = -6,8:1,05 = \underline{\underline{-6,5}}.$$

So whether one takes  $a$  as temperature function or  $b$  — in both cases one will find  $\tau'_k=0$ , and  $\tau''_k$  not far from 7, resp. — 7.

And as to the dependence of the quantity  $b$  on  $v$ ,  $b'_k$  will be at most 0,1,  $v_k b''_k$  at most — 0,4 (see § 1).

By the side of  $\tau/v^2$  no function of  $v$  can occur which could account at the same time for the course of the quantity  $\varphi$  at  $T_k$ , and for the known values of the critical quantities. So not VAN DER WAALS'S factor  $(1 - \frac{1}{2}x)^2$  either, in which  $x$  is a function of  $v$  (see § 3).

<sup>1)</sup> It is of course impossible that  $\tau'_k$  is absolutely  $=0$ , for then the critical temperature would have an exceptional meaning in the series of temperatures between  $T=\infty$  and  $T=0$ , to which it cannot lay claim. For quantities which have only significance in the *heterogeneous* region, where liquid and vapour coexist, there can indeed be question of a factor  $1-m$  in the neighbourhood of  $T_k$ , which factor would become  $=0$  at  $T_k(m=1)$  — but never for quantities as  $a$  and  $b$ , for which the critical temperature is no more than an ordinary temperature. So  $\tau'_k$  can only be exceedingly small.

These are accordingly the inevitable conclusions to which the investigation of the preceding paragraphs has led us.

5. *The reduced equation of state.* Already in previous papers (v. L. III, p. 568, IV, p. 719) I made use of the reduced form of the equation of state, when  $b = f(v)$  was assumed in consequence of association. VAN DER WAALS has, however, (see particularly v. D. W. II) given such a form to the reduced equation of state, that the law of corresponding states was brought forward in a new form. For this purpose it was only necessary to divide the former reduced volume (expressed in  $v_k$ ) by  $\frac{3}{r} = \sqrt{\frac{f-1}{3}}$ . (The relation  $b_k : b_0$  or  $b_g : b_0$  may be left out of consideration for the present; we shall return to it in our concluding paper).

VAN DER WAALS's results are naturally more or less approximative: first because the factors  $\lambda_1$  and  $\lambda_2$  have been disregarded, and secondly because not  $r = v_k : b_k$ , but again  $r' = v_k : b_g$  was introduced.

There is now no longer any approximation, and we get — also by a simpler way — the results found by VAN DER WAALS, perfectly defined, when  $p, T$  and  $v$  are not expressed in the *real* critical quantities  $p_k, T_k$ , and  $v_k$  — but in the *ideal* critical quantities, i.e. those which would hold for the ideal equation of state with  $a$  and  $b$  constant. If we call the latter quantities  $p'_k, T'_k$ , and  $v'_k$ , then

$$RT_k = \frac{8}{27} \lambda_1 \frac{a}{b_k} \quad ; \quad p_k = \frac{1}{27} \lambda_2 \frac{a}{b_k^2} \quad ; \quad v_k = r b_k$$

$$RT'_k = \frac{8}{27} \frac{a}{b_k} \quad ; \quad p'_k = \frac{1}{27} \frac{a}{b_k^2} \quad ; \quad v'_k = 3b_k.$$

Then from:

$$\left( p + \frac{a}{v^2} \right) (v - b) = RT$$

follows the equation

$$\left( \epsilon' p'_k + \frac{a}{n'^2 v'^2_k} \right) (n' v'_k - \beta' v'_k) = m' RT'_k,$$

when  $\epsilon', n', \beta'$ , and  $m'$  resp. represent  $p : p'_k, v : v'_k, b : v'_k, T : T'_k$ , just as formerly  $p : p_k, v : v_k, b : v_k, T : T_k$  were represented by  $\epsilon, n, \beta$ , and  $m$ .

After substitution of the above given values of  $RT'_k, p'_k$ , and  $v'_k$ , we get therefore as before:

$$\left( \epsilon' \cdot \frac{1}{27} \frac{a}{b_k^2} + \frac{a}{n'^2 \cdot 9b_k^2} \right) (n' \cdot 3b_k - \beta' \cdot 3b_k) = m' \cdot \frac{8}{27} \frac{a}{b_k},$$

i.e.

$$\left( \varepsilon' + \frac{3}{n'^2} \right) (n' - \beta') = \frac{8}{3} m' \dots \dots \dots (10)$$

Had we expressed everything in the *real*  $RT_k$ ,  $p_k$  and  $v_k$ , we should have got:

$$\left( \varepsilon \lambda_2 + \frac{27 : r^2}{n^2} \right) (n - \beta) = \frac{8}{r} \lambda_1 m,$$

or also:

$$\left( \varepsilon + \frac{27 : \lambda_2 r^2}{n^2} \right) (n - \beta) = \frac{8}{r} \frac{\lambda_1}{\lambda_2} m = sm, \dots \dots \dots (10a)$$

in which  $\beta = b : v_k = b : r b_k$ .

Hence the new reduced quantities  $\varepsilon$ ,  $m$ ,  $n$ , and  $\beta$  of equation (10) are to the original ones in the following simple relations:

$$\left. \begin{aligned} \varepsilon' &= \lambda_2 \varepsilon = \varepsilon \times (p'_k : p_k) \\ m' &= \lambda_1 m = m \times (T_k : T'_k) \\ n' &= \frac{1}{3} r . n = n \times (v_k : v'_k) \end{aligned} \right\} \dots \dots \dots (11)$$

Substitution of (11) in (10a), of course, immediately leads to (10), and vice versa.

VAN DER WAALS has retained  $\varepsilon' = \varepsilon$ ,  $m' = m$ , and therefore his new reduced equation of state will in this respect only hold by approximation, though the difference will be exceedingly slight. But as VAN DER WAALS does not put  $n' = \frac{1}{3} r . n$  (or  $n' = n : \frac{3}{r}$ ), but  $n' = n : \frac{3}{r'}$ , in which  $r'$  does not represent  $v_k : b_k$ , but  $v_k : b_g$ , while  $b_g$  and  $b_k$  can differ 4 or 5%, the difference with the reduced equation of state (10) will be much greater for the quantity  $n : \frac{3}{r'}$ , because in (10) the specific element [embodied in the quantity  $r$  ( $\lambda_1$  and  $\lambda_2$  left out of consideration), which quantity  $r$  can be different for different classes of bodies] has been entirely removed.

If  $a$  and  $b$  are still functions of the temperature, the term  $3 : n'^2$  in (10) will have evidently to be replaced by  $3f(m') : n'^2$ , or  $\beta'$  by  $\beta'f(m')$ .

As according to (6)  $\lambda_2(f-1) : 3 = 9 : r^2$ , also:

$$\frac{3}{r} = \sqrt{\lambda_2 \frac{f-1}{3}},$$

and we may also write instead of  $n' = n : \frac{3}{r}$ :

$$n' = n : \sqrt{\lambda_2 \frac{f-1}{3}},$$

now perfectly accurate.

In a following (concluding) paper some remarks will be made about the dependence of  $a$  or  $b$  on the temperature, and some general considerations will be given about the nature of the function  $b = f(v)$ .

*Fontanivent sur Clarens, March 1913.*

**Chemistry.** — “*Colloids and the phase rule.*” By Dr. E. H. BÜCHNER.  
(Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of April 25, 1913.)

The question, whether the phase rule can be applied to systems, in which a colloïd occurs, and if so, in what way, has been discussed more than once. Some investigators have concluded, that it is not allowed; the greater part, however, think, that — under certain restrictions — it can be done; systems, in which irreversible reactions occur, must, for instance, be excluded<sup>1)</sup>. The question has been examined most closely by PAVLOV<sup>2)</sup> and JONKER<sup>3)</sup>. Both consider a colloïd a system of two phases, but, whilst JONKER applies the usual rule, PAVLOV introduces a new independent variable, namely the specific surface of a phase, i.e. the ratio of its surface to its quantity. He gives the phase rule then naturally the form

$$F = n + 3 - r,$$

without applying it practically or giving any experimental proof of its exactness. It is certainly easy to see, that such a proof will be impossible, since the number of degrees of freedom is found to be just as great if one applies the ordinary phase rule, provided that the colloïd is taken as one phase. If we take e.g. a solution of gelatine in equilibrium with its vapour at a certain temperature,  $n = 2$ , and according to PAVLOV  $r = 3$ ; the system has therefore one degree of freedom. If, on the other hand, we consider the solution one phase, and apply the familiar rule, then it follows from  $F = n + 1 - r$  (1, because the temperature is fixed), that in like manner  $F = 1$ , because now  $r$  is taken  $= 2$ . Thus it will never be possible to decide by experimental evidence, which of the two formulae has to be applied; this must be deduced from considerations a priori: we should ask ourselves whether really a new independent variable must be introduced, and whether a colloïd actually consists of two phases. As to these questions, JONKER has adopted the view, that neither the surface-tension, nor any other quantity must be taken into consideration, and that therefore the ordinary rule may be maintained. Taking a colloïdal solution as composed of two phases, one will find — ceteris paribus — one degree of freedom less than in an ordinary solution, and JONKER thinks this to be confirmed by the absence of the depression of the freezing point and the other quantities connected therewith in typical colloïdal

<sup>1)</sup> HENRI, Z. phys. Chem. 51, 31.

<sup>2)</sup> Z. phys. Chem. 75, 48.

<sup>3)</sup> Kolloid-Zeitschrift 8, 15.

solutions. From the formula  $F = n + 3 - r$  it would indeed follow, that the freezing point depends on the concentration, whereas  $F = n + 2 - r$  would lead to the conclusion, that the freezing point does not vary with the concentration, which is in agreement with the observations.

It seems to me that new light is thrown upon these questions, if we take a view, which was brought forward, a few years ago, by EINSTEIN and PERRIN. Our starting-point then will be EINSTEIN'S declaration<sup>1)</sup> that the only difference between a dissolved molecule and a suspended body lies in their size, and that one cannot see, why a number of suspended bodies should not exert an osmotic pressure just as well as a number of dissolved molecules. It will be superfluous to point out, how rich in results this conception has become in PERRIN'S hands. I only wish to mention that PERRIN<sup>2)</sup>, with the help of considerations on that very osmotic pressure, deduced a formula for the distribution of a suspension under the influence of gravity, which was fully confirmed by the experiments. Should objections be raised against his reasoning, LORENTZ<sup>3)</sup> has shown, that the formula can be obtained with perfect strictness. Moreover we find it developed by VAN DER WAALS—KOHNSTAMM<sup>4)</sup> in a third way; in fact these authors apply to PERRIN'S suspensions a formula, deduced rigorously for ordinary diluted solutions, only making those alterations that are necessary and permissible because of the enormous molecular weight of one of the components. It is quite evident from all this, that suspended granules may really be treated as enormous molecules.

Now it is only a short step to the conception, which I propose, namely, that a colloidal substance must be considered one phase, as well as a solution of sugar in water is one phase. Let us confine ourselves for the present to the sols, cases, that are usually treated as suspensions or emulsions. For these the given conception leads to the conclusion, that they really exhibit a diminution of the vapour pressure, that, therefore, the freezing point changes with the concentration, but at the same time it shows this depression to be exceedingly small, because the molecular weight or the quantity, which we may in this case regard as such, the weight of the particles floating in the liquid — is so considerable. The proposed assumption is therefore in agreement with the experimental results,

<sup>1)</sup> Ann. d. Phys. [4] 17, 549.

<sup>2)</sup> Ann. d. Chim. et de Phys. 8e Sér. T. 18.

<sup>3)</sup> Chem. Weekbl. 7, 827.

<sup>4)</sup> Lehrb. der Thermodyn. II, p. 567.

as was that of JONKER; perhaps very exact observations on colloids, the molecular weight of which is not too great, as for instance tannin, may assist in clearing up this point. SVEN ODÉN's<sup>1)</sup> solutions of sulphur also, which melt sharply and reversibly, seem to be a favourable subject for the determination of the depression of the freezing point, or, perhaps still better, of the osmotic pressure.

If this idea is accepted, one must evidently reject PLANCK's opinion<sup>2)</sup>; that the alteration of the vapour pressure would afford a means of distinguishing between emulsion and real solution. Emulsions too will show diminution of the vapour pressure, but in such a slight degree, that it escapes observation.

It is curious to note, that the workers in this field have made their experiments as if the colloid consisted of one phase, although they were, of late at least, theoretically convinced, that it was composed of two phases. A striking example is found in JONKER's second paper<sup>3)</sup>. This investigator takes a solution of tannin in water as having two phases; when adding a definite amount of ether, he observes a division into three liquid layers, the composition of which is determined to 0,5 %, 3,1 % and 44,3 % tannin respectively. Now he calls the system, at fixed pressure and temperature, an invariant one, because it is composed of three components and three phases. That is quite correct in my opinion; but, if one conceives tannin in water two phases, why then does tannin in water with some percentage of ether added suddenly become one phase? <sup>4)</sup>

Everyone who is acquainted with, for instance, OSTWALD's Kolloidchemie, will see, that my conception is absolutely contrary to the current views of the present time. I think this to be caused by the fact, that one has gradually been led to confuse the notions "heterogeneous" and "composed of several phases." OSTWALD<sup>5)</sup> for instance, says: colloidal systems, especially colloidal solutions, belong to the systems, which are called in physical chemistry heterogeneous or plural phase systems, and FREUNDLICH<sup>6)</sup> joins him by remarking, that it is appropriate to consider generally systems of two components to be two-phase systems: real solutions, especially the dilute ones, form extreme

<sup>1)</sup> Z. phys. Chem. **80**, 709.

<sup>2)</sup> Thermodynamik, § 223, 3rd ed., p. 205.

<sup>3)</sup> Kolloid-Zeitschr. **10**, 126.

<sup>4)</sup> It will be evident, that I certainly think JONKER's determination of the critical solution temperature of the two phases with a slight percentage of ether to be conclusive.

<sup>5)</sup> Grundriss der Kolloidchemie, 3rd ed., p. 23.

<sup>6)</sup> Kapillarchemie, p. 308.

cases, to be regarded as one-phase systems. This view, the consequence of which would be, that an ordinary solution of salt would consist of two phases, and that even one phase would be composed of separate molecules, is the fundamental difference between OSTWALD and FREUNDLICH on one side, and myself on the other. As to this point I wish to refer to BAKHUIS ROOZEBOOM's clear representation <sup>1)</sup> of the fact, that the notion "homogeneous" is only a relative one, and that, what is called by us a homogeneous system, deserves this name only, because the molecules are so small and our observations not delicate enough. When defining later the "phase" ideal he speaks of homogeneous states (it is clear now, what is meant by this), and further of internally uniform forms of appearance of a substance, differing in state of aggregation, composition or energy. Of course, one cannot speak of a state of aggregation, when treating of molecules; further, the energy content of different molecules will differ, so that one will have to consider each molecule as a phase and there should be as many phases as molecules. Those, who desire a more thermodynamical treatment of the idea phase, will find it in VAN DER WAALS-KOHNSTAMM's text-book <sup>2)</sup>. When giving a definition of phase, these authors claim that there must exist a relation between the different thermodynamical factors, potentials, pressure and temperature. How can there be any question of that, so long as we have not a complex, composed of numerous molecules, whose number permits us to apply statistical methods? To carry the idea phase so far seems to me to be in complete contradiction to the notion itself, as we are used to apply it. An other question is connected herewith. The defenders of the two-phase conception add, that the systems are complicated by this fact, that the surface of contact between the phases is very great, and that consequently surface forces must play an important role. But this, too, only holds good within certain limits; for, once more I put the question, what, if one of the so-called phases is composed of separate molecules — not an impossible state of affairs, when we think of the size of albumen-molecules? Do the laws of surface action, which are known to us, hold good in that case? It requires no argument to show that the special forces, which certainly come into action in sharply curved surfaces, are always calculated and measured in cases, in which we still have a great many molecules,

<sup>1)</sup> Heterogene Gleichgewichte I, 9.

<sup>2)</sup> Vol II, p. 11. Professor KOHNSTAMM was kind enough to direct my attention to the fact, that in the same book, vol. I, p. 123 the condition, that a phase must consist of a great number of particles, is plainly stated.

and that, when we pass on to the molecules themselves, the ordinary attractive forces — the  $a_{12}$  in VAN DER WAALS'-equation — must be able to explain the phenomena in first approximation.

Of course, in this conception we are breaking to a certain extent with homogeneity as a necessary element of the notion "phase". But, as I pointed out above, homogeneous is only relative, and so it is only the limits, which are removed. An emulsion too may after all be homogeneous, as long as we do not divide it in parts of too small a size. It depends on the circumstances, how far one may go on with that. As long as we have in the separated part so many molecules — either "really" dissolved, or suspended granules or droplets of liquid — that statistical methods are applicable, that therefore mean values of velocity, energy etc. may be calculated, so long are we allowed to speak of homogeneity. If we go further so that finally one granule in a quantity of liquid is left, then we must call this heterogeneous. A system, for instance, consisting of one drop of oil, floating in a mixture of water and alcohol, is decidedly heterogeneous. For the rest, the remarks just made turn out to be the same in principle as the question, how to consider a gas in such extreme dilution, that there is only one molecule in the unity of volume.

To summarize, my opinion is, that when we desire to treat the questions, usually dealt with by means of the phase rule, for the case, that any one of the phases is a colloidal solution, we have to apply the rule in its ordinary form; only when making quantitative determinations, we have to pay attention to the size of the molecules. When, however, we wish to investigate as to whether the so-called suspended granules exclusively consist of one component or — as probably the ions do — condense a mantle of liquid-molecules around themselves, we are not likely to succeed with the phase rule, and we shall be obliged to have recourse to other methods, as for instance those in use for the electrolytic or gaseous ions just mentioned.

Although I have restricted myself to sols, I see no objection at present — in connexion with the results of a previous investigation <sup>1)</sup> — to extending the given considerations to gels.

After the above paper had been written, the April number of the Journal of the American Chemical Society came into my hands, in which TOLMAN treats the same question in an analogous manner as PAVLOV did, though he obtains different results. I shall return to this point shortly in another periodical.

*Inorg. Chem. Lab. University of Amsterdam.*

<sup>1)</sup> WOLFF and BÜCHNER, These Proc. 15, 1078.

**Physiology.** — “*Velocity of the intestinal movements in different mammals.*” By Dr. E. LAQUEUR and W. R. VAN DER MEER.  
(Communicated by Prof. HAMBURGER).

It is a well-known fact that the metabolism of the smaller kinds of mammals is more intensive than that of the larger kinds. The smaller species not only take comparatively more food, but the need of food makes itself *more frequently* felt. To explain the latter fact it must be assumed that in the smaller animals the food passes much more rapidly through stomach and intestinal canal than in the bigger ones. This is also borne out by the fact that the smaller species defecate much more frequently than the larger ones. The velocity with which the food passes through the intestinal canal is certainly dependent on the velocity of the intestinal movements.

Generally speaking the movements of the larger mammals are slow and heavy as compared with the movements of the smaller kinds. The problem relating the velocity of the intestinal movements is the more important since it seems that it is not absolutely certain if the quality mentioned just now, which holds good for (transversely) striated muscles is also found in lissed (non-striated) muscular cells.

Immediately on the abdominal cavity being opened, it becomes manifest that the movements of stomach and intestinal canal are indeed much more rapid in smaller mammals (e. g. rat and mouse) than for instance in the rabbit. The difference becomes still more conspicuous when an intestinal coil is extirpated and allowed to move in a suitable warm salt-solution which has been saturated with O<sub>2</sub> (e. g. the one suggested by TYRÖDE).

A further investigation of this difference is the object of these researches. For this purpose we adopted the method applied by MAGNUS when studying the qualities of the “surviving” intestine. As we know he suspended a piece of an intestinal coil in a solution of 37° through which a current of oxygen was led. The contractions of the longitudinal muscle were transferred to a lever and registered. The intestines of smaller animals present some difficulty since the absolute value of the intestinal muscular force is but small. We have examined the intestinal movements of 8 kinds of mammals (mouse rat, guinea-pig, rabbit, cat, dog, pig, cow) and that nearly always on duodenum and ileum <sup>1)</sup>.

<sup>1)</sup> I avail myself of this opportunity to tender my best thanks to Prof. C. F. A. KOCH, who enabled me to examine also pieces of intestines of man, which it had been necessary to remove by operations. Until now however, only pieces of coecum and processus vermiformis could be supplied; both parts showed very slow movements.

Though the contractions of the isolated piece of intestine cannot be considered identical with the movements taking place in the body in normal circumstances, yet it must be assumed that certain properties of the living intestine may be studied by means of the isolated one.

The results obtained with the 2 kinds of animals mentioned last, are not absolutely certain, as we were not able to study for a long time at a stretch the intestinal movements of these animals, which were killed at the slaughter-house. This was only the case with those which were killed at the laboratory.

Perhaps it is more difficult to feed the thick-walled intestines of pig and cow sufficiently with  $O_2$ . Moreover the intestines of the animals killed, cannot be exposed at once to a current of oxygen, because the intestines have to be taken from the slaughter house to the laboratory. This was done as carefully as possible in a so-called Thermos-flask (DEWAR'S flask) which had been filled with a Tyrode solution of  $37^\circ$  saturated with  $O_2$ . Thus we were enabled to prevent the intestine from being cooled down.

As a rule the movements of the duodenum are somewhat more rapid than those of the ileum. Here, however, we shall give only the average values; the extreme values are not absolutely certain.

I. Intestinal movements of various species of animals: at ca.  $36.5^\circ$

Animal	Per minute
mouse	32—48
rat	28—35
guinea-pig (cavia)	26—34
rabbit	11—14
cat	10—12
dog	7—11
pig	? 5
cow	? 8

II. After the preceding remarks (effect of the size of an animal) it was not impossible that the *age* of the animal might affect the velocity of the intestinal movements. It might be expected then that the intestines of a young animal would move more rapidly than those of an older animal of the same kind.

The result of these experiments is that only the intestines of the very youngest animals of some species move somewhat more rapidly. A rabbit of 88 grammes for instance (3 days old) had 16—18 intestinal movements a minute. A rabbit of 235 grammes (3 weeks old) had 14

movements a minute i.e. the same number as found in full-grown animals.

III. As yet no support has been found for the opinion that small but full-grown individuals of a certain species have more rapid intestinal motion than bigger individuals of the same species.

The following experiment shows that it is not the size or the age, but the kind of individual which affects the intestinal movements.

The intestine of a half-grown rat of 86 grammes (i.e. as heavy as the above-mentioned rabbit of 3 days) as well as the intestine of a guinea-pig 9 times this weight, (777 grammes) contracted exactly twice as rapidly as the intestine of the rabbit (rat and guinea-pig 35, rabbit 16—18 a minute).

A number of questions are connected with these facts. First the movements of the various parts of stomach and intestinal channel must be compared. Further birds and cold-blooded animals must be examined. These experiments we have partly carried out already. It is not sufficient to study the velocity of the intestinal movements, but it should also be investigated how much labour is performed by the intestine.

In short not only the anatomy, but also the *mechanical function* of the intestine and the various parts of the stomach and intestinal channel must still more be submitted to a *comparative* examination in the different species of animals.

*Physiological Laboratory of the  
University of Groningen*

February 1913.

**Paleontology.** — “*The orientation of the shells of Beyrichia tuberculata* KLÖDEN sp.” By Dr. J. H. BONNEMA. (Communicated by Prof. MOLL.)

Among the smaller fossil Ostracoda the best-known is certainly *Beyrichia tuberculata* KLÖDEN sp., illustrations of which are found in nearly all the text-books on paleontology (1, p. 527) and stratigraphical geology (2, p. 130).

From the figures found in these books it appears that these valves present a lateral aspect which is more or less oval. One of the long edges is straight; the other is curved, which is also the case with the two short edges. On the side there are two nodes near one

short edge, and near the other there is a lobe, cut across by two furrows into three parts. In the space left between these lobes and the straight edge, there is an oval node, the long axis of which stands at right angles on the straight edge. This latter node is situated nearest to that short edge close to which the two nodes are found. Of these latter the one that is at the greatest distance from the straight edge, is sometimes considerably swollen. Such valves are assumed to have originated from female individuals and the swollen node to have served as ovarian pouch.

That this Ostracod is so universally known is undoubtedly due to its frequent occurrence in the upper silurian Beyrichian limestones of which a great many erratic boulders of Lower Germany consist. In our diluvium too such boulders are by no means rare.

But however well-known this species of Ostracoda may be, it soon appears on examining the literature on the silurian forms that the orientation of the shells is still doubtful, in other words which valves are to be considered as right ones and which as left.

Now the purpose of this paper is to solve this problem.

Before proceeding to this, however, I will first give a short account of the history of this problem.

The first person whom we may suppose to have been acquainted with this Ostracod, is LEOPOLD VON BUCH (3, p. 71). In 1828 he gave a representation of a piece of Beyrichian limestone and in this described *Chonetes striatella* DALM. sp., which he called *Leptaena lata*, and to which he gave the shells of *Tentaculites* as spines. To the Ostracoda found in this rock he gave the name of "*Leptaenenbrut*." It is quite possible that among these there were also valves of *Beyrichia tuberculata*, but this cannot be ascertained from the pictures. VON BUCH does not mention the orientation of the shells.

Neither do KLÖDEN (4, p. 112) and BURMEISTER (5, p. 72), who took the Ostracoda valves for cephalic and caudal shields of Trilobites. KLÖDEN was the first who in 1834 gave a clear representation of *Beyrichia tuberculata* as one of the forms which he classified among *Battus tuberculatus*.

Not until 1845 does BEYRICH (6, p. 47) assert that *Battus tuberculatus* is no trilobite on account of the asymmetry of the remains, but must be classified among the Ostracoda as it has a bivalved carapace. Later, in 1846, M'COY (7, p. 57) and independently of him, BOLL (8, p. 127) in 1847 instituted the genus *Beyrichia*. Only the former gives a sufficient account of the criteria of the new genus.

This author is the first in whose works we can find something about the question we are going to solve.

This, however, may first be divided into two parts. We shall first decide which edge is to be regarded as hinge line, or in other words along which edge the two valves moved with respect to each other, and next try to find out which edge is to be considered as anterior end, or in other words which of the two short edges was situated nearest the head of the animal. The first part of the question will be discussed first being easiest to solve.

M'Coy had got so accustomed to the position which was to be given to the valves when they were still regarded as cephalic shields of trilobites that, in mentioning the criteria of the genus *Beyrichia*, he described the long curved edge as dorsal side and the straight edge as ventral. He did this also in a later publication (9, p. 135), though in the meantime SALTER (10, p. 351) in the description of a species of *Beyrichia* had taken the straight side as the dorsal edge. Later investigators always followed SALTER's example and in my opinion this is quite in accordance with what we see elsewhere in nature in similar cases, so that I agree with him and consider this part of the question settled.

Now the second part of the problem remains to be solved and this will take us longer.

In mentioning the criteria for the genus *Beyrichia*, M'Coy states that the least developed end is to be regarded as anterior also recognized by the location of the median furrow and the oval node in it nearest to that end. There are no data given for this assertion.

Nor does JONES (11, p. 85) mention any. Among the criteria of the genus *Beyrichia* he states that the posterior end of the valves is higher than the anterior end. From the description of *Beyrichia tuberculata*, however, it appears that he regards the end with the two nodes as the anterior end whereas this part is the highest. At a later date BOLL (12, p. 118) and KRAUSE (13, p. 30) did the same.

BARRANDE (14, p. 467) is the first who tries to prove that the position of the *Beyrichian* shells suggested by JONES, is probably the right one. He does this, however, by comparing the nodes at one end of the shells of some Bohemian Ostracoda with the lobes of the Tribolite-glabella. As these nodes occur on the tapering part of the shells, he takes this to be the cephalic part. As for myself, I would not follow this line of evidence; nor does it lead us any further towards the orientation of the *Beyrichian* shells, as the latter have nodes at both ends. BARRANDE himself admits this too.

Contrary to all former writers REUTER (15, p. 625) assumed that the end with the three bulb-like parts, was the anterior end. He did this because measuring showed him that this very end is the

lowest and that in recent Ostracoda the lowest end is generally anterior. Another reason for his line of conduct was the conjecture that the large node into which the lower of the two nodes has sometimes passed at one end, must be considered as the lodging place of the genital apparatus of the female individuals, whereas ZENKER had said that in recent Ostracoda this genital apparatus fills the widened and heightened posterior part of the shell.

This conception of REUTER was again refuted by JONES (16, p. 339) and KIESOW (17, p. 2) but like REUTER, they failed in furnishing convincing evidence.

Therefore KRAUSE (18, p. 12; 19, p. 4) proposed to retain the position most assumed till it should be proved wrong.

At a later date ULRICH (20, p. 630) was also of opinion that for the time being the best plan would be to follow the rule indicated by JONES and regard the least developed end as anterior.

In 1908 ULRICH and BASSLER (21, p. 280) in a paper on the *Beyrichiidae* devoted a chapter to this question and tried to solve it by the following way of reasoning.

With the species of the genus *Leperditia* the shells have on both valves near one end a so-called eye-tubercle, which as is universally accepted by paleontologists is to be connected with the visual organs. Therefore in *Leperditia* shells the end with the eye-tubercles is the anterior end. As the shells are lowest in front here and most developed behind, owing to a strong retral swing of the posterior edge, they assume that this is also the case with the *Beyrichiidae*. They apply these rules also to *Beyrichia tuberculata* and find then that the position suggested by REUTER, is the right one.

Soon after the publication of ULRICH and BASSLER's paper I found an opportunity of indicating that the rules given by these writers, as far as the Ostracoda of the Kuckers formation are concerned, were altogether at variance with the results I had found.

MOBERG and GRÖNWALL (23, p. 55), who the year after gave a terminology for the *Beyrichian* valves, accepted the position such as it had been suggested by JONES, but added :

“Dock bör framhållas, att denna terminologi på paleontologiens nuvarande ståndpunkt är endast hypotetisk, äfven om mycket talar till gunst för densamma.”

And this is the present state of the question.

As I have said already, I think I have enough data now to solve the problem and from this it will appear that the position suggested by JONES, is the right one. In doing so I must make use of what

I found some years ago in *Primitia Tolli* BONNEMA (22, p. 16) from the Kuckers formation and besides of what I noticed in valves of *Beyrichia tuberculata* KLÖDEN sp.

In *Primitia Tolli* (fig. 1) I found in the first place that the shells

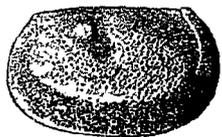


Fig. 1.

Left valve of *Primitia Tolli*  
BONNEMA.  $\times 15$ .



Fig. 2.

Transverse section of the entire  
carapace of *Primitia Tolli* BONNEMA,  
through the part of the lateral eyes,  
anterior view.  $\times 13$ .

are very thin on the spots where the valves have a more or less distinct node (fig. 2). As according to ZENKER (24, p. 8) this is also the case with Ostracoda living in the sea, on the spots where the two composite eyes are located, the short edge of the two valves which is nearest to the node, appears to be the anterior edge. As the straight edge is to be regarded as hinge line, accordingly as dorsal edge, the orientation of the shell of this Ostracod is settled.

Besides I found that the two valves have a furrow behind the node. In this furrow there is a round spot in the lower part indicating the place where on the interior of the valve the adductor is fastened.

Further it appeared that the free edges of the right valve are sharp and that on those of the left valve there is a deep furrow. When the valves are closed the sharp edges of the right valve lie in the deep furrow of the left one.

In order now to determine which of the two short edges of the valves of *Beyrichia tuberculata* is to be regarded as anterior, I investigated in the first place whether there was any sign of a muscle impression. I succeeded in discovering this in valves originating from an erratic boulder of Beyrichian limestone found at Vollenhove. Now the muscle impression is located in the furrow between the oval node and the three bulb-like parts, as a light oval spot, the edge of which passes upward into a curved line, which runs to the superior part of the oval node (fig. 3).

From the location of the muscle impression I think I am justified in concluding that the oval node may be identified with the node

of *Primitia Tolli*; the part of the valve of *Primitia Tolli* which is situated in front of the node, and the part of the valve with the three bulb-like parts with that part of the valve of *Primitia Tolli*

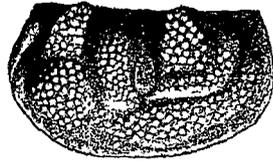


Fig. 3.

Left valve of *Beyrichia tuberculata* KLÖDEN sp.  $\times 10$ .

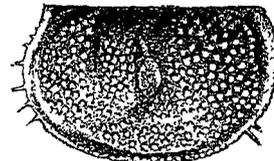


Fig. 4.

Left valve of *Beyrichia protuberans* BOLL.  $\times 10$ .

which is located behind the lateral groove. My opinion that this comparison was correct, was corroborated on comparing the valves of the Ostracoda mentioned above with one of *Beyrichia protuberans* BOLL, originating from an erratic boulder of Beyrichian limestone found at Groningen, which lies between the two others in structure (fig. 4).

From this then we may conclude that the edge near which the two nodes are located, is to be regarded as anterior.

Next I began to investigate if the structure of the free edges of the two kinds of valves was in accordance with the conclusion drawn from the location of the muscle impression.

For this purpose sections were made of the two kinds of valves at right angles to the dorsal edge, somewhere about the muscle impression. I then found that the structure of the free edges entirely corroborated my conclusion. The valve which I had interpreted as

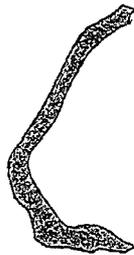


Fig. 5.

Transverse section of the right valve of *Beyrichia tuberculata* KLÖDEN sp., through the part of the muscle impression. anterior view.  $\times 19$ .



Fig. 6.

Transverse section of the left valve of *Beyrichia tuberculata* KLÖDEN sp., through the part of the muscle impression, anterior view.  $\times 20$ .

the right one (fig. 5) appeared to have sharp free edges and the

left one (fig. 6) appeared to possess a deep furrow as is the case with *Primitia Tolli*.

This, I think, shows sufficiently that JONES' orientation of the valves of *Beyrichia tuberculata* is the correct one.

As further result of my investigation I may tell that the dorsal edge of the right valve of *Beyrichia tuberculata* has a less deep furrow, in which the sharp dorsal edge of the left valve lies.

A more or less identical structure of the edges was also found in *Beyrichia Jonesii* BOLL var. *clavata* KOLMODIN (17, p. 15), of which

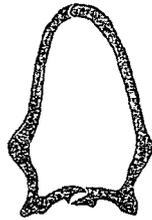


Fig. 7.

Transverse section of the entire carapace of *Beyrichia Jonesii* BOLL var. *clavata* KOLMODIN through the part where the muscle impression is undoubtedly located, anterior view.  $\times 20$ .



Fig. 8.

Part of the last figure magnified four times.

I possess entire carapaces originating from the clay of Mulde in Gotland (fig. 7 and 8). Here, however, the dorsal edge of the left valve is rounded off.

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**Physics.** — “*A Viscosimeter for volatile liquids*”. By Prof. J. P. KUENEN and S. W. VISSER.

In determining the viscosity of a volatile liquid it is necessary to take the measurements in a closed viscosimeter. It is moreover desirable that the apparatus should be small, so that it can be easily handled and the temperature can be easily kept constant in all parts and that the liquid does not come in contact with mercury; the use of mercury at temperatures below its freezing point is in any case excluded.

In designing an apparatus that should fulfil these requirements, we based ourselves upon OSTWALD's viscosimeter<sup>1)</sup>. His viscosimeter consists of a glass *U*-tube with one wide and one capillary arm; the wide tube has a bulb at the bottom and the capillary tube one at the top. The capillary tube opens at the bottom into a wider tube, which curves into the lower bulb. The time which the liquid takes to pass from the bulb through the capillary tube into the bottom bulb is observed. The experiment begins, when the liquid surface passes a contraction above the bulb, and ends, when it reaches the capillary tube. Before each determination the liquid is drawn up through the capillary or pressed up from the other side.

The first thing that we tried to do was to make this viscosimeter into a closed apparatus by joining the two branches of the *U*-tube above into an *O*; our intention was to collect the liquid every time in the upper bulb by simply turning the apparatus upside down.

This was not successful, as the liquid would not join in this position, some of it remaining in the wide tube above the capillary.

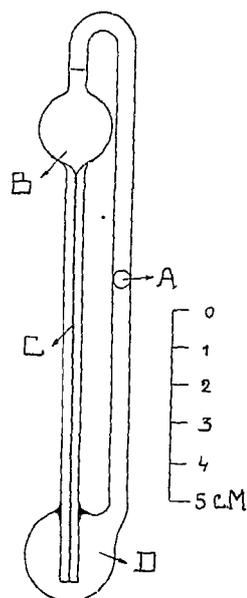
On this account the bottom reservoir was blown directly on to the capillary tube and the wide tube was then sealed to it in the immediate vicinity of the capillary tube. By this means the apparatus became more compact, as the curved portion of the wide tube disappeared.

Still liquid remained above the capillary tube, which prevented it readily flowing back. Moreover the time which the liquid took to pass through appeared to depend upon the way in which the liquid flowed out of the capillary tube along the walls of the bulb.

Finally, the capillary tube was provided with a continuation reaching nearly to the bottom of the bulb. When the apparatus is tur-

<sup>1)</sup> W. OSTWALD, Hand- und Hilfsbuch zur Ausführung physiko-chemischer Messungen, p. 195, 1893.

ned upside down the extremity of the capillary tube projects above the liquid, and the liquid runs back without any difficulty. During the determination the liquid now flows out continually under the liquid surface. As the figure shows, in making this apparatus a hole is blown in the bulb; through this the capillary tube is introduced and the two are then sealed together. The final form of the apparatus



is sufficiently clear from the figure. The liquid is introduced by the side tube *A*; after filling this is sealed off. In the inverted position the liquid fills the bulb *B* and part of the wide tube. If the viscosimeter is then turned up the liquid flows partly out of the wide tube to the bulb in which the capillary tube ends; the flow through the capillary tube begins at the same time and the meniscus passes along the upper curve; at the moment that the liquid passes a mark above the bulb *B*, a chronometer is set going. This mark takes the place of the contraction in OSTWALD'S viscosimeter, where a drop of liquid is apt to collect. Through the capillary tube *B* is now emptied and the chronometer is stopped when the liquid dips into the capillary; when the apparatus is turned

upside down, the bulb quickly empties itself.

The viscosimeter is placed in a wider tube, in which a bath of constant temperature is maintained; this tube is put up in such a way, that it can easily be turned upside down.

The whole apparatus is not more than 15 cm. long and by taking a finer capillary tube, or a larger bulb, it can be made even a little shorter.

No absolute determinations were made: the times of flow for various liquids were compared to that of water.

Some preliminary measurements were made with a larger experimental tube. In the final apparatus the dimensions used were such, that in determining the viscosity of normal butane a period of flow of at least three minutes could be reckoned upon. In the preliminary determinations a difficulty showed itself; in turning the apparatus over, the small bulb did not easily fill itself, on account of the great capillarity of water. With liquids such as ether and alcohol no difficulty was experienced. It seemed probable that determinations with water would be impossible with a much narrower tube. The apparatus was therefore standardized with water before the *U*-tube

was closed, while the apparatus was still used like OSTWALD'S viscosimeter.

*Influence of the quantity of liquid.*

The time of flow depends upon the total amount of liquid in the apparatus. The more liquid there is, the higher the surface is in the lower bulb and the smaller is the pressure under which the liquid flows.

In OSTWALD'S viscosimeter the same volume is taken of the various liquids: in this way the influence of the filling of the viscosimeter is eliminated. When the apparatus is filled with a liquid of high vapour-pressure or liquid gas, it is difficult to fulfil accurately the condition of equal volumes and it becomes necessary to investigate experimentally the influence of the volume of liquid. This can be done by measuring the time of flow of the same liquid, e.g. water, with various fillings. If we then know the weight of another liquid used and its specific gravity, we know the total volume. From the measurements previously made with water we can then find the time of flow for the same amount of water. From the ratio of the times of flow ( $t$  and  $t_w$ ) the viscosity ( $\eta$ ) is then calculated by the equation

$$\eta : \eta_w = dt : d_w t_w.$$

*Influence of capillarity on the time of flow.*

In consequence of the capillary action the pressure is not that of the mean difference of height, but is smaller. It is sufficient to make an estimation of this correction.

The capillary rise in a tube which is placed inside a second tube is given by the formula

$$h = \frac{2\sigma}{dg} \left( \frac{1}{r} - \frac{1}{R-r_1} \right),$$

in which  $\sigma$  represents the capillary constant,  $d$  the density,  $r$  the internal and  $r_2$  the external radius of the first tube,  $R$  the internal radius of the second tube. By this formula the capillary rise was calculated for a series of positions of the liquid surface during the flow; further the volumes between the chosen positions were estimated and by means of these the times elapsing between the moments at which the positions were reached. The capillary ascension was then represented graphically as a function of the time and by means of the curve the mean rise was determined. This divided by the mean height of the liquid gives the correction for the capillarity in percentages.

For water at  $0^\circ$  with  $\sigma \approx 75.5$  we found: mean capillary rise

0.034 cM.; the mean height of pressure is 11.6 cm., which gives for the correction 0.3%. For water at 30° with  $\sigma = 71.0$  it is also 0.3%.

The capillary rise of water in the capillary at 0° was 8.0 cm., that of butane at the same temperature 2.4 cm.; the correction for the time of flow was therefore for butane 0.09%: this may be regarded as constant in the field of temperature used.

*REYNOLDS'S critical velocity.*

To make sure that the velocity of the liquid remained below REYNOLDS'S critical value, an estimation was made. The volume of the upper bulb was about 3.5 cm.; the capillary tube was fully 11 cm. long, the diameter of the capillary tube  $D$  was 0.038 cm., the viscosity  $\eta$  is about 0.002, the density  $d$  at 0° is 0.60, and the time of flow 300 seconds. With these data we find for  $\frac{Ddv}{\eta}$  the value 117, which is far below REYNOLDS'S critical value (2000).

*Determinations with water. Influence of the temperature.*

The water used was doubly distilled. Great care was taken to keep it free from dust. It was renewed from time to time, which had however very little influence upon the results.

The viscosimeter was placed in a water-bath, which was kept in circulation by a rotating screw and at constant temperature by means of an adjustable number of platinum spirals through which an electric current was passed. Everything was bound round with cotton wool, which was partially removed at the beginning and end of the time determinations. The temperature was read every minute. The greatest difference during one observation was 0.07°, in the second series during 54 minutes it was 0.

During the measurements at 0° the viscosimeter stood in ice.

The two ends of the U-tube were covered by glass caps. After each determination the liquid was sucked up by a water pump.

I			II		
	temp.	time		temp.	time
31 Oct. '12	26.05	12 m. 11.4 s.	1 Nov.	26.48	12 m. 6.8 s.
	25.99	11.4		26.48	6.7
	26.03	11.6		26.48	6.2
	26.03	11.7		26.48	6.6
	26.05	11.2			
mean	26.03	731.5 s.		26.48	726.6 s.
Corrected for capillarity		729.3 sec.			724.4 sec.

III			IV		
	temp.	time		temp.	time
5 Nov.	0.00	24 min. 59.7 s.	7 Jan. '13	0.00	24 min. 57.2 s.
		59.7			57.2
		59.6			56.9
					57.0
					56.7
mean	0.00	1499.7 s.		0.00	1497.0 s.

Mean time of flow at 0° 1498.5 sec.

Corrected for capillarity 1494.0 sec.

Specific gravity of water at 0° 0.9999; at 26.48° 0.9967; at 26.03° 0.9968.

$$\eta_0 : \eta_{26.48} = 1493.9 \times 0.9999 : 724.4 \times 0.9967 = 2.069$$

$$\eta_0 : \eta_{26.03} = 1494.0 \times 0.9999 : 729.3 \times 0.9968 = 2.055$$

THORPE and RODGER<sup>1)</sup> give for the viscosity of water at

$$0^\circ \quad 0.01778$$

$$25^\circ \quad 0.00891$$

$$30^\circ \quad 0.007975$$

BINGHAM<sup>2)</sup> assumes the reciprocal of  $\eta$  as a linear function of the temperature. From THORPE and RODGER's figures follows:

$$\text{at } 0^\circ \quad \frac{1}{\eta} = 56.2$$

$$\text{,, } 25^\circ \quad 112.0$$

$$\text{,, } 30^\circ \quad 125.4$$

From this follows:

$$\text{at } 26.48^\circ \quad \frac{1}{\eta} = 115.97 \quad \text{at } 26.03 \quad 114.76$$

For the ratio of the viscosities at 26.48° and 0° we find from this:

$$\frac{\eta_0}{\eta_{26.48}} = \frac{115.96}{56.2} = 2.063$$

and

$$\frac{\eta_0}{\eta_{26.03}} = \frac{114.76}{56.2} = 2.042.$$

Our result at 26.48, 2.069, agrees with this to less than  $\frac{1}{3}\%$ , which may be regarded as sufficient. The agreement of the other figures is a little less satisfactory (about 0.7%), which is probably the consequence of the less perfect equilibrium of temperature.

<sup>1)</sup> THORPE and RODGER, On the relations between the viscosity of liquids and their chemical nature. Phil. Trans. 185 A, p. 449, 1894.

<sup>2)</sup> EUGENE C. BINGHAM and Miss J. PEACHY HARRISON, Viskosität und Fluidität. Z. f. Physik. Ch. 66, p. 1, 1909.

EUGENE C. BINGHAM Viscosity and Fluidity, A Summary of Results. Phys. Rev. XXXV, p. 407, 1912; Phys. Rev. (2) I, p. 96, 1913.

*Influence of the total quantity of water.*

All the determinations were made at 0°.

Small quantities of water were added or drawn off. After each series of determinations the viscosimeter was weighed with water and at the end the empty viscosimeter. From this follows the volume of water at each determination. Usually two measurements were made in each series. The greatest difference between them was 1.4 sec. in a total time of 25 minutes, a difference of less than 0.1 %.

The results were the following:

	weight of water.	time of flow.
10 Jan. 1913	3,24 gr.	1470,3 sec.
10 „ 1913	3,53 „	1480,2 „
7 and 8 Jan.	4,06 „	1497,0 „
8 „	4,41 „	1516,3 „
11 „	4,42 „	1517,2 „
9 „	4,88 „	1528,3 „
9 „	5.24 „	1544,4 „

Graphically represented these figures give a curve with two points of inflexion. If the bottom reservoir were cylindrical, the curve would be a hyperbola, as the product of pressure and time of flow is constant. The deviation from the hyperbola which the curve shows can be explained in every particular by the irregular form of the bottom reservoir (bulb with a tube sealed in at the side).

*Determinations with Normal Butane.*

The side tube A was connected to the reservoir which contained the butane prepared according to GRIGNARD's method <sup>1)</sup>. After the viscosimeter had been pumped out, the butane was distilled over. For this purpose the lower bulb was cooled in a mixture of ice and salt. After cooling the side tube was sealed off.

The determinations above 0° were made in a water-bath, like the determinations with water. The glass jacket, which consisted of two coaxial tubes fastened by an india-rubber ring, was turned round with the viscosimeter. The latter was clamped between two corks in which a number of holes were bored. No determinations were made above 35°, as then the internal pressure may exercise a very uncertain influence upon the volume. The vapour-pressure of butane at 35° is 3.5 atmospheres.

At 0° the viscosimeter was placed in a wide test-tube which was closed by a cork. Two glass tubes, fastened with sealing wax into

<sup>1)</sup> J. P. KUENEN Comm. Phys. Lab Leiden, No. 125, p. 4. 1911.

a strip of cork, made two openings in the ice for the observation of the beginning and end points. The test-tube stood vertically in ice, in which also two tubes left room for the observations. After one determination the test-tube was lifted out of the ice, turned upside down and put back in its place again after the upper bulb was filled.

Finally a determination was made in a bath of boiling methyl chloride.

At the suggestion of Prof. KAMERLINGH ONNES a vessel of german silver was constructed for this, in which the viscosimeter was suspended in methyl chloride in such a manner that it could be turned round while inside and that the position of the liquid in the upper bulb could be observed. In the construction connections with substances like sealing wax which come into contact with the cold liquids have to be avoided. By this means we avoid contamination of the liquid and cracking or giving way of the connections which the cold might cause. All connections are therefore made in the lid of the vessel. The three projections are represented in fig. 1, 2 and 3 at  $\frac{1}{6}$  of the actual size. The details in fig. 4—6 are actual size. The vessel consists of a neck  $H$  of circular section, a wide part, of elliptical section,  $E$ , and the bottom, which consists of a semicircularly bent strip  $R$ , the diameter of which is equal to the large axis of the ellipse and two curved sideplates  $P_1$  and  $P_2$  which complete the vessel. The vessel is provided with a number of strengthening rings  $v$  (necessary for working at low internal pressure) and stands in a box filled with cotton wool.

The viscosimeter hangs in the lower part of the vessel in a frame,  $BG$ , which is attached to a german silver tube  $TS$ , which projects above the vessel through an opening. This opening is made air-tight by a stuffing box  $PB$  (fig. 4). The tube has a bend by which the opening in the lid comes just outside the middle, which is necessary in view of the available space. This tube can be moved up and down in the stuffing box.

The viscosimeter can be turned round an axle. (fig. 5). The two tubes of the viscosimeter wound round with silk are clamped between two blocks  $B_1$  and  $B_2$  by two screws  $S_1$  and  $S_2$ .  $B_1$  is soldered to the axle. The axle is provided with a pulley  $K_1$ , which is worked by means of an endless spiral spring  $SV$  (fig. 1 and 2) by a second pulley  $K_2$  in an air-tight box above the lid of the vessel; the axle projects outside through a stuffing box (see fig. 6). This pulley is raised up out of the way of the other parts on two tubes  $B_1$  and  $B_2$  soldered on to the cover, and through which the spiral spring runs.

-6

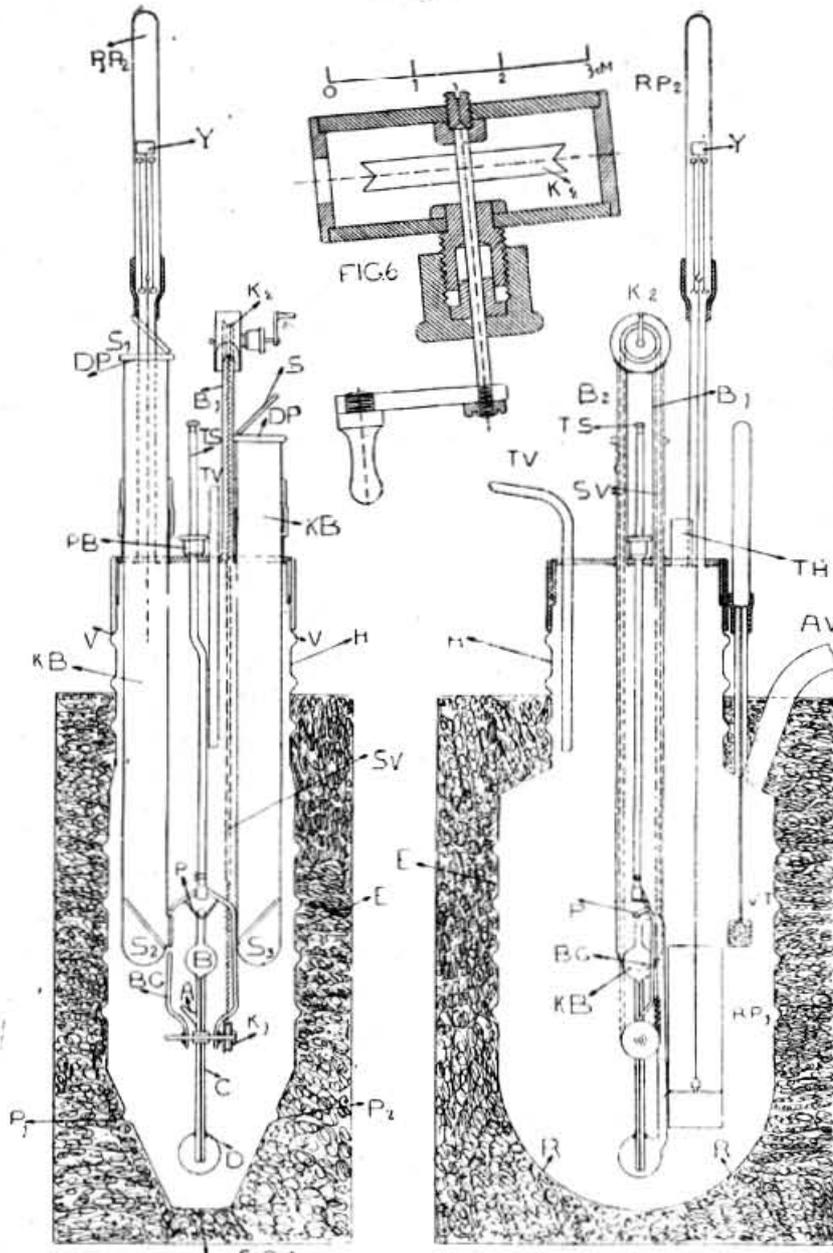


FIG. 1

FIG. 2

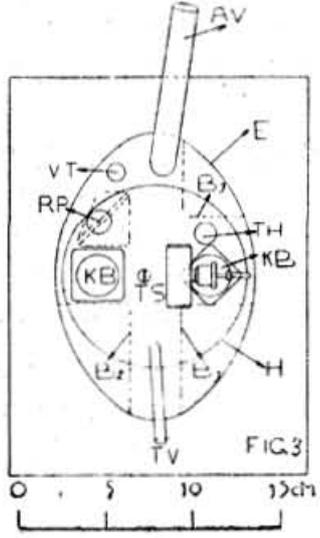


FIG. 3

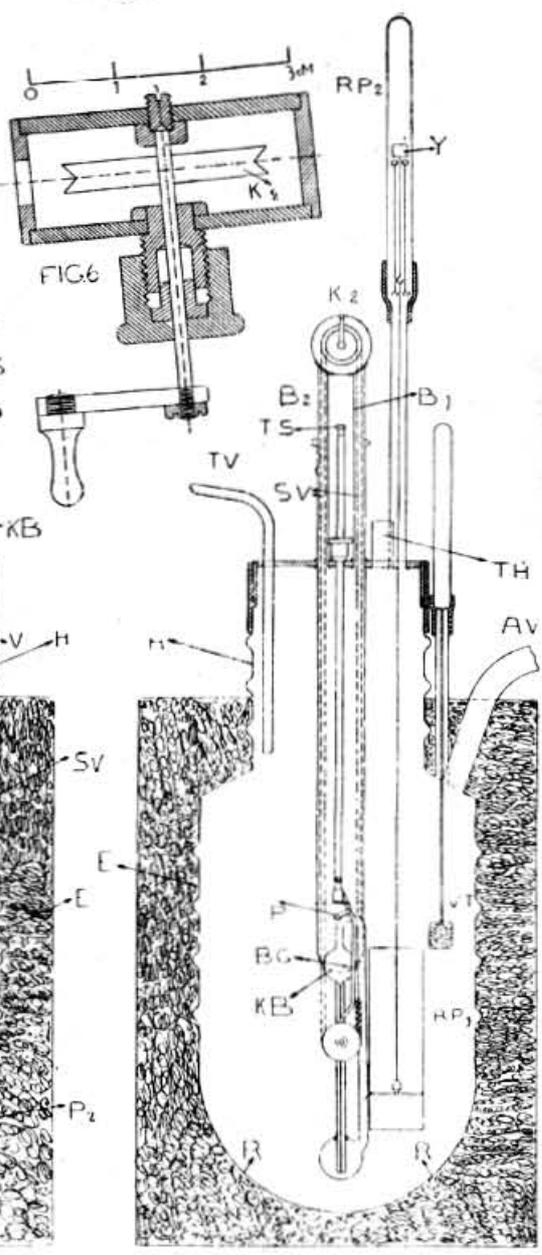


FIG. 4

FIG. 5

FIG. 6

FIG. 7

FIG. 8

The frame  $BG$  is provided with a pall bound with silk, which prevents the viscosimeter going beyond the vertical position. The turning takes place in a plane parallel to the long axis of the ellipse.

For the observation of the viscosimeter there are two view tubes  $KB$  fastened into the cover in the direction of the short axis of the ellipse, which reach below the upper bulb, (fig. 1 and 3). (In fig. 2, part of one of the tubes is shown). These tubes are closed air-tight above the cover by thick glass covering plates  $DP$ . The light of a glowlamp is thrown upon the viscosimeter by the mirrors  $S_1$  and  $S_2$ , it can be viewed by the mirrors  $S_3$  and  $S$  (fig. 1). The mirrors  $S_2$  and  $S_3$  (fig. 7) are attached to a copper cross which is soldered on to a hoop of copper wire  $K$ , resting upon the bottom of the view-tube, and by which the mirrors can be easily adjusted. When they are in the right position the wire is fastened with paraffine. Opposite to the mirror the view-tubes have a side opening ground flat, on to which a covering glass is fastened with fish-glue. This connection remains firm even in liquid air. By this means the light falls through a plan-parallel layer of liquid, so that the bulb does not appear distorted. To avoid the glue being exposed to pressure, there are openings higher up in the view-tubes (fig. 1). By moving the viscosimeter a short distance up and down with the handle  $TS$  the mark above the bulb or the beginning of the capillary tube can be brought into view. The spiral spring remains tight the whole time.

In addition the vessel contains :

1°. an electro-magnetic stirring pump  $RP$  (fig. 2 and fig. 3; in fig. 1 a part of it). The iron core  $Y$  is moved up and down by an electro-magnet round the tube  $RP_2$ . The bottom of the cylinder  $RP_1$  and the piston are provided with suitable valves, turning on an axis represented in fig. 3 by a double dotted line. The shape of the cylinder is here shown also.

2°. a floater which indicates the height of the boiling liquid.

3°. a platinum resistance-thermometer, of which only the tube sealed into the cover is shown:  $TH$  (fig. 2 and 3).

4°. a supply tube for the liquid  $TV$ , which is closed after filling.

5°. a tube  $AV$  to lead off the vapour, when working at low pressure.

6°. three tubes  $B_1$ ,  $B_2$  and  $B_3$  (fig. 3) which fill up the superfluous space, to save liquid and trouble.

When tested this cryostat appeared to be in every way satisfactory, the distinctness of the readings left nothing to be desired. At the same time the volume of the butane was so much diminished by contraction that it was difficult to get sufficient pressure, when

the viscosimeter was turned round, to drive the remaining liquid out of the capillary. Only one determination was successful. We hope later on to be able to publish more extensive determinations at low temperatures.

Our results are given in the table.

The liquid-densities were measured by a dilatometer.

temp.	time	corrected	density	$\eta$
34.5°	235.5	235.2	0.556	0.00163
18.5°	258.5	258.2	0.577	176
0.0	291.8	291.5	0.601	207
-23.6	352.6	352.3	0.631	265

The method of calculation of  $\eta$  from the data is made clear by the following example.

The viscosimeter when filled weighed 16.78 gr. and empty 14.26 gr.

The weight of the butane was therefore 2.52 gr. with a volume of 4.20 ccn.

The time of flow of 4.20 ccn. water at 0° is 1504.0 sec. (according to table on page 80; of the butane 291.8 sec.

Corrected for capillarity these times become 1499.8 and 291.5.

$$\eta_w = 0.01778 \text{ } ^1) \text{ therefore } \eta_b = 0.01778 \frac{0.601 \times 291.5}{1498.9 \times 0.9999} = 0.00207.$$

THORPE and RODGER (p. 590) give for the viscosity at the boiling point for

	$\eta \times 10^5$		
normal pentane	200	isopentane	203
„ hexane	204	isohexane	205
„ heptane	199	isoheptane	198
„ octane	198		

As the boiling point of butane is just below 0°, the value we find for  $\eta$  corresponds well with that for the other hydrocarbons.

**Physics.** — “*On the law of the partition of energy.*” III. By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS Sr.).

§ 9. *The distribution in configuration.*

In § 7 of my preceding note on this subject I have called attention to the deviations of BOLTZMANN's law for the distribution in configuration, but then I did not give a possible formula for it. Nor can I give a formula for the general case now. I will however try for

<sup>1)</sup> THORPE and RODGER l. c. p. 449.

a simple special case to draw up a formula here, which is in agreement with what is known concerning the kinetic energy. This special case is the following.

A large number  $n_0$  of particles move in a space  $V$ , which has the following properties: the particles can move freely in a part of the space without being subjected to forces. I will call this part the free space. In another part  $v$  forces will act which are directed towards a centre; the intensity of these forces will be proportional to the distance from that centre. We will assume that not only one centre of this kind is present in the space, but  $n_1$ , each of them surrounded by a region  $v$ . Every region  $v$ , however, will be surrounded by a transition region, which is characterised by the property that a particle lying in it has a much higher potential energy than one in the free space. In other words: when the particles come from the free space and penetrate into the transition-regions they are at first repulsed, and not until they have approached towards the centre to within a definite distance  $R$  will they experience the forces directed towards the centre, which I will call the quasi-elastic forces. I will assume, that the sum of all the regions  $v$  and also of the transition-regions will be small compared with the free space. This latter may therefore also be represented approximately by  $V$ .

It is obvious that in each of the regions  $v$  particles can move which execute harmonic vibrations. The period of these vibrations will be determined by the mass of the particles and by the intensity of the quasi-elastic forces. We will raise the question, what will be the distribution in velocity and the distribution in configuration of these particles.

I will assume that the component of the velocity in the direction of the radius-vector towards the centre of attraction will show a smaller amount than would agree with the equipartition law; but that the components perpendicular to it will show the normal equipartition amount. I make this assumption in order to account for the energy of di-atomic molecules, which corresponds at ordinary temperatures with five degrees of freedom. In reality, however, the properties of di-atomic molecules will probably be somewhat different from those assumed by me. The average kinetic energy of the component of the velocity in the direction of the radius vector of particles which lie in the regions  $v$  will be represented instead of by

the normal  $\frac{1}{2} \theta$ , by the value ascribed to it by PLANCK:  $\frac{1}{2} \frac{v^2 h}{e^{\theta} - 1}$ .

The supposition would now naturally suggest itself, 1<sup>st</sup>. that the mean value of the kinetic energy for this degree of freedom would be the same for the different points of the region  $v$ ; 2<sup>nd</sup>. that the partition of the velocities for this component would be represented

by  $Ce^{-\frac{1}{2}mv^2/U} dv$ . This expression however leads to an untenable formula for the distribution in configuration. I will therefore assume that the radial component of the velocity does not follow MAXWELL'S law for the distribution of velocities, and that the mean kinetic energy belonging to it is different for different points of the region  $v$ .

For points at a distance  $r$  from the centre e.g. it will amount to  $F(r)$ . This function  $F(r)$  is unknown; we only know that its mean value for different values of  $r$  will amount to  $\frac{1}{2}U$ . The components of the velocity perpendicular to the radius vector will be denoted by  $s'$  and  $t'$ . Their mean kinetic energy will be equal to the normal equipartition-amount.

In a harmonic vibration kinetic and potential energy are periodically converted into one another; therefore the distribution in configuration will follow the same law as the distribution in velocity. We are therefore justified in the following assertions concerning it. Let us take all molecules with a definite velocity  $v$ , and investigate their deviations from the position of equilibrium. We will call the component of the deviation in the direction  $v, r_v$ , the components normal to this direction  $r_s$  and  $r_t$ . The mean value of  $\frac{1}{2}fr_v^2$  for these molecules will again amount to  $F(v)$ , which function again is unknown, whereas its average value for different values of  $v$  amounts to  $\frac{1}{2}U$ . The average values of  $\frac{1}{2}fr_s^2$  and  $\frac{1}{2}fr_t^2$  present the normal equipartition-amount.

In this way we are induced to represent the number of particles whose coordinates and momenta are included between definite limits by:

$$N_e = \frac{e_p + e_q}{U} \chi(mr, ms', mt', r_v, r_s, r_t, v) dmr dm's' dmt' dr_v dr_s dr_t \dots \quad (14)$$

Here  $e_p = \frac{1}{2}m(\dot{r}^2 + \dot{s}'^2 + \dot{t}'^2)$  and  $e_q =$  the potential energy. In the space  $V$  this potential energy has a constant amount  $\epsilon_0$ ; in the

<sup>1)</sup> These Proc. Vol. XV, p. 1355 I really have expressed the opinion that this partition of velocities would probably exist. I have however written erroneously  $\frac{1}{3}U$  in the numerator of the exponent instead of  $U$ . If  $U$  represented the total kinetic energy of a particle with three degrees of freedom,  $\frac{1}{3}U$  would be the right value.  $U$  represents however the kinetic energy for one degree of freedom.

regions  $v$  it is equal to  $\varepsilon_1 + \frac{1}{2}fr^2$ , where  $\varepsilon_1$  is the energy of a particle lying in a centre of a region  $v$ .  $\chi$  is an unknown function, which for  $v=0$  (i. e. in  $V$ ) assumes the value unity, whereas in the regions  $v$  it must satisfy the following equations:

$$\left. \begin{aligned} \frac{\int \frac{1}{2}mr^2 Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi(r) dm r dm s' dm t' dr_v dr_s dr_t}{\int Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi(r) dm r dm s' dm t' dr_v dr_s dr_t} &= \frac{1}{2} \frac{vh}{\frac{vh}{\theta} - 1} \end{aligned} \right\} \quad (15a)$$

and a corresponding formula for the mean value of  $\frac{1}{2}fr_v^2$ ; and

$$\left. \begin{aligned} \frac{\int \frac{1}{2}ms'^2 Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi(r) dm r dm s' dm t' dr_v dr_s dr_t}{\int Ne^{-\frac{\varepsilon_p + \varepsilon_q}{\theta}} \chi(r) dm r dm s' dm t' dr_v dr_s dr_t} &= \frac{1}{2} \theta \end{aligned} \right\} \quad (15b)$$

and three corresponding formulae for the average values of  $\frac{1}{2}mt^2$ ,  $\frac{1}{2}fr_s^2$  and  $\frac{1}{2}fr_t^2$ .

In consequence of the formulae (15b) we no doubt must assume, that  $\chi$  is independent of  $s'$ ,  $t'$ ,  $r_s$  and  $r_t$ . If this is so we can divide in (15a)

the numerator and the denominator by  $\int e^{-\frac{1}{2}ms'^2}{\theta} dm s'$  and by three corresponding integrals. We get therefore, if we add the two equations (15a):

$$\frac{\int (\frac{1}{2}mr^2 + \frac{1}{2}fr_v^2) e^{-\frac{mr^2 + fr_v^2}{2\theta}} \chi(r, r_v, v) dm r dr_v}{\int e^{-\frac{mr^2 + fr_v^2}{2\theta}} \chi(r, r_v, v) dm r dr_v} = \frac{vh}{\frac{vh}{\theta} - 1} \quad (16)$$

The integrations with respect to  $v$  should be extended between 0 and  $\infty$ , properly speaking those with respect to  $r$  however only between 0 and  $R$ . If  $R$  and  $f$  are sufficiently great and  $\theta$  sufficiently small, it will be allowed to introduce also  $\infty$  as superior limit for the integration with respect to  $r$ .

If we call the denominator of the left hand member of (16)  $J$ , then the numerator may be represented by  $\theta^2 \frac{dJ}{d\theta}$ . The equation may therefore be written in the following form:

$$\frac{1}{J} \frac{dJ}{d\theta} = \frac{\frac{vh}{\theta^2}}{\frac{vh}{\theta} - 1} = \frac{e^{-\frac{vh}{\theta}} \cdot \frac{vh}{\theta^2}}{1 - e^{-\frac{vh}{\theta}}} \dots \dots \dots (17)$$

from which we deduce:

$$J = \frac{C}{1 - e^{-\frac{vh}{\theta}}} \dots \dots \dots (18)$$

The value of  $C$  may be determined, because we know that for  $v = 0$  the function  $\chi$  assumes the value 1. Then the integral becomes

$\sqrt{2\pi m\theta} \cdot \sqrt{2\pi \frac{\theta}{f}}$  and the right hand member  $C \cdot \frac{vh}{\theta}$ . In connection with  $v = \frac{1}{2\pi} \sqrt{\frac{f}{m}}$  this yields:

$$C = h \cdot 1)$$

§ 10. Application to chemical equilibrium.

We will apply these results for the derivation of a formula for the dissociation equilibrium of a di-atomic gas. For this purpose we will assume, that  $n_1$  free atoms are present in a unit of volume. Each atom has a region  $v$ , whose properties are described in the preceding paragraph. When another atom penetrates into the region  $v$ , a di-atomic molecule is formed. According to our considerations in the preceding paragraph we have:

$$n_1 = Ne^{-\frac{\epsilon_0}{\theta}} \int e^{-\frac{\epsilon_p}{\theta}} dm_r dms' dmt' = Ne^{-\frac{\epsilon_0}{\theta}} (2\pi m\theta)^{3/2} \dots (19)$$

$\chi$  being unity for free space. The number of particles in one region  $v$  amounts to:

$$n_v = Ne^{-\frac{\epsilon_1}{\theta}} \int e^{-\frac{\epsilon_p + 1/2 f (r_v^2 + r_s^2 + r_t^2)}{\theta}} \chi(r, r, v) dm_r dms' dmt' dr_v dr_s dr_t =$$

$$= Ne^{-\frac{\epsilon_1}{\theta}} \cdot 2\pi m\theta \cdot 2\pi \frac{\theta}{f} \cdot \frac{h}{1 - e^{-\frac{vh}{\theta}}}$$

<sup>1)</sup> Properly speaking  $C$  can be a function of  $v$ , and therefore we should write for  $C = h \times F(v)$ , where  $F(v)$  is a function of  $v$ , which for  $v = 0$  is unity. In the following, however, we will use the simple solution  $C = h$ .

So the total number of associated molecules is:

$$n_g = n_1 \times n_v = n_1^2 e^{\frac{\epsilon_0 - \epsilon_1}{\theta}} (2\pi\theta)^{1/2} \frac{1}{fV/m} \frac{h}{1-e \cdot \frac{vh}{\theta}}$$

or

$$n_g = n_1^2 e^{\frac{\epsilon_0 - \epsilon_1}{\theta}} \sqrt{\frac{\theta}{8\pi^3 m^3}} \frac{\frac{h}{v^2}}{1-e \cdot \frac{vh}{\theta}} \dots \dots \dots (20)$$

So we have found a general formula for the dissociation of di-atomic molecules. I hope to discuss this formula later more fully. At present I will only observe, that it shows a certain analogy with the results of NERNST's "Wärme-theorem". This analogy consists in the circumstance, that the equilibrium-constant is determined by  $\epsilon_0 - \epsilon_1$  (i. e. the heat developed by the reaction at the absolute zero of temperature) and by  $r$ , which quantity is closely connected with the store of energy and the specific heat. Besides the molecular weight occurs in the formula. The chemical volumes (i. e. BOLTZMANN's "kritische Raume") to which we should be inclined to ascribe an influence on the equilibrium-constant do *not* occur in the formula. The cause of this is that in equation (16) we have extended the integrations with respect to  $r$  between 0 and  $\infty$  instead of between 0 and  $R$ . If the conditions on which we thought we were justified in doing so are not satisfied, then the formula would of course have to be modified in such a way that the chemical volumes would occur in it. In this case, however, the number of molecules dissociating in one second would be so large, that we should be in circumstances in which we consider the substance to be totally dissociated. We should no longer have occasion to speak of chemical combination, but only of grouping or quasi-association.

A difference with the considerations of NERNST constitutes the circumstance that we started in the usual way from gasreactions, whereas NERNST takes reactions in solid condition as starting-point. Whether this is only a difference of method, or whether it leads to different results is a question which I hope to investigate on a later occasion.

I will still make one single remark in connection with equation (20), namely that it agrees with the law of the equilibrium change.

If namely we put  $\frac{n_g}{n_1^2} = K$ , then we get:

$$\frac{dK}{dO} = \frac{1}{O^2} \left\{ \varepsilon_1 - \varepsilon_0 + \frac{1}{2} \theta + U \right\} \dots \dots \dots (21)$$

The expression between braces represents the thermal value of the reaction. For in the free space the potential energy is  $\varepsilon_0$  and the mean kinetic energy  $\frac{3}{2} \theta$ . In associated condition the potential energy would be  $\varepsilon_1$ , if the particles were always in the centres of the regions  $v$ . For the average potential energy of the deviation from that position of equilibrium in the direction  $v$  we have found  $\frac{1}{2} U$  and for the two components of the deviation normal to  $v$  each  $\frac{1}{2} \theta$ . For the kinetic energy we assumed in the same way  $\frac{1}{2} U + \theta$ . So we get for the thermal value of the reaction:

$$\varepsilon_1 + 2 \theta + U - \left( \varepsilon_0 + \frac{3}{2} \theta \right) = \varepsilon_1 - \varepsilon_0 + \frac{1}{2} \theta + U.$$

It is by no means superfluous to investigate whether this law is satisfied. If e.g. we had assumed MAXWELL'S law for the distribution

$-\frac{1}{2} f r_v^2$

of  $r$  and if in connection with this we had written  $C e^{-\frac{U}{dr_v^2}}$  for the probability of a deviation  $r_v$  in the direction  $v$  then we should have found a formula for  $K$  which in general would not satisfy the law of the equilibrium change. Artificial additional suppositions would be required if we wished this law to be satisfied.

§ 11. *The distribution in configuration in arbitrary fields of force.*

The above considerations only refer to particles subjected to forces, under the influence of which they can execute tautochronic harmonic vibrations. About the question what the formula for the distribution of particles in arbitrary fields of forces will look like, I should not venture to express so much as a supposition, except of course in those cases in which BOLZMANN'S original formula is a sufficient approximation. I will only express the following surmise.

For quasi-elastic forces the energy of the particles is governed by the quantity  $v$ , which in its turn is again determined by the quantity  $f$ . The conclusion now naturally suggests itself that for an arbitrary field of forces the quantity  $\frac{dF}{dv}$  ( $F =$  the force that acts on a particle) will be decisive for the energy of the particles. This supposition comes to this, that we assume that the particles, when they get into a very inhomogeneous field of forces, in consequence of this are subjected to changes in properties (shape, mass etc.), which changes are not governed by the laws of classical mechanics, and give rise to the deviations from the equipartition law.

**Chemistry.** — “*On the reduction of aromatic Ketones*”. By Prof. J. BOESEKEN and W. D. COHEN. (Communicated by Prof. A. F. HOLLEMAN).

1. This research originated in the observation by one of us that in the reduction of benzophenone by aluminium amalgam in 80% alcohol, therefore in a neutral medium, are formed considerable quantities of benzopinacone in addition to benzhydrole. As according to statements in the literature which are supported by our own observations, benzophenone may be quantitatively converted into benzhydrole by zinc dust in a faintly alkaline alcoholic solution, whereas reduction in an acid solution causes the formation of pinacone<sup>1)</sup> (or of the pinacoline secondarily resulting there from) it struck us that a systematic research as to the progressive change of this reduction would not be devoid of interest.

In the reduction of benzophenone may be formed, besides alcohol and pinacone, also diphenylmethane. KLAGES and ALLENDORF<sup>2)</sup> have even succeeded in obtaining a quantitative yield of this hydrocarbon by means of sodium and ethyl alcohol. Evidently this total reduction takes place owing to a powerful action in a concentrated alkaline medium. Presumably, stress must be laid here on the nature of the reduction agent because on using zinc dust in a strongly alkaline alcoholic solution benzhydrole is formed almost exclusively, whereas on using aluminium amalgam diphenylmethane may be detected. Working according to MONTAGNE's<sup>3)</sup> directions with zinc dust we have obtained from 25 grams of benzophenone 25 grams of crude hydrole which was practically odourless consequently free from diphenylmethane.

With magnesium amalgam (obtained by heating 2 grams of Mg with 200 grams of Hg) was obtained, in absolute alcohol solution, mainly benzhydrole besides a little diphenylmethane, but no pinacone.

As magnesium and aluminium stand nearer to sodium than zinc, this result is not astonishing.

In order not to complicate the reaction too much we have tried to avoid the formation of diphenylmethane as much as possible.

As reduction agents we have chosen: zinc dust and aluminium, the latter in the form of amalgam in so far as it concerned the reduction in a neutral or acid medium.

Again, when using the latter metal we have avoided a too power-

<sup>1)</sup> LINNEMANN Ann **133**, 6

<sup>2)</sup> Berichte **31**. (1898).

<sup>3)</sup> Recueil **25**, 402 (1906).

fully acid or alkaline reaction, because diphenylmethane is then also formed.

As solvent we selected in all cases a liquid containing 80% ethyl alcohol to which the acid, alkali, etc. was eventually added.

In 80% alcohol benzophenone is practically insoluble whilst the hydrole is readily soluble therein, so that the determination of the two substances in a mixture is a simple matter.

Solubility of pinacone: Shaken in a thermostat for one day at 25°.

In supersaturated solution 100 cc. retained 0.124 gram.

„ unsaturated „ „ „ dissolved 0.110 „

The solubility of benzhydrole = ± 35 grams.

We have also ascertained that the solubility of pinacone is not appreciably influenced by quantities of hydrole up to 5 grams.

The *modus operandi* was very simple. Quantities of 5 grams of benzophenone were boiled for some time in a reflux apparatus, with the requisite amounts of the reduction agent, in 50 cc. of 80% alcohol; the solution was filtered hot, the residue was extracted with small quantities of boiling 80% alcohol, the filtrate made up to 100 cc. and then shaken at 25° for one day.

In 50 cc. of the solution the hydrole was determined by evaporation. The residue was tested as to its purity by the determination of its odour, melting point, and crystal-habit.

This evaporation was always carried out in the same manner, for the hydrole is somewhat volatile; for instance, if the evaporation lasts 30 minutes, 12 mg. of benzhydrole get lost.

For this loss a correction was made as well as for the pinacone eventually present.

## 2. *Reduction in a neutral medium.*

This was only possible with aluminium amalgam. This was prepared by shaking aluminium grit with 1% HgCl<sub>2</sub> solution for 15 minutes at the ordinary temperature, filtering off rapidly and washing with 96% alcohol. It was then at once used for the reduction in the proportion of 10 grams of the aluminium to 5 grams of benzophenone.

The following figures were obtained: (see table page 93).

Hence, the result shows that the proportion in which hydrole and pinacone are formed is constant, namely 68% : 32%, independent of the time of the reduction.

Pinacone once formed is not reduced any further in a neutral solution within seven hours, so it cannot be considered as an intermediate product.

No. of experiment	Time of reduction	Benzhydrole formed	Remarks
1	1 uur	3.37 gr.	The residue on evaporation was odourless and melted at 68° hence contained no benzophenone and diphenylmethane. The insoluble part contained 1.55 grams of pinacone.
2	2 "	3.45 "	
3	3 "	3.41 "	
4	4 "	3.4 "	Preliminary experiments, where the solution after boiling was left for 24 hours. After filtering, the residue was washed with cold alcohol. The insoluble part contained 1.6 grams of pinacone.
5	5 "	3.2 "	
6	6 "	3.3 "	
7	7 "	3.4 "	

### 3. Reduction in a faintly acid medium.

#### A. With zinc dust.

After it had been ascertained that no appreciable change had taken place on boiling benzophenone with 80% alcohol and zinc dust for 6 hours, the operation was repeated in a *current of carbon chloride*.

After boiling 10 and 12 hours 4.19 and 4.00 grams of residue were obtained on evaporation; this however, melted just below 48° and had the usual properties of benzophenone. The remaining of the 5 grams was benzpinacone.

On again subjecting the residue a few times to the same process (in order to concentrate hydrole formed eventually) the quantity became less, namely 2.9 and 1 gram, but it remained benzophenone. The quantity of the product insoluble in 80% alcohol increased, it was pinacone, but not very pure.

With zinc dust in a very faintly acid medium the reaction therefore proceeds very slowly and with exclusive formation of pinacone.

This same result was also obtained when instead of carbon dioxide ammonium chloride was taken. 10 grams of zinc, 3 grams of NH<sub>4</sub>Cl and 50 cc. of 80% alcohol were chosen for 5 grams of benzophenone.

The operation here had to be modified somewhat because the residue on evaporation contained zinc and nitrogen; it was boiled with hydrochloric acid (1 part of acid 1.19 — 1 part of water), washed and dried.

After boiling for 3½, 6 and 12 hours we obtained as a purified residue: 2.22, 1.87, and 0.99 gram of a substance melting below 48° and having a strong odour of benzophenone.

The insoluble part was a not very pure pinacone; after extraction with benzene and evaporation it melted at 170°.

In a somewhat stronger acid medium pinacone (pinacoline) was also obtained exclusively.

For this was used a mixture of 80% of alcohol and 20% of glacial acetic acid; quantities of 15 grams of zinc dust and 75 cc. of the acid mixture were chosen for 5 grams of benzophenone.

The reaction takes place more energetically and much zinc acetate is deposited. The liquid is therefore diluted with water and the remaining zinc rapidly dissolved by means of dilute HCl. A solid substance is now left which is shaken for a day with 100 cc. of 80% alcohol as directed above.

On boiling for 2 and 6 hours, respectively only 0.45 and 0.35 gram of a substance readily soluble in 80% alcohol had formed; its melting point was, however, situated below 25°; it did not crystallise in the shape of felt-like needles and had the typical odour of diphenylmethane; the residue consisted of pinacone.

Hence, the reduction proceeds in dilute acetic acid and zinc dust much more rapidly than in a nearly neutral medium, but otherwise in the same direction.

This result agrees with that of ZAGOMENNI<sup>1)</sup>, who obtained 92% of pinacone in glacial acetic acid solution.

With sulphuric acid (80 cc. of 96% alcohol, 20 cc. of H<sub>2</sub>SO<sub>4</sub>, 1—1) exactly the same result was obtained. After boiling for 2—4 hours, respectively there was obtained only 0.28—0.27 gram of a product: soluble in alcohol having the odour of orange peels and a very pale yellow colour with a low melting point; the part not soluble in alcohol was, presumably, mainly pinacoline.

#### B. Reduction in a faintly acid medium with aluminium.

Aluminium grit was not attacked by the above acetic acid-alcohol mixture (15 grams of Al, 75 cc. of acid mixture to 5 grams of benzophenone). Therefore, a little HgCl<sub>2</sub> was added which caused the reaction to set in. After three hours' boiling the product was treated as stated above; no hydrole could be detected, only a little of a pale yellow product soluble in alcohol and having an odour of orange-peels, all the rest consisted of pinacone. The melting point 165° also again pointed to formation of pinacoline. Contrary to the reduction in a neutral solution *no* hydrole is formed.

#### 4. Reduction in a faintly alkaline medium.

##### A. With zinc dust.

For this was chosen a mixture of 50 cc. of 96% alcohol, 25 cc.

<sup>1)</sup> B 14, 102 (1881),

of ammonia density 0.93 and 10 grams of zinc dust, which was boiled with 5 grams of benzophenone.

After 2 and 5½ hours' boiling, respectively 4.21—4.34 grams of pure hydrole were formed; the balance consisted of pinacone, which could be isolated by the extraction of the insoluble part with benzene.

After 2 hours nearly all the ammonia was boiled off; after 5½ hours it had quite disappeared.

*B. With aluminium amalgam.*

For 5 grams of ketone were taken 40 cc. of alcohol, 10 cc. of ammonia and 10 grams of aluminium amalgam and the whole was boiled until all the ammonia was expelled (3 hours). 4.81 grams of very beautiful benzhydrole and 0.21 gram of pure pinacone were obtained.

From this we notice that the reduction is almost independent of the metals and that the result is mainly governed by the reaction of the medium.

5. In a stronger alkaline medium with alcoholic sodium hydroxide not a trace of pinacone was obtained, with zinc dust as well as with aluminium; the product was very readily soluble in 80% alcohol. During the aluminium reduction, which was particularly violent, a product was obtained having a pale yellow colour and which judging from the odour, contained a little diphenylmethane.

Let us tabulate the results obtained in the subjoined survey (also including sodium).

Medium	Zinc dust	Aluminium	Magnesium	Sodium
acetic acid	pinacone	pinacone	—	—
	in presence of some diphenylmethane and pinacoline			
very faintly acid: carbonic acid, NH <sub>4</sub> Cl.	pinacone	—	—	—
neutral	—	pinacone 32% hydrole 68 "	—	—
faintly alkaline (NH <sub>3</sub> )	pinacone 15% hydrole 85 "	pinacone 4 " hydrole 96 "	—	—
strongly alkaline	hydrole	hydrole	hydrole	hydrole
	in presence of diphenylmethane			

When we disregard the formation of diphenylmethane it is beyond all doubt that the formation of pinacone or benzhydrole is in the first instance dependent on the reaction of the medium.

The nature of the metal is apparently of secondary importance and can only exert an influence in so far as it yields OH-ions. (Magnesium, sodium).

So long as the reaction is acid, even ever so feeble, pinacone is exclusively formed; but no sooner do OH-ions occur than we notice the appearance of the hydrole.

This even takes place with aluminium-amalgam in 80 % alcohol where we may take it for granted that the liquid is practically neutral, although the possibility is not excluded that at the boundary layer of the metal a very small excess of OH is temporarily present.

If the excess of OH-ions is small we can still detect the pinacone in the presence of hydrole, but when it becomes more considerable pinacone is soon no longer present.

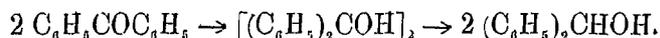
The cause of the non-occurrence of pinacone in strongly alkaline solutions is now very easy to explain. If we boil a solution of pinacone with sodium ethoxide it gets converted into a mixture of benzophenone and hydrole.

During the reduction in an alkaline medium the pinacone generated will be continuously converted into the above mixture of which the keton will be again reduced, so that finally all will have been converted into hydrole.

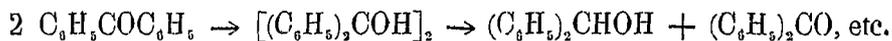
Apparently the latter, in strongly alkaline liquids, becomes the only direct reduction product.

That this, however, cannot be the case is shown from the course of the reduction in a feebly alkaline medium where also pinacone may be retained.

In a neutral solution much larger quantities of pinacone may be retained and owing to the fact that they are not reduced any further we have already come to the conclusion that pinacone cannot be an intermediate reaction product as the following scheme might express:



In an alkaline solution, pinacone can be, incidentally, an intermediate product owing to a secondary reaction:



We might assume that, apart from this secondary hydrole formation, a direct addition of an entire molecule of hydrogen to the ketone takes place under the influence of the OH-ions. Then however it would be strange that in presence of an excess of OH-ions,

however small, pinacone was still formed and retained because now two causes would cooperate to retard the formation of pinacone.

It appears to us as the most probable that the direct reduction product is in all cases the *half pinacone molecule* which afterwards :

1. will polymerise to pinacone which remains unchanged in a neutral solution and resolves into hydrole and ketone in an alkaline solution; the ketone can then again be attacked.

2. will possibly, be further reduced to hydrole and diphenylmethane.

We base this conception, besides on the above experiments from which appears a predilection for the formation of pinacone, also on observations as to the behaviour of mixtures of benzophenone and absolute alcohols and other substances in direct sunlight.

CIAMICIAN and SILBER<sup>1)</sup> have in this way obtained pinacone quantitatively from benzophenone and ethyl alcohol, we have been able to confirm this result with a series of other alcohols<sup>2)</sup>. Not a trace of hydrole is formed in these neutral liquids *absolutely free from hydroxyl-ions*.

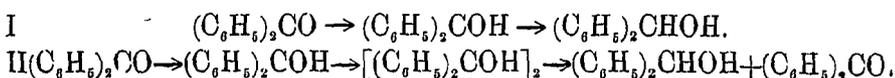
With benzyl alcohol and with ether the two Italian chemists found, besides pinacone, substances such as  $(C_6H_5)_2COHCHC_6H_5OH$  and  $(C_6H_5)_2COHCHCH_3OC_2H_5$ , whose formation, like that of pinacone may be explained in the simplest manner by a primary addition of one hydrogen-atom to the ketone-oxygen which will here be followed immediately by an attachment of the molecular residues to the carbon of the CO-groups.

Hence, in the above formulated assumption it has been taken for granted that the half pinacone molecule  $(C_6H_5)_2COH$  is the sole real intermediate product.

It is now very well possible that this, in an alkaline solution, is straightway reduced to hydrole (2).

But it is, however, also not excluded that the polymerisation to pinacone takes place, also in alkaline solution, with such velocity that this latter product is formed first also in these circumstances, then to be secondary converted into hydrole in the manner suggested above.

The two alternatives may be represented as follows:



If the latter is the case it is to be expected that the ketones which yield pinacones that are rapidly resolved by OH-ions into a mixture

<sup>1)</sup> B 33, 2911; 36, 1577; 43, 1536; 44, 1557.

<sup>2)</sup> This research will become the subject of a further communication.

of ketone and hydrole will yield on reduction in a (OH-containing) neutral medium a slight amount of pinacone.

In order to verify this experimentally we have commenced by reducing a series of ketones by means of aluminium amalgam in 80 % alcohol.

The subjoined table gives a survey of the results concerned :

Ketone (5 grams)	m.p. ketone	Quantity of hydrole		m.p. hydrole	Quantity of pinacone <sup>1</sup>		m.p. pinacone
		in gr.	in %		in gr	in %	
Benzophenone	48°	3.40	68	67°5	1.60	32	178°—180°
4 methoxybenzophenone	62°	3.22	64	60°	1.84	36	158°—160°
4 methylbenzophenone	55°	2.94	59	48°	2.07	41	164°—165°
4,4' dimethylbenzophenone	94°	2.58	52	67°—68°	2.40	48	180°—181°
4 Bromobenzophenone	81°	4.22	84	64°—65°	0.73	15	169°—170°
4 Chloro4'meth.benzoph.	118°	4.96	100	67°5	0.04		
2 Chloro4'meth.benzoph.	99.°5	4.35	87	67°	0.65	13	175°—176°
2 Chlorobenzophenone	45.°5	4.77	85	67°5	0.29	6	174°—175°
3 Chlorobenzophenone	81°	4.87	97	1)	0.12	2	
2,4' dichlorobenzophenone	52°	4.87	97	1)	0.14	3	
4,4' dichlorobenzophenone	144.°5	4.82	96	89°	0.19	4	180°
2,4,2',4' tetrachl.benzophen.	78°	5.0	100	100°	0.01		
4 Chlorobenzophenone	76°	4.27	85	78°5	0.72	14	179°

Disregarding a few irregularities, the following is now apparent from this table :

1. The methoxy- and methyl group appear to promote in a slight degree the formation of pinacone.

2. Halogen in the nucleus favours in a high degree the formation of the hydrole so that, particularly with plural substitution, the formation of pinacone is nearly, or entirely, prevented.

3. The position of the substituent in the nucleus does not appear to be of considerable influence on the proportion in which hydrole and pinacone are generated; on the other hand the nature of the group entered seems to be of more importance.

Hence, many important differences may be observed in the relation

<sup>1</sup>) These hydroles have low melting points; as only small quantities were at our disposal we did not succeed obtaining them in a perfectly pure condition.

pinacone: hydrole, which are dependent on the group introduced.

It is to be expected that these differences will continue to exist also in another medium provided this remains neutral, for instance when we reduce with aluminium amalgam in another saturated alcohol. This indeed proved to be the case.

Ketone	Solvent	Formed hydrole
Benzophenone	C <sub>2</sub> H <sub>5</sub> OH	68%
	CH <sub>3</sub> OH	68 "
o-Chlorobenzophenone	C <sub>2</sub> H <sub>5</sub> OH	94 "
	CH <sub>3</sub> OH	93 "

On the other hand it was ascertained that a ketone which in a neutral solution gave almost exclusively hydrole, yet yielded in a feebly acid solution nothing else but pinacone.

2 grams of *pp'* di-chlorobenzophenone yielding in a neutral solution with AlHg 96 % of hydrole gave with zinc dust and the acetic acid-alcohol mixture 1.99 grams of pure pinacone m. p. 180°.

0.1820 and 0.1926 gram gave 0.2060 and 0.2207 gram AgCl

Calculated for C<sub>12</sub>H<sub>10</sub>O<sub>2</sub>Cl<sub>2</sub> 28.1 % Cl (Found 28.0—27.7).

This also agrees with the assumption that the formation of pinacone, in the absence of OH-ions and in this method of reduction, takes place very much more rapidly than that of other possible reduction products and that the hydrole formation in a neutral medium must be attributed to the presence of OH-ions at the boundary layer.

The measurement of the velocity with which some pinacones are converted into the mixture of ketone and hydrole will be the subject of a following communication.

*Lab. Organic Chemistry  
Technical University.*

*Delft, May 1913.*

**Chemistry.** — "*Equilibria in ternary systems*". VIII. By Prof. SCHREINEMAKERS.

Let us now consider the case when a liquid *L* is saturated with the solid compounds *F* and *F'* and at the same time in equilibrium with a vapour *G*. As the system *F* + *F'* + *L* + *G* contains the three components in four phases it is monovariant; hence we can consider the vapour pressure of the system and the composition of *L* and *G* as functions of the temperature.

7\*

On a change in  $T$  the liquid therefore traverses a curve in a concentration diagram; this is also the case with the correlated vapour. We will call these curves the saturation and vapour saturation curves of  $F + F'$  under their own vapour pressure, or also the liquidum and the vapour curve of the four-phase equilibrium  $F + F' + L + G$ . The relation between pressure and temperature will also be represented by a curve in a  $P, T$ -diagram.

In fig. 4 this  $P, T$ -curve is represented by  $LSDR$ ; in fig. 1, 2 and 3  $ac$  is the liquidum and  $a_1c_1$  the vapour curve of the system  $F + F' + L + G$ . Point  $a$  of the curve  $ac$  therefore represents a liquid saturated at a definite  $P$  and  $T$  with  $F + F'$ ; point  $a'$  indicates the correlated vapour.

Let us represent the composition, the entropy, the volume and the  $\zeta$  of  $F$  by:  $\alpha, \beta, 1-\alpha-\beta; \eta, v$  and  $\zeta$   
 that of  $F'$  by:  $\alpha', \beta', 1-\alpha'-\beta', \eta', v'$  and  $\zeta'$   
 that of the liquid by:  $x, y, 1-x-y, H, V$  and  $Z$   
 that of the vapour by:  $x_1, y_1, 1-x_1-y_1, H_1, V_1$  and  $Z_1$

The conditions of equilibrium then are:

$$\left. \begin{aligned} Z - (x - \alpha) \frac{\partial Z}{\partial x} - (y - \beta) \frac{\partial Z}{\partial y} &= \zeta \\ Z - (x - \alpha') \frac{\partial Z}{\partial x} - (y - \beta') \frac{\partial Z}{\partial y} &= \zeta' \\ Z_1 - (x_1 - \alpha) \frac{\partial Z_1}{\partial x_1} - (y_1 - \beta) \frac{\partial Z_1}{\partial y_1} &= \zeta \\ \frac{\partial Z}{\partial x} = \frac{\partial Z_1}{\partial x_1} \quad \frac{\partial Z}{\partial y} = \frac{\partial Z_1}{\partial y_1} \end{aligned} \right\} \dots \dots \dots (1)$$

Hence, we have five relations between the six variables  $x, y, x_1, y_1, P$ , and  $T$ , so that we can consider the vapour pressure of the system and the composition of  $L$  and  $G$  as functions of the temperature as stated above. If we differentiate the equations (1) and eliminate  $dx$ , and  $dy$ , we obtain:

$$[(x - \alpha) r + (y - \beta) s] dx + [(x - \alpha) s + (y - \beta) t] dy = AdP - BdT \quad (2)$$

$$[(x - \alpha') r + (y - \beta') s] dx + [(x - \alpha') s + (y - \beta') t] dy = A'dP - B'dT \quad (3)$$

$$[(x_1 - \alpha) r + (y_1 - \beta) s] dx + [(x_1 - \alpha) s + (y_1 - \beta) t] dy = CdP - DdT \quad (4)$$

$A, B, C$  and  $D$  have herein the values indicated in communication II;  $A'$  and  $B'$  are found from  $A$  and  $B$  by substituting in the latter  $\alpha, \beta, v$  and  $\eta$ , by  $\alpha', \beta', v'$  and  $\eta'$ . If we eliminate  $dx$  and  $dy$  from (2), (3) and (4) we get:

$$\frac{dP}{dT} = \frac{n \eta + n' \eta' + m H + m_1 H_1}{n v + n' v' + m V + m_1 V_1} \dots \dots \dots (5)$$

In this:

$$\left. \begin{aligned} n &= [\beta' (x-x_1) + \alpha' (y_1-y) + x_1 y - x y_1] \lambda \\ n' &= [\beta (x_1-x) + \alpha (y-y_1) + x y_1 - x_1 y] \lambda \\ m &= [x_1 (\beta'-\beta) + y_1 (\alpha-\alpha') + \alpha' \beta - \alpha \beta'] \lambda \\ m_1 &= [x (\beta-\beta') + y (\alpha'-\alpha) + \alpha \beta' - \alpha' \beta] \lambda \end{aligned} \right\} \dots \dots \dots (6)$$

in which  $\lambda$  is an arbitrary factor. The significance thereof is as follows: In each fourphase equilibrium  $F + F' + L + G$  a reaction can always take place, which we represent by:

$$n \text{ quant. } F + n' \text{ quant. } F' + m \text{ quant. } L + m_1 \text{ quant. } G = 0 \quad (7)$$

It is evident that the four reaction coefficients in (7) cannot have the same sign. With the aid of the known compositions of the four phases we find from (7) that  $n$ ,  $n'$ ,  $m$  and  $m_1$  have the values given in (6). The numerator of (5) therefore represents the change in entropy, the denominator the change in volume occurring in reaction (7). If we call the heat to be supplied or withdrawn in this reaction  $\Delta W$  and the change occurring in volume  $\Delta V$ , then (5) changes into the well-known relation:

$$T \frac{dP}{dT} = \frac{\Delta W}{\Delta V} \dots \dots \dots (8)$$

which, of course, we might have deduced in a different manner.

Before applying this formula we will first investigate more closely the liquidum and the vapour curve and the reactions which can appear in the system  $F + F' + L + G$ .

Let us first consider the point of intersection  $S$  of the liquidum curve  $ac$  (fig. 1, 2 and 3) with the line  $FF'$ ; the vapour appertaining to this liquid  $S$  is indicated by  $S_1$ . As the three points  $F$ ,  $F'$ , and  $S$  of this four-phase equilibrium  $F + F' + \text{liquid } S + \text{vapour } S_1$  are situated on a straight line, a reaction occurs in which the vapour does not take part. According to the situation of the three points  $F$ ,  $F'$ , and  $S$  in regard to each other this reaction will be  $F + F' \rightleftharpoons L$  or  $F' \rightleftharpoons F + L$  or  $F \rightleftharpoons F' + L$ .

If the three points are situated as in fig. 1 or 2, the reaction is  $F + F' \rightleftharpoons L$ ; the liquid  $S$  is then formed by the joint fusion of the compounds  $F$  and  $F'$ , so that the point  $S$  is a point of the melting point line of the complex  $F + F'$ . As this liquid, however, can be also in equilibrium with a vapour  $S_1$ , the point  $S$  is the minimum melting point of the complex  $F + F'$ .

If the three points are situated as in fig. 3 the reaction  $F' \rightleftharpoons F + L$  occurs; the point  $S$  is then the incongruent minimum melting point of the complex  $F + F'$ .

In the point of intersection  $D_1$  of the vapour line  $a_1c_1$  with the line  $FF'$  the correlated liquid has the composition  $D$ . As of this four-phase equilibrium  $F + F' + \text{liquid } D + \text{vapour } D_1$  the three phases  $F, F'$  and  $D_1$  are situated on a straight line, a reaction occurs in which the liquid takes no part. According to the situation of the three points  $F, F'$  and  $D_1$ , in regard to each other this reaction is:  $F + F' \rightleftharpoons G$  (fig. 1) or  $F' \rightleftharpoons F + G$  (fig. 2) or  $F \rightleftharpoons F' + G$  (fig. 3).

The point  $D_1$  is, therefore a point of the congruent or incongruent sublimation curve of the complex  $F + F'$ . As, however, this vapour  $D_1$  may also be in equilibrium with a liquid  $D$ , the point  $D_1$  is the maximum sublimation point of the complex  $F + F'$ .

Hence, we find: the point of intersection  $S$  of the line  $FF'$  with the liquidum curve of the four-phase equilibrium  $F + F' + L + G$  represents the minimum melting point (congruent or incongruent); the point of intersection  $D_1$  of this line with the vapour curve of this four-phase equilibrium represents the maximum sublimation point (congruent or incongruent) of the complex  $F + F'$ .

Let us now ascertain which reaction can occur in the four-phase equilibrium  $F + F' + L + G$  if the liquid is represented by a point in the proximity of  $S$ . We will call that side of the line  $FF'$ , where the vapour  $S_1$  conjugated with the liquid  $S$  is found, the vapour side, the other side of  $FF'$  the liquidum side. We distinguish three cases.

1. In the point  $S$  the reaction  $F + F' \rightleftharpoons L$  takes place. We imagine in fig. 1 or 2, on the part of the liquidum curve situated at the vapour side of  $FF'$ , a liquid  $L$  in the vicinity of the point  $S$ , the correlated vapour  $G$  will then be represented by a point of the vapour curve situated in the vicinity of  $S_1$ . As the point  $L$  now lies within the triangle  $FF'G$  the reaction  $F + F' + G \rightleftharpoons L$  will occur. If we take a liquid  $L$  situated in the vicinity of  $S$  at the liquidum side of  $FF'$ , the lines  $FF'$  and  $LG$  then intersect each other in a point between  $F$  and  $F'$  and also situated between  $L$  and  $G$  so that the reaction  $F + F' \rightleftharpoons L + G$  takes place.

It is evident that this goes on independently of the situation of the point  $D_1$ .

2. In the point  $S$  the reaction  $F' \rightleftharpoons F + L$  occurs. If we take in fig. 3 a liquid  $L$  in the vicinity of  $S$  and at the vapour side of the line  $FF'$ , and a vapour  $G$  in the vicinity of  $S_1$ , the lines  $FL$  and  $F'G$  will intersect each other so that the reaction  $F' + G \rightleftharpoons F + L$  occurs. If we take a liquid  $L$  in the vicinity of  $S$  at the liquidum side of the line  $FF'$ ,  $F'$  then lies within the triangle  $FLG$  and so the reaction  $F' \rightleftharpoons F + L + G$  takes place.

3. In the point  $S$  the reaction  $F \rightleftharpoons F' + L$  occurs. In the previous reactions  $F$  and  $F'$  should then, however, be exchanged.

We can allow the liquid of the four-phase equilibrium  $F + F' + L + G$  to traverse the liquidum curve from  $a$  to  $c$ ; the vapour then traverses the vapour curve from  $a_1$  to  $c_1$ . We will call this direction, where the equilibrium arrives first in the minimum melting point and then in the maximum sublimation point of the complex  $F + F'$ , the positive direction:

We now allow the equilibrium to move over a short distance from the one side of the minimum melting point towards the other. At the one side, as noticed above, a four-phase reaction takes place different to that at the other side; in the minimum melting point itself both reactions coincide and the vapour does not participate in the reaction. Hence, in this moving we obtain a succession of three reaction types which we will call a reaction series.

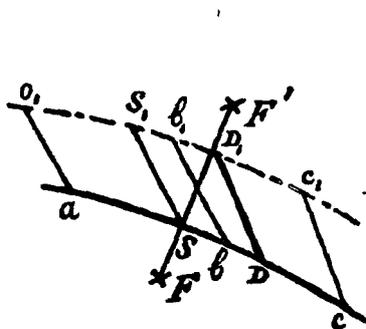


Fig. 1.

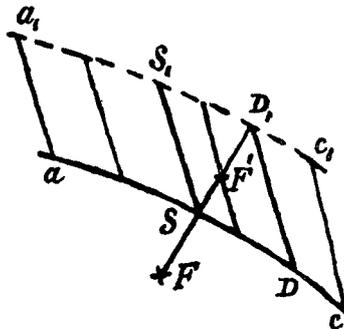


Fig. 2.

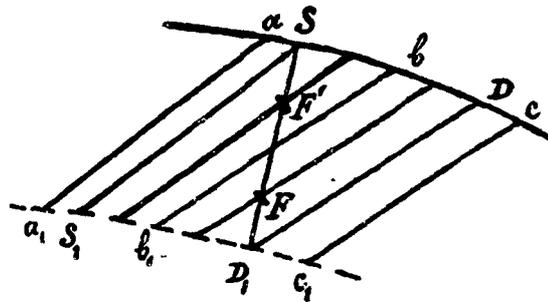
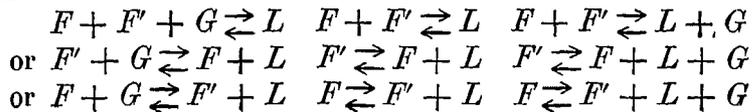


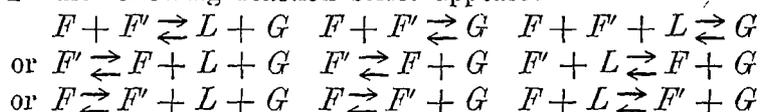
Fig. 3.

We now may summarise the previous results in the following manner; if a four-phase complex  $F + F' + L + G$  moves in a positive direction through the minimum melting point of the complex  $F + F'$  there occurs the reaction series:



which we will call  $A$ ,  $B$ , and  $C$ , respectively. It is evident that this only applies so long as the four-phase equilibrium is found in the vicinity of the minimum melting point.

If we ascertain what reactions can occur in the four-phase equilibrium  $F + F' + L + G$  when the vapour is represented by a point in the vicinity of  $D_1$  we find in an analogous manner as above: if a fourphase equilibrium  $F + F' + L + G$  moves in a positive direction through the maximum sublimation point of the complex  $F + F'$  the following reaction series appears:



which we will call  $A_1$ ,  $B_1$ , and  $C_1$  respectively. We notice that the last reaction of series  $A$ ,  $B$  and  $C$  agrees with the first reaction of series  $A_1$ ,  $B_1$  and  $C_1$ .

The above reaction series, as has been already stated, are only valid so long as the four-phase equilibrium is present in the vicinity of the minimum melting point or the maximum sublimation point; at a greater distance other reactions may occur besides the above mentioned ones. We will explain this with a single example and choose therefore fig. 1. If the system is found in the maximum sublimation point, hence the liquid in  $D$  and the vapour in  $D_1$ , the reaction  $F + F' \rightleftharpoons G$  takes place. If now the system moves in a positive direction, hence the liquid from  $D$  towards  $c$  and the vapour from  $D_1$  towards  $c_1$ ,  $G$  gets within the triangle  $FF'L$  causing the reaction  $F + F' + L \rightleftharpoons G$  to take place. (Also see reaction series  $A_1$ ).

If now the system moves further in a positive direction, the point  $G$  can arrive outside the triangle  $FF'L$ , this, for instance, is the case with the system  $F + F' + L_c + G_{c_1}$ .

The reaction  $F + F' + L \rightleftharpoons G$  then becomes  $F' + L \rightleftharpoons F + G$ ; by way of transition the three-phase reaction:  $F' + L \rightleftharpoons G$  occurs. This is the case at the moment that the conjugation line liquid-vapour passes through the point  $F'$ .

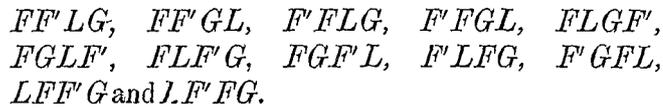
If the four-phase equilibrium moves still further in a positive direction, the point  $L$  can arrive within the triangle  $FF'G$ ; the reaction  $L \rightleftharpoons F + F' + G$  then takes place. By way of transition, at the moment that the conjugation line liquid-vapour passes through the point  $F$ , the three-phase reaction  $L \rightleftharpoons F + G$  appears.

On moving the four-phase equilibrium in a positive direction we thus get first the reaction series  $A$  and  $A_1$  followed by the reactions:  $F' + L \rightleftharpoons G$ ;  $F' + L \rightleftharpoons F + G$ ;  $L \rightleftharpoons F + G$  and  $L \rightleftharpoons F + F' + G$ . This latter reaction is the same as the first reaction in series  $A$ .

From all this it follows that in the system  $F + F' + L + G$  many reactions are possible as a rule; in the vicinity of the minimum melting point, however, always one of the reaction series  $A$ ,  $B$  or  $C$  occurs and in the vicinity of the maximum sublimation point one of the series  $A_1$ ,  $B_1$  or  $C_1$ .

Let us now consider the four points  $F$ ,  $F'$ ,  $S$  and  $D_1$  situated on a straight line. In fig. 1 these lie in the order  $FSD_1F'$  or in the reverse order  $F'D_1SF$ ; in fig. 2 the order is  $FSF'D_1$  or  $D_1F'SF$ ; in fig. 3 it is  $D_1FF'S$  or  $SF'FD_1$ .

In all, we can distinguish 24 cases; as, however, each succession from the right to the left corresponds with a succession from the left to the right, there are only twelve types. If we replace the point  $S$  of the liquidum curve by  $L$  and the point  $D_1$  of the vapour curve by  $G$  we find:



We now allow the four-phase equilibrium to move in a positive direction starting from a point just before the minimum melting point, to a point just behind the maximum sublimation point. To this movement belongs a definite reaction series which however, is dependent on the situation of the points  $F$ ,  $F'$ ,  $S$  and  $D_1$ , in regard to each other, so that to each type belongs a definite reaction series. Each of these series commences of course, with one of the series  $A$ ,  $B$  or  $C$  and terminates with one of the series  $A_1$ ,  $B_1$  or  $C_1$ .

From a consideration of the different cases we can deduce the following table in which the different types and their correlated reaction series are united.

Type:	Reaction series:
1) $FLGF'$	$A; A_1$
2) $FGLF'$	$A; A_1$
3) $FF'LG$	$B; B_1$
4) $FF'GL$	$B; B_1$
5) $F'FLG$	$C; C_1$
6) $F'FGL$	$C; C_1$
7) $FLF'G$	$A; F' \rightleftharpoons L + G; B_1$
8) $F'LFG$	$A; F \rightleftharpoons L + G; C_1$
9) $FG'FL$	$B; F' \rightleftharpoons L + G; A_1$
10) $F'GFL$	$C; F \rightleftharpoons L + G; A_1$
11) $LF'FG$	$B; F' \rightleftharpoons L + G; F + F' \rightleftharpoons L + G; F \rightleftharpoons L + G; C_1$
12) $LFF'G$	$C; F \rightleftharpoons L + G; F + F' \rightleftharpoons L + G; F' \rightleftharpoons L + G; B_1$

The last reaction of  $A$  being the same as the first of  $A_1$ , the reaction series  $AA_1$  consists of five reactions, two of which are three-phased. The same applies to the series  $BB_1$  and  $CC_1$ . In the cases marked 7—10 each series consists of seven reactions of which three are three-phased; in the cases marked 10—12 each series consists of nine reactions, four of which are three-phased.

From the above table we also notice that if the liquidum point  $L$  and the vapour point  $G$  appear in direct succession (type 1—6) the reaction series consists of 5 reactions; if the points  $L$  and  $G$  are separated from each other by a solid phase the reaction series consists of 7 reactions (type 7—10) and if  $L$  and  $G$  are separated from each other by both solid phases (type 11—12) it consists of 9 reactions.

The reaction series appertaining to a definite type may be readily deduced from a diagram in which the points  $F$ ,  $F'$ ,  $S$  and  $D_1$  are situated according to that assumed type. In fig. 1 they lie according to type 1 or  $FLGF'$ , in fig. 2 according to type 7 or  $FLF'G$ , in fig. 3 according to type 11 or  $GFF'L$ . We now allow the four-phase equilibrium in these figures to move in a positive direction, starting from a point just before the minimum melting point, to a point just behind the maximum sublimation point. The liquid then traverses curve  $ac$  from a point close to  $S$  and situated between  $S$  and  $a$  to a point close to  $D$  and situated between  $D$  and  $c$ . The vapour then traverses curve  $a_1c_1$  from a point situated close to  $S_1$  and situated between  $S_1$  and  $a_1$  to a point close to  $D_1$  and situated between  $D_1$  and  $c_1$ .

If now we consider the situation of the four points  $F$ ,  $F'$ ,  $L$  and  $G$  in regard to each other and the changes occurring in this system owing to the moving of the system, we notice that in fig. 1 occurs the reaction series 1 or  $AA_1$ , in fig. 2 the reaction series 7 and in fig. 3 the reaction series 11.

The three-phase reactions  $F \rightleftharpoons L + G$  or  $F' \rightleftharpoons L + G$ , which we find in the series 7—12 can only appear in exceptional circumstances; we shall see later that in this case the four-phase curve of the complex  $F + F'$  comes into contact with the three-phase curve of the compound  $F$  or  $F'$ .

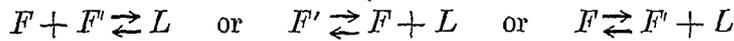
We will now consider more closely the  $P, T$ -curve of the four-phase equilibrium  $F + F' + L + G$  and for this take the relation

$$T \frac{dP}{dT} = \frac{\Delta W}{\Delta V}.$$

As noticed previously this curve meets in the minimum melting

point  $S$  the melting point curve  $Sd''$ , and in the maximum sublimation point  $D$  the sublimation curve  $\alpha''D$  of the complex  $F + F'$ . These curves are indicated in fig 4 by the same letters.

If the system  $F + F' + L + G$  is found in the minimum melting point  $S$  the reaction:



takes place (Series  $A$ ,  $B$  or  $C$ ). We always take these and the following reactions in the direction from the left to the right. As we always assume that in these reactions heat must be supplied for the formation of liquid from the solid substance,  $\Delta W$  for each of these reactions is positive.

During the fusion or transformation the volume may, however, increase as well as decrease;  $\Delta V$  can, therefore, be positive as well as negative. Here, we will call  $\Delta V$  positive so that in agreement with fig. 4,  $\frac{dP}{dT}$  is positive in the point  $S$  in case of the four-phase curve as well as of the melting point line  $Sd''$ .

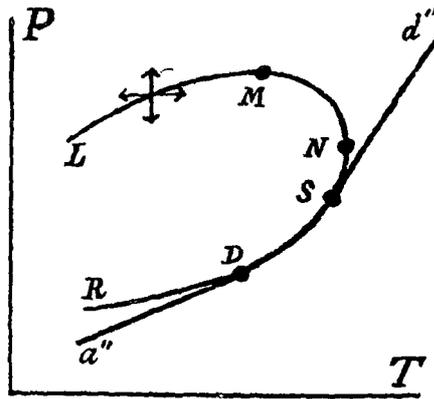
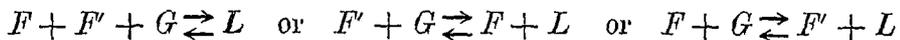


Fig. 4.

We now consider the equilibrium  $F + F' + L + G$  in a point  $X$  (not drawn in the figure) on branch  $LS$  in the immediate vicinity of the point  $S$ . The equilibrium has thus been shifted in the negative direction. From the reaction series  $A$ ,  $B$ , and  $C$  it follows that the reaction



now occurs. These differ from the previous three-phase reactions only in so far that in the first term only the vapour phase has been introduced. So long as the point  $X$  lies very close to  $S$ , only a very little quantity of vapour will take part in the reaction:  $\Delta W$  and  $\Delta V$  are, therefore, both still positive.

If, however  $X$  gets removed from  $S$  still further in the negative

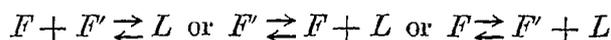
direction, the quantity of vapour taking part in the reaction becomes greater. Now, at the same  $P$  and  $T$ , a substance has in the gaseous condition a much larger volume than in the liquid or solid state; at a definite position of  $X$  the small increase in volume that occurs at the formation of liquid will be just compensated by the condensation of the vapour taking part in the reaction. Let this be the case in the point  $N$  of fig. 4. In this point  $N$ , therefore,  $\Delta V = 0$  so that the tangent stands vertically. The point  $X$ , thus traverses a curve as  $SN$  in fig. 4 on which the pressure increases with a rising temperature.

If the point  $X$  moves further in the negative direction  $\Delta V$  becomes negative;  $\Delta W$ , however, is still positive. Hence, the point  $X$  traverses a curve like  $NM$  in fig. 4 on which the pressure increases with a falling temperature.

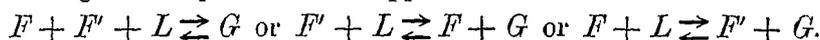
When, however, the point  $X$  moves away further from  $N$ , the quantity of vapour taking part in the reaction accordingly increases. The quantity of heat generated at the condensation of this vapour will, therefore, also increase. This, in a definite point  $M$  will now just compensate the heat required for the formation of liquid so that  $\Delta W$  becomes  $= 0$ . In the point  $M$  the tangent is therefore horizontal.

On further moving the point  $X$  in the negative direction  $\Delta W$  becomes negative;  $\Delta W$  and  $\Delta V$  now being both negative the point  $X$  will traverse a curve like  $ML$  in fig. 4 on which with a falling temperature the pressure decreases likewise.

We now allow the point  $X$  to move away from  $S$  as far as just past the point  $D$  (fig. 4). The three-phase reaction:



occurring in the point  $S$  then appears in one of the reactions:



This transition takes place according to one of the reaction series 1—12 and depends on the situation of the points  $F$ ,  $F'$ ,  $L$  and  $G$  in regard to each other. As in each of these reactions  $\Delta W$  and  $\Delta V$  are positive the point  $X$  will traverse a curve  $SDR$  on which the pressure diminishes with a falling temperature.

If the point  $X$  moves away further in a positive direction, other reactions may again take place as we have already demonstrated by a single example; hence exists the possibility that the curve  $DR$  in its further progress changes its direction. We will refer to this later. From the above considerations follows: on moving in a positive direction the fourphase equilibrium  $F + F' + L + G$  attains

successively a pressure and a temperature maximum, the minimum melting- and the maximum sublimation point.

We have assumed in the above considerations that, in the three-phase reaction appearing in the point  $S$ , the volume increases. If the volume decreases, the point  $S$  arrives on the branch  $MN$  of the four-phase curve and the melting point line  $Sd''$  proceeds from  $S$  towards lower temperatures.

We have noticed above that the four-phase equilibrium  $F + F' + L + G$  is represented in fig. 4 by points of the curve  $LSDR$ . On supply or withdrawal of heat or on change in volume one of the four three-phase equilibria:

$F + F' + L$ ,  $F + F' + G$ ,  $F + L + G$  or  $F' + L + G$   
is formed from this equilibrium.

The question now arises: by which points of the  $P, T$ -diagram are these equilibria represented.

Let us take at the temperature  $T_x$  and the pressure  $P_x$  a correlated point  $x$  of the curve  $LSDR$ . As we have already stated, to such a point applies the rule that we find:

to the right of  $x$  the three-phase systems formed from the four-phase system  $F + F' + L + G$  on supply of heat ( $\Delta W > 0$ ), to the left of  $x$  those formed on withdrawal of heat ( $\Delta W < 0$ ), above  $x$  those formed with decrease in volume ( $\Delta V < 0$ ) and below  $x$  those formed with increase in volume ( $\Delta V > 0$ ).

Here, the supply or withdrawal of heat must take place at the constant pressure  $P_x$  and the change in volume at the constant temperature  $T_x$ .

In order to apply the above rule we must, of course, know the reaction to take place in the point  $x$ . Let us take as an example a four-phase complex belonging to type 1 so that the reaction series  $A$  and  $A_1$  appear.

Let us first take the point  $x$  on the branch  $LM$  (fig. 4). From series  $A$  it follows that in this point the reaction  $F + F' + G \rightleftharpoons L$  takes place; further we have noticed that in this reaction  $\Delta V$  and  $\Delta W$  are negative in the point  $x$  (in the direction from the left to the right). We now easily find which three-phase equilibria are situated to the right or to the left of  $x$  and which above or below that point. As this applies to all points of the branch  $LM$  we find: at the right of and below branch  $LM$  exists the system  $F + F' + G$ ; at the left of and above this branch exist the three other systems:  $F + F' + L$ ,  $F + L + G$  and  $F' + L + G$ .

If we take the point  $x$  on branch  $MN$  (fig. 4) the reaction will still be  $F + F' + G \rightleftharpoons L$ , but  $\Delta W$  is positive and  $\Delta V$  negative. We now find: at the left of and below branch  $MN$  exists the sys-

tem  $F + F' + G$ , at the right of and above this branch exist the three other systems.

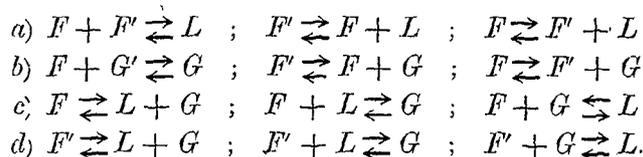
If the point  $x$  is situated on the branch  $NS$  the reaction will still be the same, but  $\Delta W$  and  $\Delta V$  are both positive. Hence, we find the system  $F + F' + G$  at the left of and above branch  $NS$ , the three other systems at the right of and below this branch.

If the point  $x$  gets on the branch  $SD$  a quite different reaction, namely  $F + F' \rightleftharpoons L + G$  takes place; in this reaction  $\Delta V$  and  $\Delta W$  are both positive. From this we deduce: at the left of and above branch  $DS$  we find the systems  $F + F' + L$  and  $F + F' + G$ ; at the right of and below this branch we find the two other systems.

If the point  $x$  gets on the branch  $DR$  the reaction again changes and becomes  $F + F' + L \rightleftharpoons G$  (see the last reaction of series  $A_1$ );  $\Delta V$  and  $\Delta W$  are both positive. From this we deduce: at the left of and above branch  $DR$  we find the system  $F + F' + L$ , at the right of and below this branch the three other systems.

Above we have deduced the situation of the four three-phase systems in regard to the curve  $LSDR$  in the assumption that the four-phase equilibrium belongs to type 1: if, however, the system appertains to one of the other types 2—12 the situation may be found in the same manner.

When the four-phase equilibrium traverses the curve  $LSDR$  (fig. 4) one of the following three-phase reactions will occur in definite points.



In each of the reaction series 1—6 are found two of these three-phase reactions; in each of the series 7—10 three, and in each of the series 11—12 four of the same. The last two of the group  $c$  and  $d$  can only take place when the four-phase equilibrium moves away further from the point  $S$  or from  $D$ .

Previously we already found:

If in the four-phase equilibrium a reaction of group  $a$  takes place it finds itself in the minimum melting or conversion melting point of the complex  $F + F'$ ; in a  $P, T$ -diagram the four-phase curve then meets the melting point curve or the conversion curve of the complex  $F + F'$  (Point  $S$  in fig. 4).

If in the four-phase equilibrium appears a reaction of group  $b$  it finds itself in the maximum sublimation or conversion sublimation

point of the complex  $F + F'$ ; in a  $P, T$ -diagram the four-phase curve then meets the sublimation curve of the complex  $F + F'$  (Point  $D$  in fig. 4).

Further we have:

If in the four-phase equilibrium occurs a reaction of group  $c$  (or  $d$ ) the four-phase curve meets in a  $P, T$ -diagram the three-phase or boundary curve of  $F$  (or  $F'$ ).

We may readily deduce this last property in the following manner. Suppose in a point  $x$  appertaining to the temperature  $T_x$  and the pressure  $P_x$  of the four-phase curve there occurs a three-phase reaction of group  $c$ . If now we remove from the equilibrium  $F + F' + L + G$  the compound  $F'$  we retain in the point  $x$  the three-phase equilibrium  $F + L + G$ . As according to our assumption a reaction of group  $c$  occurs between these three phases, they have such a composition that between them a phase reaction is possible. Now, as we have noticed previously, such an equilibrium  $F + L + G$  is represented in a  $P, T$ -diagram by a curve that we have called the three-phase or boundary curve of  $F$  ( $KF$  in fig. 3 (II);  $mKFM$  in fig. 4 (IV)). From this it follows that the boundary curve of the compound  $F$  passes through the point  $x$  of the four-phase curve.

As the direction of both curves is determined by  $T \frac{dP}{dT} = \frac{\Delta W}{\Delta V}$  and as in the point  $x$   $\Delta W$  and  $\Delta V$  are the same for both curves, these curves must meet in the point  $x$ .

We may summarise the previous considerations as follows: if in a point  $x$  of a four-phase curve occurs a three-phase reaction the four-phase curve in the  $P, T$ -diagram comes into contact with a three-phase curve appertaining to that reaction. To a reaction of group  $a$  appertains the melting point curve, to one of group  $b$  the sublimation curve of the complex  $F + F'$ ; to one of  $c$  the boundary curve of  $F$  and to one of  $d$  the boundary curve of  $F'$ .

From the reaction series 1—12 it appears that in each four-phase equilibrium occurs one reaction of group  $a$  and one of group  $b$ . In harmony with our previous considerations it follows that each four-phase curve meets the melting-point curve and the sublimation curve of  $F + F'$ . If now in a four-phase system occurs one of the series 7—10 the four-phase curve meets the boundary curve of  $F$  (series 8 and 10) or of  $F'$  (series 7 and 9); if one of the series 11 or 12 appears, it meets the two boundary curves. These points of contact lie between the minimum melting and the maximum sublimation point of the curves coming into contact with each other.

If one of the reaction series 1—6 occurs the curves  $KF, K'F'$

and  $SD$  will be situated in regard to each other as in fig. 1 (VII); if series 7 or 9 appears  $K'F'$  meets the curve  $DS$ ; if 8 or 10 occurs  $KF$  meets  $DS$  and if 11 or 12 appears  $K'F'$  as well as  $KF$  meets that curve.

As a rule the case drawn in fig. 1 (VI) and corresponding with series 1—6 is the one likely to occur. If, however, the minimum melting or the maximum sublimation point of the complex  $F + F'$  is situated but a very little lower, or somewhat higher, than the same points of one or of both compounds separately,  $KF$  or  $K'F'$  or both will then lie in the vicinity of  $DS$  and contact may take place.

We now imagine drawn in the figs. 1, 2, or 3 the straight lines  $aF$  and  $aF'$ ; the first may be considered as being part of a rectilinear solution path of  $F$ , the second as a part of such a path of  $F'$  under its own vapour pressure. We have noticed previously (communication IV) that the  $P, T$ -curves of these paths meet the melting point line of the compound in the minimum melting point. We now imagine drawn, as in fig. 1 (VII), the melting point lines  $Fd$  and  $Fd'$  in fig. 4 also.

We now take on the four-phase curve  $LSDR$  of fig. 4 a point corresponding with point  $a$  of fig. 1—3 which we will also call  $a$ . From this point  $a$  the two  $P, T$ -curves of the solution paths of  $F$  and  $F'$  then proceed; the one meets the melting point line of  $F$ , the other that of  $F'$  in the minimum melting point.

It is now evident that from each arbitrary point  $X$  of the curve  $LSDR$  in fig. 4 proceed two solution paths of which the one meets the melting point line of  $F$  and the other the melting point line of  $F'$ ; in fig. 1 (VII) are drawn only the two paths proceeding from the point  $S$ .

The paths proceeding from an arbitrary point  $X$  of the four-phase curve generally intersect this curve in  $X$ . Contact takes place if in the point  $X$  occurs a reaction of group  $c$  or  $d$ ; in the first case the solution path of  $F$ , in the second case that of  $F'$  meets the four-phase curve in the point  $X$ .

We have seen previously (communication IV): if in a point  $X$  of a solution path of  $F$  a reaction is possible between the three phases it comes into contact in the point  $X$  with the boundary curve of  $F$ . Previously we have deduced also: if in the point  $X$  of a four-phase curve occurs a reaction of group  $c$  it meets in the point  $X$  the boundary curve of  $F$ . From this now follows: if in a point  $X$  of a four-phase curve occurs a reaction of group  $c$ , the four-phase curve, the boundary curve of  $F$  and the solution path of  $F$  come into contact with each other in the point  $X$ .

This may be also shown in the following manner. The direction of the solution path of  $F$  is determined by 5 (IV), that of the boundary curve by 16 (IV) and that of the four-phase curve by 8.

If now between the phases occurs a reaction of group  $c$  we get:

$$\frac{y-\beta}{x-\alpha} = \frac{y_1-y}{x_1-x} = \frac{y_1-\beta}{x_1-\alpha}.$$

From this relation follows:

$$\frac{M}{N} = \frac{x-\alpha}{x_1-x}$$

so that 5 (IV) passes into 16 (IV).

With the aid of the above relation we readily find from (2) and (3) the formula 16 (VI), with which the above mentioned property is indicated.

(To be continued).

**Physics.** — “Further experiments with liquid helium. H. On the galvanic resistance of pure metals etc. VII. The potential difference necessary for an electrical current through mercury below 4°.19 K.” By Prof. H. KAMERLINGH ONNES. (Continued.)

§ 11. *Local nature of the loss of heat by a mercury thread enclosed in a glass capillary carrying a current, when the temperature sinks below 4°.19 K.* While the supposition that the thread should accidentally consist of some other substance than mercury for a small part of its length, is in contradiction to the regularity of the potential phenomena, yet on the other hand the supposition that the mercury thread has a microresidual resistance similar to the ordinary resistance in OHM’s law (therefore independent of the strength of current, see § 4), gives rise to no less difficulties <sup>1)</sup>. Such a microresistance proper to the mercury will be evenly distributed over the whole thread. If we calculate from the potential differences observed during the warming up at low temperatures and the strength of current to which they belong, the resistance of the thread under the conditions of the experiment, then we find that the thread, when the threshold value of the strength of current is only very slightly exceeded, must for a part of its length be partly heated distinctly above the vanishing point. Let us take for example the experiments

<sup>1)</sup> Besides those mentioned in § 9, the difficulties here treated also present themselves if we try to explain the potential phenomena by an even distribution of additive mixture-resistance.

of Dec. 1911 in table I. We find from the threshold value of the current at  $4^{\circ}.19$  K., that the resistance of the thread at this temperature may be put at  $< 3.10^{-6} \Omega$ . In the experiment at  $3^{\circ}.65$  K. we find that when the strength of current rises to 1 amp. the resistance,  $11.5.10^{-6} \Omega$ , was already distinctly greater than when the whole thread was at  $4^{\circ}.19$  K., while the ends must still be at  $3^{\circ}.65$  K. The portion that comes above the vanishing point by this heating, as it assumes ordinary resistance, need only be very small to produce the potential differences observed; in the case in point only 0.1 mm. If we assume that the giving off of heat to the bath may be calculated by the same data as were found for it above the vanishing point in § 7, then we find that, if the whole surface of the thread were at the mean of the temperature of the bath and of the vanishing point, the loss of heat per second should be about 20000 microjoules, while in reality only 14.0 microjoules, or about 1400 *times less*, are given off.

We conclude from this that the rise of temperature in the thread, which is in a bath of a temperature below the vanishing point is only local. If there were anywhere else a rise of temperature (although of a smaller amount) the thread must have ceased to give off heat to the glass to a perceptible degree, except at certain points. The heat could therefore only flow to the extremities or the remaining points of conduction. This might be the consequence, for instance, of the mercury having come away from the glass everywhere except at the places indicated. But this is contradicted by the fact that in freezing the mercury adheres to the glass, and that immediately above the vanishing point the contact has not yet ceased. The supposition that everywhere where the temperature remains above the vanishing point (and perhaps close to it) the mercury thread gives off heat, and that it does not where the temperature is lower, is confirmed by the way in which the resistance disappears below the vanishing point (see Table II and fig. 7). If we determine, from the proportion of the resistance remaining to that just by the vanishing point, the length of the portion of the thread which is at the temperature of the vanishing point, then the JOULE-heat that it must give off at the existing strength of current corresponds more or less to that which is to be expected at the assumed difference of temperature of bath and vanishing point if the heat is given off to the glass over the whole length of that portion; more or less, for there remain unexplained and apparently systematic differences, with which perhaps the difference of the curves for different strengths of current in fig. 7 is connected.

In supposing, however, that the development of heat which brings a part of the thread to the temperature of the vanishing point is of a local nature, we give up the supposition that the microresidual resistance is evenly distributed over the thread. Assuming the whole of the path of the current to be of pure mercury, there could possibly only be an *apparent microresidual resistance*, in consequence, for instance, of the mercury not being homogeneous, or not free from mechanical tension. These disturbances would then be the cause of threads showing a resistance throughout, while the pure homogeneous tension-free mercury would have an imperceptible microresidual resistance.

If we remember that with lead the increase of resistance by pressure <sup>1)</sup> becomes less at low temperatures, and has almost disappeared at hydrogen temperatures, then it is not probable that tensions, although they could cause PELTIER-effects, and although their regularity corresponds to that of the phenomena, should really play a part in the disturbances.

It would be more natural to suppose a lack of homogeneity in the thread, which might be the consequence of difference of the state of crystallization. When we turn down a block of very pure KAHLBAUM-lead on the lathe, we can sometimes see a moiré effect on the surface, which indicates different alternating states of crystallization, each of which extends over more than a centimetre. In this way a thread of solid mercury might consist of a series of differently crystallized portions, the dividing surfaces of which would be at the same time usually cross sections of the thread.

At a dividing surface of this kind, a local heating such as we have treated above, might take place, at the expense of current energy. For instance a transitional resistance might give an apparent microresidual resistance to such a dividing surface. But the relation between the threshold value of current density and the temperature of the bath, points (see. § 8) rather to a PELTIER-effect at this transitional place. We should then have to imagine that when the current density reaches the threshold value, the temperature at the dividing surface between two states of crystallisation, even if not high enough to occasion a thermoelectric force equal to the potential difference observed, yet reaches the vanishing point, and that, therefore, by further increase of the current density ordinary resistance must appear at this dividing surface. The length of the thread which takes an ordinary resistance would then increase with the excess of

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<sup>1)</sup> H. KAMERLINGH ONNES and BENGT BECKMAN. Comm. No. 132b, Nov. 1912.

the development of heat above that which produces locally the vanishing point temperature; it would be further determined by the circumstances under which the excess of the heat developed would be given off. When we compare the potential difference observed in the different cases, there are one or two things that seem to confirm this supposition<sup>1)</sup>.

Taking all this together we are brought back to the idea that the potential phenomena must be ascribed to "bad places", although in a different sense to that in § 9. But the regularity of the phenomena remains a weighty objection to this hypothesis<sup>2)</sup>. For although, with the explanation of the local development of heat by a difference in the states of crystallization, the difficulty disappears which in the explanation by foreign resistances arose out of the circumstance that the whole section must be blocked up, still the appearance of a dividing surface between two states of crystallization is governed by chance. In any case, to come to an explanation on this principle, we should have to assume, that there are various PELTSER-places of the kind meant in each mercury thread of any length and that they are not too unevenly distributed.

But in this manner we should add a new indefinite hypothesis to the one which has to be tested and it is only by a complete quantitative working out of a perfectly definite theory that the question with which we are dealing can be answered: for the answer involves some far-reaching inferences. If we might assume that the potential phenomena in mercury-threads at a current density exceeding the threshold value are entirely due to disturbances then, on account of the systematic connection of the potential phenomena, there would be every reason to assume that we get a truer idea of the actual degree of conductivity of the superconductive mercury, the lower the temperature at which we determine the threshold value of current density of a thread<sup>3)</sup>. And as at the lowest temperatures the disturbances still have an influence, although a smaller one, the actual conductivity would therefore have to be placed higher, perhaps a good deal higher, than the value found in § 7, which was already  $0,5 \cdot 10^{10}$  times that at the ordinary temperature,

<sup>1)</sup> Too indefinite to be published.

<sup>2)</sup> The existence of a real microresidual resistance is also made probable by that the ratios between the resistances for the mercury in the capillary tube and the frozen mercury thread at  $4^{\circ}25$  K. seems to run parallel to the threshold values, so that the difference of the threshold values might be ascribed to differences of the local deviations of the cross sections from the mean.

<sup>3)</sup> In this train of thought there is no reason for not supposing that the conductivity assumes its large value immediately below the vanishing point.

in other words the conductivity of the super-conducting mercury might *practically* be considered *infinite*.

§ 12. *Failure of the relations of WIEDEMANN and FRANZ and of LORENZ with super-conductors.* *a.* If the conclusion concerning the non giving off of heat to the glass by a mercury thread below  $4^{\circ}.19$  K. which we discussed in § 11, were applicable, we should arrive at a different view concerning the potential phenomena, from that arrived at above. If the mercury has an appreciable real micro-residual-resistance, so that heat is developed throughout the thread, and if we need not take any account of apparent micro-residual-resistances, the distribution of temperature in the part of the wire that is below the vanishing point, is governed by the ordinary formula for the rise of temperature of a wire conveying a current without external conduction of heat.

Let us keep as near as possible to the well known ordinary case in order to show the nature of the phenomena that are to be expected in the case in point, and for the sake of simplicity, as it is principally a question of order of magnitude, let us assume that below the vanishing point the ratio of the electric conductivity  $k$  to that of heat  $\lambda$ , is given by the same formula as holds approximately above the vanishing point, with the difference that the constant has a different value  $10^7$  times smaller, so that while above the vanishing point;

$$\frac{\lambda}{k} = aT \quad \text{with } a = 0,023.10^{-6} \text{ (watt, ohm, degree}^{-1}\text{),}$$

below the vanishing point

$$\frac{\lambda}{k} = a'T \quad \text{with } a' = a.10^{-7}.$$

We arrive at the low value which we ascribe to  $a'$  amongst other things in consequence of the fact that  $\lambda$  remains of the same order of magnitude below the vanishing point as above it, as appears when on the supposition that all the heat in the experiments is developed in the middle of the thread and only flows away at the extremities, we deduce an upper limit for the heat conductivity<sup>1)</sup>.

<sup>1)</sup> This conclusion is confirmed by preliminary determinations of the heat-conductivity of mercury above and below the vanishing point made by me and Mr. G. HOLST. We conclude from these that this constant does not undergo any considerable change at the vanishing point, and the same is true for the specific heat, which we have also investigated, however important this point may be for the electric conduction.

[Our preliminary yet very uncertain values are: for the conductivity between  $4^{\circ}.5-6^{\circ}.5$  K.,  $k = 0,25$  cal. cm. sec., between  $3^{\circ}.8-4^{\circ}.2$  K.,  $k = 0,46$  cal. cm. sec., for the specific heat between  $4^{\circ}.2-6^{\circ}.5$  K.,  $C_p = 0,0014$  and between  $3-4^{\circ}$  K.,  $C_p = 0,00053$  (Added in translation)].

With the assumption indicated the maximum temperature  $T_{max}$  of a thread, the extremities of which are at the temperature  $T_b$ , with a potential difference of  $E$  volts at the extremities is determined by

$$T_{max}^2 - T_b^2 = \frac{1}{4a'} E^2.$$

From this formula can be seen at once that the well known property of good conductors, that comparatively small potential differences, when external heat conduction is excluded, produce considerable heating, which may even lead to melting, becomes enormously more prominent in the superconducting condition.

In fact we find that at the smallest, potential difference  $E$  of 0.5 microvolts, which is only a little above that which at 2°45 K. is first observed, such comparatively great heating can take place, that even at the lowest values of  $T_b$ ,  $T_{max}$  rises to 4°20 K. At higher bath temperatures of course smaller potential differences are sufficient to reach the vanishing point, or at the same potential difference  $a'$  can be placed lower, at 4°18 K. for instance  $a' = a \cdot 10^{-5}$ .

With the rough estimation of  $a'$  given, and assuming that the mercury thread where its temperature has fallen below the vanishing point gives off no heat to the glass<sup>1)</sup>, we can, therefore, without the assumption of heating caused by local disturbances, predict phenomena such as threshold value of the current density and the differences of potential, that appear at greater current densities.

At current strengths below the threshold value, the thread will all along be in the condition of superconduction, without external heat conduction, at current densities above the threshold value this only exists for portions below the vanishing point temperature; for the portion of the thread that is above the vanishing point, the regime of ordinary conduction with loss of heat at the surface comes in its place<sup>2)</sup>. In this way there can, however, be no question of the deduction of the law of dependence of the thres-

<sup>1)</sup> This calls our attention to the question of the distribution of temperature along a thread through which a current passes without external conduction of heat for different laws of dependence of  $\lambda, k$  and  $T$ . Laws might be imagined, which would cause the rise of temperature to run through the values from 0 to  $T_{max} - T_b$  practically within a very small length of the thread, in which case the heating by a microresidual resistance could not be distinguished from a heating caused by a local disturbance. For the present, however, we adhere to the simpler supposition that the thread gives off no heat to the glass.

<sup>2)</sup> The divergence of the lines for 0,4 and 0,004 amp. in fig. 7 may also indicate the transition from the one regime to the other.

hold value on the temperature, because it is determined by the temperature function, which we have arbitrarily assumed as constant  $\alpha'$  while we have seen that in the train of reasoning followed it might have very different values at different temperatures, from  $\alpha' = 10^{-5}a$  to  $\alpha' = 10^{-7}a$ . And it is very questionable if, when the necessary data are known for working out the sketch taking note 1 into consideration, the potential phenomena would correspond quantitatively to those observed. For the supposition with regard to the absence of external conduction of heat, upon which the theory in this § is based, might be untrue. (Cf. § 16  $\sigma$  of VIII).

It would be of great importance<sup>1)</sup> to cool by immediate contact the thread over its whole surface with liquid helium; if the potential phenomena are to be ascribed to a real micro-residual resistance of the mercury, then the threshold value of the current density could probably be raised considerably higher than was now possible. This is too difficult with mercury. Thus for further experiments the use of tin and lead (see § 1) was indicated, these metals being more easily manipulated than solid mercury, and with them the conditions of the external conduction of heat being more easily regulated<sup>2)</sup>. We shall treat of these investigations in future papers.

$\beta$ . We may here add a few remarks concerning the superconducting condition.

The experiments described above leave no doubt that for mercury below  $4^{\circ}.19$  K. there is no question of an approximate validity even as regards the order of magnitude of the relations established by WIEDEMANN and FRANZ and by LORENZ. The failure of this relation between  $\lambda$ ,  $k$  and  $T$  indicates a difference between the super-conducting and the ordinary conducting state which may be regarded as a *characteristic difference* of both.

Both according to § 11 and to § 12 $\alpha$ , we come to a conductivity of mercury which is say  $10^{10}$  times as great, or even more, than that at the ordinary temperature. If we assume that the number of free electrons per unit of volume at the transition from the ordinary to the super-conducting condition undergoes no important change, and then calculate according to the ordinary electron theory from the conductivity the free path of the electrons, we arrive at values which are comparable to the *lengths* of the mercury threads used in

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<sup>1)</sup> Less, when the particular circumstances mentioned in note 1 should exist.

<sup>2)</sup> The purity of both can probably not be made so high as that of mercury so that disturbances from a trace of additive admixture resistance in the super-conductive state do not seem impossible.

the experiments, in fact are considerably larger <sup>1)</sup>. With such large free paths there would be every reason to believe that the peculiarities of the movements of the electrons pointed out in § 4, which are not consistent with OHM's law, would begin to play a part (which perhaps might resemble a PELTIER-effect such as seems to reveal itself in the potential phenomena). It is, however, questionable whether the whole hypothesis developed in § 4 in connection with Comm. N° 119, concerning the movement of free electrons through the metal and which is also mentioned in § 10, must not be replaced by an essentially different one for the super-conducting condition, according to which the movement of the electrons is carried on by the current for considerable distances, but each separate electron which takes part in the progress, only moves one molecular distance.

To illustrate this idea we may take as an example the well known case of the propagation of a blow by a row of billiard balls which just touch each other. In a super-conductor the flow of electricity might consist in this, that an electron jumping across onto an atom of the super-conductor from one side causes an electron on the other side of the atom <sup>2)</sup> to jump onto the next one, etc. till finally at the further end of the superconducting wire as many electrons would be carried away in the direction of the current, as were thrown in at the beginning <sup>3)</sup>.

<sup>1)</sup> Taking the free path at ordinary temperature at  $10^{-7}$  cm., it becomes  $10^2$  cm. at  $2^{o}.45$  K., yet taking no account of the decrease of the number of free electrons. We do not consider collisions of the electrons mutually, as these would cause microresidual-resistance phenomena.

<sup>2)</sup> To express it more accurately, in the same layer of atoms taken across the path of the current, more passes over in a given time than is sent out (or thrown back) through the same layer in the same time to the side from which the electrons taken up come. We here give only the simplest possible sketch, to characterise the super-conducting condition.

<sup>3)</sup> The taking up of an electron on one side of an atom and the giving off on the other side of one to another atom, would then be accompanied by a moving up of the electrons (through or) over the surface of the atom, by which each electron moves along a part (if the number of electrons on the surface of an atom is large, then a small part) of the diameter of the atom. The connection of the electrons of two different atoms with each other and with these atoms probably does not differ very much from the connection between the electrons of one atom with each other and with the atom, so that the passing of an electron from the one atom to the other in the super conducting state would be similar to the movement of the electrons in a single atom. The conductivity of the super-conductor would thus be that of the atoms united into one continuous whole (see § 4).

If the numerous electrons in the atom, which belong to the framework of it, in the described process only pass on the blow from the one electron that jumps on to the atom, onto the one that is given off without themselves taking part in the

The migration speed is thereby propagated through the superconductor without the performance of work<sup>1)</sup>. If the superconducting metal is converted into an ordinary conducting metal by heating above the vanishing point, (if the point is not much exceeded it will still be strongly conducting) then, according to this hypothesis the OHM resistance is due to the action of the vibrators (between the atoms) which bring the atoms to a distance from each other such that the electrons cannot jump from one atom to another without doing work, but in traversing the space made by the vibrators between the atoms give off some of the energy taken up by them.<sup>2)</sup> The representation given of the conduction in the superconductors seems thus to be most easily combined with the conduction theory developed by LENARD.

In my rough sketch (Comm. N<sup>o</sup>. 119) of the application of the quanta-theory to the electron-theory of conductors, in order to judge

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movement and if the moving electrons are the valency electrons, then our hypothesis, although arrived at by a different road, may be regarded as an application to the superconducting state of the hypothesis of STARK concerning the movement of the framework of the valency electrons along the shearing surfaces of the metal crystals. It thus shows the usefulness of the fundamental idea of STARK. As in the above hypothesis this idea is supplemented by the notion of the free moving electrons of the original electron theory viz. the jumping across of the electrons, the connection with the electron theories of the ordinary conducting state, especially with that of LENARD, is maintained.

<sup>1)</sup> In so far as we may disregard real microresidual resistance.

<sup>2)</sup> We will not discuss whether this happens through electrons with migration speed being taken up and electrons without migration speed being given off or by elastic collision of the electrons against the surface of the atoms between which they move backwards and forwards: through energy of ordered motion being transformed into energy of unordered motion. We must remark that for the explanation of the superconducting state the assumption that in contrast to non elastic collision in ordinary, only elastic collision takes place in the superconducting state is inadequate. As LORENZ has taught us (comp. REINGANUM, Heidelb. Akad. 1911, 10 p. 7) even with elastic collision the above mentioned transformation must take place and show itself as development of heat.

By the transition from the superconducting state to the ordinary in proportion as the atoms begin to vibrate separately in larger numbers and room is made for the movement of the electrons between the atoms, the mechanism develops which leads to the approximate relations of WIEDEMANN and FRANZ and of LORENZ. The communication of the movement of the electrons inside the atoms to each other perhaps plays a chief part in the conduction of heat. The continuity of the heat conduction above and below the vanishing point would then be explained by the small change which the process undergoes when the peculiar connection the atoms which makes super-conduction possible, is destroyed.

The change of the distance between the atoms also clearly plays a part in change of the resistance at the melting point.

whether the hypothesis that resistance is caused by vibrators (the electrons otherwise moving freely through the metal with speeds in accordance with the kinetic theory of gases <sup>1)</sup>) is well adapted to deduce the change of resistance with temperature, I put the mean free path of the free electrons inversely proportional to the mean amplitude of PLANCK's vibrators, which disturb them in their movements, while this mean amplitude was calculated by the formula which PLANCK at the time gave for the mean energy of the vibrators. The way in which mean values were introduced by this (comp. the reasonings in WIEN's theory, which clearly show the deficiencies of mine) could not allow us to expect more than a qualitative representation. Yet, as is rather remarkable, a close agreement was obtained with the observations between the ordinary temperature and that of liquid hydrogen. It is more difficult to judge of the suitability of the new hypothesis for reproducing the observations with metals above the vanishing point. According to the note at the end of Comm. N<sup>o</sup>. 119 the energy of the vibrators would also determine the increase of the volume of the metal from  $T=0$ . The mean distance of the surface of the atoms may thus perhaps be taken proportional to the square of the mean amplitude calculated according to PLANCK's just mentioned formula. We may perhaps further conclude that the idea of the condition above the vanishing point at which we arrived starting from the hypothesis concerning the super-conducting state, will appear to be not unsuitable, and in any case gives no ground for objecting to the last named hypothesis.

On both assumptions, however, the assumption that the free path is continuously described by the same electron, and also the other that it is broken by the movement being transferred from one electron to another, a difficulty arises in the explanation of normal resistance, because PLANCK's previous formula has been replaced by a new one. In the discussions at the Conseil SOLVAY <sup>2)</sup> (Oct. 1911) I pointed out that according to the theory developed in Comm. N<sup>o</sup>. 119, if we introduce the new formula, and further calculate in the same way, i.e. with only one frequency, the resistance could not fall below a certain value determined by the "internal temperature"

<sup>1)</sup> KEESOM (Verslag Akademie XXII, p. 108, Suppl. No. 30b) not yet translated in These Proceedings) has come to the important conclusion, by the application of the quanta-theory to the free electrons in a metal (considered as a monatomic gas) that at low temperatures the velocity of the free electrons becomes independent of the temperature, and has called this field of temperature the "WIEN field".

<sup>2)</sup> La théorie du rayonnement et des quanta, Rapports et discussions de la réunion à Bruxelles sous les auspices de M. SOLVAY. Paris 1912 p. 129.

(according to  $\frac{h\nu}{2} = \frac{1}{2} k_3 \nu$  and  $\beta\nu = 200^\circ \text{K.}$  for silver  $100^\circ \text{K.}$ ) multiplied by  $\sqrt{T}$ , while above  $T = 0$  (for various metals above helium temperatures) it seems to become practically nothing. We must therefore adhere to the old formula <sup>1)</sup> for calculating the amplitude, or rather, accepting the new formula on account of the more satisfactory representation that it gives in many respects, we must assume that the amplitude of the vibrators that comes into consideration for the determination of free path and of the distance between the atomic surfaces (the part of the path between their old and their new positions, upon which the electrons experience resistance in their movement from one atom to another) <sup>2)</sup> is only determined by that part of the energy of the vibrators, which is dependent on the temperature. In addition, in order to explain the existence of the super-conducting state one would have to assume that when the excess of the energy above the zero point energy has fallen to the small value which corresponds to the temperature of the vanishing point, the resistance to the motion of the electrons between the atoms suddenly becomes zero. <sup>3)</sup>

In the reasonings of Comm. N<sup>o</sup>. 119 it was assumed that all vibrators in the metal have the same frequency. As the resistance is mainly determined by  $e^{-\frac{\beta\nu}{T}}$  one need only assume as the single difference between the super-conducting condition and the normal that the frequency of the vibrators is say four times higher in order to find at the vanishing point a micro-residual resistance  $10^4$  smaller than the ordinary resistance at the same temperature and at  $2^\circ \text{K.}$  one which is  $10^9$  times smaller. But against this explanation it may be adduced that in order to bring the formula of Comm. N<sup>o</sup>. 119 into agreement with the observations at the lowest temperatures the frequency has to be taken lower as the temperature falls <sup>4)</sup>. WIEN

<sup>1)</sup> As WIEN does in his theory. Sitz. Ber. Ak. d. Wiss. Berlin 1913, p. 200.

<sup>2)</sup> We may remark that it is not necessary that when an electron jumps over with resistance the whole surplus velocity which it has to propagate should be lost.

<sup>3)</sup> Perhaps the distance of the surfaces of neighbouring atoms has then become equal to that of two neighbouring electrons in the same atom (comp. KEESOM's paper cited above p. 108 note 1) and the connection of the electrons of two atoms similar to that of the electrons in one and the same atom (comp. the speculations on "atom-fast" compounds in KAMERLINGH ONNES and KEESOM, Encyclop. d. Math. Wissensch. V 10, Suppl. No. 23 Nr. 57.

<sup>4)</sup> As I pointed out at the discussion of the Conseil Solvay (l. c. p. 298) one might suppose considering that the vibrations take place in the system of mutually connected molecules that there are two kinds of vibrations, a longitudinal and a

in taking into account in the calculation of the free path of the electrons all the frequencies which play a part in the specific heat has succeeded in explaining this peculiarity: the resistance according to his theory diminishes at very low temperatures only as  $T^2$  or as  $T^{3/2}$ , (depending on the choice of a subsidiary hypothesis). But then it becomes much more difficult to explain the extremely small value of the possible micro-residual resistance by considering the super-conducting metal simply as a metal with slightly modified properties. It thus seems as if at the vanishing point something occurs by which the small frequencies lose their influence on the resistance although they continue to play a part for the specific heat. The spectrum of the frequencies of the vibrators which are operative in the resistance would thus become limited to a few high frequencies or at least be cut off on the side of the small frequencies, in the same way as this happens according to DEBIJSE on the side of the high frequencies<sup>1)</sup>.

**Astronomy.** — *“Investigation of the inequalities of approximately monthly period in the longitude of the moon, according to the meridian observations at Greenwich.”* By J. E. DE VOS VAN STEENWIJK. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

(Communicated in the meeting of April 25, 1913).

It is now about a year ago that Prof. VAN DE SANDE BAKHUYZEN brought under my notice the calculations that he and others had made to determine the corrections needed by HANSEN-NEWCOMB's tables of the moon, which still show systematic deviations. I willingly undertook to continue his calculations on the errors of the longitude, and gratefully acknowledge his frequent advice and ready helpfulness.

My investigation is confined to the inequalities in the longitude of transversal kind. Perhaps above the vanishing point only two vibrations play a part in the resistance, a transversal and a longitudinal one, so that according to PLANCK the small frequency becomes prominent at the lower temperatures, and at the vanishing point this frequency changes into a very high one, so that the original higher one assumes the more important part.

A rotation in opposite senses of two neighbouring atoms with small frequency above the vanishing point, might perhaps, by the atomic surfaces overlapping below the vanishing point, change into a rotation with high frequency. [The caloric investigation of what happens in passing the vanishing point will throw light on this question. As to the specific heat above and below the vanishing point compare the addition to note 1 page 117.

<sup>1)</sup> This raises the question whether above the vanishing point also the small frequencies do not in some way lose their influence on the resistance all the more the smaller they are.

approximately monthly period, or to speak more accurately, periods differing only slightly from the anomalistic time of revolution, which can also be taken as inequalities of long period in the eccentricity and the longitude of the perigee, and to the comparison of them with the values found for the same by E. W. BROWN in his new lunar theory.

My method was exactly the same as that used by Prof. E. F. VAN DE SANDE BAKHUYZEN, in his two papers in 1903, and previously by NEWCOMB in his "Investigation of corrections to HANSEN's tables of the moon". I also used errors in R. A. instead of those in longitude.

NEWCOMB discussed the years 1862—1874, according to the observations made at Greenwich and Washington, and in a less thorough manner the years 1847—1858 according to the Greenwich-observations, while E. F. VAN DE SANDE BAKHUYZEN treated the years 1895—1902 also by using the observations at Greenwich. As their results pointed to terms in the eccentricity and the longitude of the perigee of about an 18 years' period, nearly agreeing with the Jovian evection as found by theory, it was natural for me to extend the material discussed by VAN DE SANDE BAKHUYZEN, so as to cover a period of 20 years.

I began a preliminary investigation with a view to the then approaching solar eclipse of April 17<sup>th</sup> 1912. I used the observations of the years 1907—1909 and the results of my calculations were published in the Proceedings of this Academy 14, 1180. On account of the short period discussed, my investigation could yield no result of general bearing.

For this first investigation I had applied beforehand to HANSEN-NEWCOMB's tables precisely the same corrections as Prof. VAN DE SANDE BAKHUYZEN had done and when later on I began to work after the more extended plan, it was first necessary to consider if any change needed be made in this.

Prof. VAN DE SANDE BAKHUYZEN had applied to the differences  $\Delta\alpha$ , which are given in the Greenwich-results in the sense calculation minus observation, the following corrections: <sup>1)</sup>

a. Corrections to the calculated mean longitude viz:

$$1^{\circ}. \text{ periodic corrections } ndz = + 1''.69 \sin D + 0''.16 \sin (D-g) - 0''.24 \sin (D+g') + 0''.09 \sin g' - 0''.33 \sin 2D - 0''.21 \sin (2D-g)^2)$$

<sup>1)</sup> Under the heading: "Comparison of the errors of the Moon from observations by Transit and Altazimuth" corrections have been applied to the  $\Delta z$  for the motion of the moon in the interval  $\Delta z$  itself, which are not yet taken into account in other parts of the Results.

<sup>2)</sup> In this the solar parallax was taken as  $\pi = 8''.796$ .

2°. a correction for the slowly varying error (secular term) which was deduced from the annual means of the  $\Delta a$ .

The sum of these corrections was reduced to corrections of the R.A. by means of NEWCOMB'S factors  $F'$  and (*v. a.*).

b. Corrections for personal errors in the observation of the times of transit of the two limbs of the moon.

After mature consideration Prof. BAKHUYZEN advised me to introduce new corrections deduced from BROWN'S lunar theory and corresponding to the solar parallax  $8''.80$ , instead of those given above under  $1''$ .

In this it was kept in view, that inequalities with small amplitude only need to be introduced for our purposes, when their period is approximately commensurable with that of the mean anomaly  $\bar{g}$ , as otherwise their influence on the average almost disappears.

The new inequalities calculated by BROWN, or their differences with those according to HANSEN, were taken from the third paper of BATTERMANN<sup>1)</sup>, where they appear on page 16—18, numbered 1—45.

Most of them are perturbations by the planets, some of them are corrections to the perturbations due to the figure of the earth, and a few are solar perturbations. The perturbations 23—29 by the planets, the solar perturbation N°. 39 and the term N°. 44 produced by the figure of the earth, when brought into the form  $a \sin(g + \chi)$  all show values of  $\chi$ , with a period between 9 and 38 years. They were not yet introduced as they stand in immediate relation to the results to be derived from my investigation.

The corrections introduced were the following:

$$\begin{aligned} &+ 1''.37 \sin D \\ &+ 0''.20 \left. \begin{array}{l} \\ \\ \end{array} \right\} \sin(D-g) \\ &+ 0''.31 \left. \begin{array}{l} \\ \\ \end{array} \right\} \sin(D-g) \\ &- 0''.20 \sin(D+g') \\ &- 0''.12 \sin(2D-g) \\ &+ 0''.25 \sin g' \\ &- 0''.19 \sin 2D. \end{aligned}$$

The values of these terms were collected in two new tables of the same form as NEWCOMB'S tables VII and VIII.

In order not to break the connection with the years 1895—1902 too much, the old corrections were used for the years 1890—1894, so that 1890—1902 form a homogeneous whole. From the results for the years 1907—1909, which have been calculated with the old and with the new corrections, which gave only insignificant differences, it appears however, that the whole period 1890—1910 may also be considered as one whole.

<sup>1)</sup> Beobachtungs-Ergebnisse der Königlichen Sternwarte zu Berlin n°. 13 1910,

The year 1891 has been left out of the calculations, as the transit-circle was not in working order for some months, and the results of the different parts of the year may differ systematically from each other.

Further, up to 1902 only observations taken with the Transit circle are used, after that also Altazimuth observations, in so far as they were taken in the meridian (which did not occur before 1903) and finally, after 1905 I could also use observations of the crater Moesting A.

The secular term was computed for every month or two months from a graphical interpolation between the annual means, given in the paper by Prof. ВАНДУЗЕН in These Proc. 14, 691 under the heading  $M-NI$ , after these values<sup>1</sup> had been diminished by a 28<sup>th</sup> part for the motion of the moon between the moments of calculated and observed transit<sup>1</sup>).

Finally we come to the corrections to be applied to the observed time of transit of the moon's limb. These depend principally upon

$D_t$ Limb I	Trans. c. 1892-94	Trans. c. 1895-1902	Trans. c. 1903-09	Altaz. 1903-09
3	-0.066 (1)	—	-0.148 (1)	—
4	-0.051 (14)	-0.121 (12)	-0.020 (17)	—
5	-0.035 (12)	-0.069 (32)	-0.036 (29)	+0.245 (2)
6	-0.065 (12)	-0.022 (36)	+0.014 (29)	+0.151 (8)
7	+0.012 (16)	-0.036 (41)	+0.026 (28)	+0.140 (10)
8	+0.014 (17)	+0.022 (50)	+0.038 (45)	+0.077 (23)
9	+0.072 (17)	+0.007 (46)	+0.022 (42)	+0.046 (30)
10	+0.019 (16)	+0.002 (43)	+0.041 (39)	+0.043 (33)
11	+0.012 (20)	+0.011 (50)	-0.019 (44)	-0.027 (36)
12	-0.029 (23)	+0.011 (54)	-0.019 (43)	-0.055 (43)
13	+0.006 (16)	+0.029 (49)	+0.009 (47)	-0.016 (37)
14	+0.012 (18)	+0.007 (49)	-0.051 (31)	-0.082 (28)
15	+0.023 (17)	0.000 (27)	-0.049 (14)	-0.081 (17)

personal errors, and can therefore in the course of years undergo great and irregular variations. On the other hand it is desirable, in order not to be too dependent upon accidental errors, not to determine the corrections for each year separately.

Taking this into consideration, the errors in observing the limbs

<sup>1</sup>) Comp. These Proc. 14, 992.

were determined for the two periods 1892—94, and 1903—09, while 1890 and 1910, which were added later, were connected to the other years as well as possible.

Like my predecessors I have arranged the  $\Delta\alpha$ , after applying all the above mentioned corrections according to the days of true age of the moon  $D_t$ , in order to investigate whether there may exist a dependence on this age. These results, as well as those found by Prof. BAKHUYZEN, I give here, viz. the mean deviation for each day diminished by the total mean for the limb. In the first table I have collected the results for limb I, in the second those for limb II; the numbers in brackets give the weights.

We must remember that the systematic errors of the observers are only correctly represented by these figures if the theoretical corrections depending on  $D$  are quite correct.

$D_t$	Trans. c. 1892—94	Trans. c. 1895—1902	Trans. c. 1903—1909	Altaz. 1903—09
Limb II				
14	+0.016 (2)	-0.027 (14)	+0.060 (4)	0.000 (1)
15	-0.060 (9)	-0.065 (33)	+0.128 (21)	+0.034 (14)
16	-0.003 (22)	+0.023 (61)	+0.057 (47)	-0.002 (31)
17	-0.011 (16)	+0.030 (49)	+0.056 (37)	+0.002 (26)
18	-0.034 (19)	-0.009 (53)	+0.103 (37)	-0.061 (16)
19	-0.035 (19)	+0.048 (45)	+0.077 (29)	+0.019 (17)
20	-0.044 (12)	+0.008 (34)	+0.104 (32)	+0.080 (22)
21	+0.007 (14)	+0.003 (31)	+0.095 (28)	+0.050 (17)
22	+0.034 (13)	+0.013 (37)	+0.062 (29)	-0.018 (14)
23	+0.085 (12)	+0.017 (38)	+0.033 (20)	-0.048 (6)
24	+0.110 (14)	-0.015 (31)	+0.037 (24)	-0.260 (1)
25	-0.140 (5)	+0.008 (19)	+0.045 (17)	+0.170 (1)
26	+0.099 (3)	+0.126 (8)	+0.047 (3)	-

This condition is certainly not fulfilled by the old set of corrections. Too much importance must therefore not be attached to the variation of these figures and by making the corrections too complicate we run the risk of introducing periodic terms and spoiling our results.

NEWCOMB, however, already indicated the possibility of one cause of divergence, viz. the tendency of observers to estimate the moon's diameter smaller by day-light, that is at very small and very great

values of its age; in the first instance this would cause a divergence in the negative direction, and in the second in the positive.

In the years 1892—94 this divergence seems to show itself, and I therefore considered it desirable to introduce for these years a separate correction of  $+0^s.06$  for  $D_t = 3, 4, 5, 6$  and one of  $-0^s.05$  for  $D_t = 23, 24, 25, 26$ ; after applying these corrections the mean deviation for each limb was determined afresh. For the years 1895—1902 Prof. BAKHUYZEN rejected the observations for  $D_t = 4$  and 26, and applied no further separate corrections. The years 1903—09 do not show these particular divergencies so conspicuously and for these I thought it advisable not to apply any separate corrections for a dependence on  $D_t$ . The years calculated later, 1890 and 1910, have been brought into connection with the others as well as possible. The correction for the observed limb for 1890 is deduced from 1890—94, and that for 1910 from 1903—10.

I now give the differences between the results from the two limbs, Limb II—Limb I, computed for each year, after the above mentioned corrections had been applied.

With one exception, these differences for the different years agree fairly well with one another.

After the corrections for the errors of observation of the limbs had been applied, a yearly mean was formed for each instrument, both for the observations of the limbs and of the crater, and further corrections were added to bring each class of observations into agreement with the total mean.

The total corrections were finally:

1892—94	$D_t = 3, 4, 5, 6$	$+0^s.08$
	$D_t = 23, 24, 25, 26$	$-0.08$
	Remaining Obs. L. I	$+0.02$
	L. II	$-0.03$
1895—99	Limb I	$+0.02$
	Limb II	$-0.02$
1900—02	Limb I	$+0.03$
	Limb II	$-0.03$
1903—09	Trans. c. Limb I	$+0.05$
	Trans. c. Limb II	$-0.07$
	Altaz. Limb I	$+0.04$
	Altaz. Limb II	$-0.01$
	Trans. c. Cr.	$0.00$
	Altaz. Cr.	$+0.01$

After the above corrections had been applied, the observations

	Limb II—Limb I	
	Trans. c.	Altazim.
1890	- 0.015	
1892	+ 0.054	
1893	+ 0.066	
1894	+ 0.037	
1895	- 0.010	
1896	+ 0.087	
1897	+ 0.008	
1898	+ 0.073	
1899	+ 0.055	
1900	+ 0.047	
1901	+ 0.053	
1902	+ 0.066	
1903	+ 0.213	+ 0.146
1904	+ 0.145	+ 0.073
1905	+ 0.098	+ 0.051
1906	+ 0.104	+ 0.089
1907	+ 0.130	+ 0.019
1908	+ 0.082	+ 0.025
1909	+ 0.107	+ 0.025
1910	+ 0.045	- 0.162

for each year were collected in groups, according to the value of  $g$ , so that each group contained a range of  $20^\circ$ ; the mean for each group was taken to hold for the mean value for  $g$  in that group.

In this way, I got for each year 18 equations of the form  $c + h \sin g + k \cos g = r$ , in which  $c$  is the residual error in the mean longitude for that year and  $h$  and  $k$  have the same meaning as in NEWCOMB'S investigation. The errors are taken in the sense calculation minus observation. These equations were now solved for each year by the method of least squares, taking the weights for each group proportional to the number of observations.

This gave the following results:

	$c$	$h$	$k$
1890	+ 1"07	+ 1"40	+ 0"48
1892	+ 0.76	+ 0.69	+ 0.87
1893	+ 0.88	- 0.45	+ 1.04
1894	+ 0.64	- 0.32	+ 1.34
1895	+ 0.07	+ 0.29	+ 0.44
1896	+ 0.05	+ 0.66	+ 1.16
1897	- 0.36	+ 0.57	+ 1.77
1898	- 0.22	+ 0.51	+ 2.10
1899	+ 0.48	- 0.93	+ 2.83
1900	+ 0.27	- 1.66	+ 1.12
1901	+ 0.46	- 1.46	+ 0.52
1902	- 0.16	- 1.18	+ 0.01
1903	- 0.05	- 0.56	- 1.64
1904	- 0.14	+ 1.32	- 2.32
1905	- 0.58	+ 2.38	- 0.66
1906	- 0.34	+ 2.98	- 0.26
1907	+ 0.52	+ 2.67	+ 0.74
1908	+ 0.18	+ 2.01	+ 1.06
1909	+ 0.09	+ 1.90	+ 2.14
1910	- 0.09	+ 1.65	+ 2.54

For the sake of comparison I here add the values of  $h$  and  $k$  for 1909, calculated with the old and the new corrections, from which it appears that this makes little difference.

$$\begin{array}{l}
 1909 \text{ old correction } h = + 1"81 \quad k = + 2"17 \\
 \text{new } \quad \quad \quad h = + 1.90 \quad k = + 2.14
 \end{array}$$

The best way to further discuss these results appeared to me to be, that first of all the values found for  $h$  and  $k$  should be corrected for BROWN'S inequalities, in which the quantities  $\chi$ , as defined above, are varying in long periods.

In this way for 1890—1910, and for the 1<sup>st</sup> and 2<sup>nd</sup> series of NEWCOMB, 1847—1858 and 1862—1874, the sum was formed of the following terms:

9\*

$$\begin{aligned}
\text{I} & + 0'' 66 \sin \{g + 298^\circ 47 + 0^\circ 101075 t\} \\
& + 0 .08 \sin \{g + 92.28 - 0.020582 t\} \\
& + 0 .07 \sin \{g + 350.40 + 0.062456 t\} \\
& + 0 .07 \sin \{g + 179.20 - 0.062456 t\} \\
& + 0 .04 \sin \{g + 87.95 + 0.035364 t\} \\
\text{II} & + 1 .14 \sin \{g + 12.85 + 0.056550 t\} \\
\text{III} & + 0 .44 \sin \{g + 322.71 - 0.026541 t\} \\
\text{IV} & + 0 .28 \sin \{g + 2 \omega + 180^\circ\} \\
\text{V} & + 0 .50 \sin (\Omega - 10^\circ 6) \cos g
\end{aligned}$$

in which  $t$  is expressed in days counted from 1900.0. For NEWCOMB'S first series, on account of their smaller accuracy, only the 5 largest terms, marked here by the numbers I—V were calculated.

As these corrections must be applied to the tabular values and as  $h$  and  $k$  have been taken in the sense calculation minus observation, I have now, indicating BROWN'S terms by  $Br$ , formed  $-h - Br$  and  $-k - Br$ , so that these differences represent the corrections which, according to the observations, must be applied to the tables after they have been corrected according to BROWN.

After this the corrected values of  $-h$  and  $-k$  were freed from their constant parts, which depend upon the corrections, which are still required for the eccentricity and the longitude of the perigee ( $-h_c = +2 \delta e$ ,  $-k_c = -2 e \delta \pi$ ). This was done in two different ways. The first time I regarded the mean values of  $-h - Br$  and  $-k - Br$  for each period as the constant parts to be subtracted from the individual values. As the two following tables, Table I and II, show, the results thus found for  $-h_c$  and  $-k_c$  for the three series are in fairly good accordance with each other.

The tables also contain the results  $-h_v$  and  $-k_v$  freed from the constant parts.

A second time I have tried to represent the constant parts for the three series together by quantities varying linearly with the time. In order to be able to dispose of 4 periods of about equal length, I divided the last into two parts, and calculated  $h_c$  and  $k_c$  for each half-series (these values differed not much from those for the whole series). I had therefore for each of the two unknown quantities four equations of the form  $-h_c = a + bt$  and  $-k_c = a' + b't$ . To the first series of NEWCOMB I gave a weight 1, and to each of the other three series a weight 3. The results found were:

$$\left. \begin{aligned}
a &= -0''.62 & b &= +0''.0034 \\
a' &= -0''.47 & b' &= -0''.0090
\end{aligned} \right\} \text{epoch 1894.5.}$$

TABLE I. Investigation of the  $h$ . 1st calculation.

	$-h$	<i>Brown</i>	$-h-Br.$	$-h_c$	$-h_v$
1847.8	+0''08	+0''03	+0''05	-0''24	+0''29
48.9	+0.55	+0.49	+0.06	"	+0.30
50.1	+0.20	+0.34	-0.14	"	+0.10
51.2	+0.32	+0.35	-0.03	"	+0.21
52.4	-0.26	+0.69	-0.95	"	-0.71
53.5	-1.10	-0.14	-0.96	"	-0.72
54.6	-1.45	-0.34	-1.11	"	-0.87
55.8	-0.77	-0.84	+0.07	"	+0.31
56.9	-1.76	-1.46	-0.30	"	-0.06
58.1	+0.17	-0.72	+0.89	"	+1.13
1862.5	-0.04	+1.74	-1.78	-0.75	-1.03
63.5	+0.64	+2.00	-1.36	"	-0.61
64.5	+1.07	+2.00	-0.93	"	-0.18
65.5	+1.03	+0.97	+0.06	"	+0.81
66.5	+0.47	+0.58	-0.11	"	+0.64
67.5	+0.93	+0.28	+0.65	"	+1.40
68.5	-0.34	-0.54	+0.20	"	+0.95
69.5	-1.67	-0.46	-1.21	"	-0.46
70.5	-1.48	-0.25	-1.23	"	-0.48
71.5	-1.65	-0.78	-0.87	"	-0.12
72.5	-2.15	-0.69	-1.46	"	-0.71
73.5	-1.91	-0.71	-1.20	"	-0.45
74.5	-1.92	-1.37	-0.55	"	+0.20
1890.5	-1.40	-0.53	-0.87	-0.66	-0.21
92.5	-0.69	-0.20	-0.49	"	+0.17
93.5	+0.45	+0.13	+0.32	"	+0.98
94.5	+0.32	+0.36	-0.04	"	+0.62
95.5	-0.29	-0.09	-0.20	"	+0.46
96.5	-0.66	+0.35	-1.01	"	-0.35
97.5	-0.57	+0.95	-1.52	"	-0.86
98.5	-0.51	+0.93	-1.44	"	-0.78
99.5	+0.93	+1.64	-0.71	"	-0.05
1900.5	+1.66	+2.10	-0.44	"	+0.22
01.5	+1.46	+1.51	-0.05	"	+0.61
02.5	+1.18	+1.28	-0.10	"	+0.56
03.5	+0.56	+0.54	+0.02	"	+0.68
04.5	-1.32	-0.62	-0.70	"	-0.04
05.5	-2.38	-1.17	-1.21	"	-0.55
06.5	-2.98	-1.43	-1.55	"	-0.89
07.5	-2.67	-2.02	-0.65	"	+0.01
08.5	-2.01	-1.52	-0.49	"	+0.17
09.5	-1.90	-0.78	-1.12	"	-0.46
0.5	-1.65	-0.72	-0.93	"	-0.27

TABLE II. Investigation of the  $k$ . 1st calculation.

	$-k$	<i>Brown</i>	$-k-Br$	$-k_c$	$-k_v$
1847.8	-0''55	+0''80	-1''35	-0''21	-1''14
48.9	+1.38	+0.76	+0.62	"	+0.83
50.1	+1.91	+1.44	+0.47	"	+0.68
51.2	+1.92	+1.20	+0.72	"	+0.93
52.4	+2.45	+1.85	+0.60	"	+0.81
53.5	+1.88	+2.03	-0.15	"	+0.06
54.6	+1.40	+1.44	-0.04	"	+0.17
55.8	-0.31	+1.31	-1.62	"	-1.41
56.9	-1.82	0.00	-1.82	"	-1.61
58.1	-0.66	-1.17	+0.51	"	+0.72
1862.5	-1.23	-1.53	+0.30	-0.17	+0.47
63.5	-1.78	-1.20	-0.58	"	-0.41
64.5	-1.09	-0.06	-1.03	"	-0.86
65.5	+0.15	+0.50	-0.35	"	-0.18
66.5	-0.10	+0.36	-0.46	"	-0.29
67.5	+0.36	+0.83	-0.47	"	-0.30
68.5	+1.46	+0.77	+0.69	"	+0.86
69.5	+1.56	+0.24	+1.32	"	+1.49
70.5	+1.14	+0.62	+0.52	"	+0.69
71.5	+0.36	+0.64	-0.28	"	-0.11
72.5	+0.12	+0.27	-0.15	"	+0.02
73.5	-0.16	+0.60	-0.76	"	-0.59
74.5	-0.60	+0.27	-0.87	"	-0.70
1890.5	-0.48	+0.20	-0.68	-0.58	-0.10
92.5	-0.87	+0.24	-1.11	"	-0.53
93.5	-1.04	-0.40	-0.64	"	-0.06
94.5	-1.34	-0.28	-1.06	"	-0.48
95.5	-0.44	-0.70	+0.26	"	+0.84
96.5	-1.16	-1.56	+0.40	"	+0.98
97.5	-1.77	-1.44	-0.33	"	+0.25
98.5	-2.10	-1.44	-0.66	"	-0.08
99.5	-2.83	-1.53	-1.30	"	-0.72
1900.5	-1.12	-0.45	-0.67	"	-0.09
01.5	-0.52	+0.38	-0.90	"	-0.32
02.5	-0.01	+0.75	-0.76	"	-0.18
03.5	+1.64	+1.70	-0.06	"	+0.52
04.5	+2.32	+1.84	+0.48	"	+1.06
05.5	+0.66	+1.10	-0.44	"	+0.14
06.5	+0.26	+0.92	-0.66	"	-0.08
07.5	-0.74	+0.16	-0.90	"	-0.32
08.5	-1.06	-0.96	-0.10	"	+0.48
09.5	-2.14	-0.98	-1.16	"	-0.58
10.5	-2.54	-1.15	-1.39	"	-0.81

TABLE III. Investigation of the  $h$  and  $k$ . 2nd Calculation.

	$-h_c$	$-k_c$	$-h_v$	$-k_v$
1847.8	-0''78	-0''05	+0''83	-1''30
48.9	"	-0.06	+0.84	+0.68
50.1	-0.77	-0.07	+0.63	+0.54
51.2	"	-0.08	+0.74	+0.80
52.4	"	-0.09	-0.19	+0.69
53.5	-0.76	-0.10	-0.20	-0.05
54.6	"	-0.11	-0.35	+0.07
55.8	"	-0.12	+0.83	-1.50
56.9	-0.75	-0.13	+0.45	-1.69
58.1	"	-0.14	+1.64	+0.65
1862.5	-0.73	-0.18	-1.05	+0.48
63.5	-0.72	-0.19	-0.64	-0.39
64.5	"	-0.20	-0.21	-0.83
65.5	"	-0.21	+0.78	-0.14
66.5	-0.71	-0.22	+0.60	-0.24
67.5	"	-0.23	+1.36	-0.24
68.5	"	-0.23	+0.91	+0.92
69.5	-0.70	-0.24	-0.51	+1.56
70.5	"	-0.25	-0.53	+0.77
71.5	"	-0.26	-0.17	-0.02
72.5	-0.69	-0.27	-0.77	+0.12
73.5	"	-0.28	-0.51	-0.48
74.5	"	-0.29	+0.14	-0.58
1890.5	-0.63	-0.44	-0.24	-0.24
92.5	"	-0.45	+0.14	-0.66
93.5	"	-0.46	+0.95	-0.18
94.5	-0.62	-0.47	+0.58	-0.59
95.5	"	-0.48	+0.42	+0.74
96.5	"	-0.49	-0.39	+0.89
97.5	-0.61	-0.50	-0.91	+0.17
98.5	"	-0.50	-0.83	-0.16
99.5	"	-0.51	-0.10	-0.79
1900.5	-0.60	-0.52	+0.16	-0.15
01.5	"	-0.53	+0.55	-0.37
02.5	"	-0.54	+0.50	-0.22
03.5	-0.59	-0.55	+0.61	+0.49
04.5	"	-0.56	-0.11	+1.04
05.5	"	-0.57	-0.62	+0.13
06.5	-0.58	-0.58	-0.97	-0.08
07.5	"	-0.59	-0.07	-0.31
08.5	"	-0.59	+0.09	+0.49
09.5	-0.57	-0.60	-0.55	-0.56
10.5	"	-0.61	-0.36	-0.78

By this formula  $-h_c$  and  $-k_c$  were then calculated for each year and with these values those for  $-h_v$  and  $-k_v$  were deduced.

We thus have two sets of values for  $-h_v$  and  $-k_v$ .

Before submitting these results to a nearer investigation, I tried to show that the introduction of BROWN'S terms is justified by the observations, at least as far as the five are concerned, which have perceptible coefficients, and were marked above in roman figures.

For this purpose tables were drawn up of  $-h_v$  and  $-k_v$ , according to the first calculation, in which all BROWN'S terms were introduced except the term to be investigated. The yearly results were then so combined, that groups were formed with values of the argument of the investigated term between  $0^\circ$  and  $10^\circ$ ,  $10^\circ$  and  $20^\circ$  etc., in such a manner that the results for the different quadrants, when necessary, were reduced by a change of sign to those for the first quadrant. The  $h$  and  $k$ , when we represent BROWN'S terms by  $\alpha \sin(g + \chi)$ , then give nine equations each of the form  $-h_v = \alpha \cos \chi$  and  $-k_v = \alpha \sin \chi$ .

Now  $\chi = \chi_0 + \mu(t - 1900.0)$  and, as we take the period or  $\mu$  as known, we can deduce from the observations the value for  $\alpha$  and  $\chi_0$  for each term by the formulae

$$\operatorname{tg}(\chi_0 + \mu(t - 1900.0)) = \frac{-k_v}{-h_v} \quad \alpha^2 = h_v^2 + k_v^2 \quad 1)$$

In this solution weights are given to the various equations proportional to the number of years that they are based upon.

The results found, compared with those according to the theory, follow below:

	$\alpha$		$\chi_0$
	Theory	Obs.	Obs.—Theory
BROWN I	+ 0''66	+ 0''61	+ 1°2
II	+ 1.14	+ 1.34	— 2.0
III	+ 0.44	+ 0.58	— 21.9
IV	+ 0.28	+ 0.19	— 26.0
V	+ 0.50	+ 0.35	+ 19.5

This agreement may be considered as satisfactory, it certainly completely justifies the introduction of BROWN'S inequalities.

Finally I endeavoured to deduce from the observed  $h$  and  $k$  for the largest term Br. II, the Jovian evection, also the length of the period. The  $-h$  and  $-k$ , corrected for all other terms, being represented for each year by

1) For Br. V we have only a coefficient  $k$ , so that the deduction for this term becomes somewhat different.

$$-h_v = \alpha \cos \chi \quad -k_v = \alpha \sin \chi^1)$$

the values of  $\chi$  were calculated for the separate years and these values were united in 7 groups, as follows:

Period	Mean Epoch	$\chi$	O—C
1847.8—58.1	1852.9	134°	+ 20°
62.5—68.5	1865.5	344	— 35
69.5—74.5	1872.0	523	+ 7
90.5—95.5	1893.3	985	+ 20
1896.5—00.5	1898.5	1112	+ 37
1901.5—05.5	1903.5	1154	— 27
1906.5—10.5	1908.5	1272	— 14

Each group gives a normal value for  $\chi$  and these are then represented by equations

$$\chi = \chi_0 + \mu (t - 1900.0).$$

To the first equation I gave the weight 0.7, to the others the weight 1. These being solved by least squares gave the result

$$\chi_0 = 1107^\circ.1 = 27^\circ.1 \quad \mu = 21^\circ.085$$

The last column of the table gives the differences between observation and calculation. The annual variation of the argument found is thus  $0^\circ.43$  larger than that which follows from the theory,  $20^\circ.65$ .

NEWCOMB found  $21^\circ.6$

BAKHUYZEN „  $19^\circ.36$ .

The argument for 1900.0 is now found  $14^\circ.3$  larger than according to the theory; for the mean epoch of the observations 1886 the difference, however, is only  $+ 8^\circ.3$ , while my previous calculation mentioned above gave Obs.—Th. =  $- 2^\circ.0$ .

We now proceed to the investigation of the residual values for  $-h_v$  and  $-k_v$ , which after correction for all BROWN's terms, still show a distinct periodicity, though the amplitude is greatly decreased.

By a graphic representation and some preliminary calculations I came to the conclusion that the best agreement would be attained by a term of a period of nine years. The values of  $h$  and  $k$  seemed to agree completely in this and together to point to the existence of a term of the form  $\alpha \sin (g + \chi)$ .

<sup>1)</sup> Our  $\chi$  is connected with the  $N$  introduced by NEWCOMB and also used by E. F. v. D. SANDE BAKHUYZEN by  $\chi = N - 90^\circ$ .

For  $h_c$  and  $k_c$  the values were taken according to the 2nd calculation.

I then examined the accurate length of the period more closely in the following manner. Proceeding from the form  $a \sin (g + \chi)$  so that  $-h_v = a \cos \chi$   $-k_v = a \sin \chi$  and from the 2<sup>nd</sup> calculation for  $h_c$  and  $k_c$ , the value for  $\chi$  for each year was found as follows

1847.8	303°	1862.5	155°	1890.5	225°	1901.5	326°
48.9	39	63.5	212	92.5	282	02.5	336
50.1	40	64.5	257	93.5	349	03.5	39
51.2	48	65.5	350	94.5	314	04.5	96
52.4	106	66.5	339	95.5	60	05.5	168
53.5	194	67.5	350	96.5	116	06.5	185
54.6	169	68.5	45	97.5	170	07.5	257
55.8	299	69.5	107	98.5	191	08.5	80
56.9	285	70.5	124	99.5	263	09.5	226
58.1	22	71.5	188	1900.5	317	10.5	245
		72.5	171				
		73.5	224				
		74.5	286				

These values for  $\chi$  were now united in 7 groups, and the mean results for these groups represented by equations  $\chi = \chi_0 + \mu(t-1900.0)$  the first group received the weight 0.7, the others weight 1.

Period	Mean Epoch	$\chi$	O-C
1847.8-58.1	1852.9	150°	+ 5°
62.5-68.5	1865.5	655	+ 2
69.5-74.5	1872.0	903	- 12
90.5-95.5	1893.3	1758	- 17
1896.5-00.5	1898.5	2011	+ 27
1901.5-05.5	1903.5	2209	+ 23
1906.5-10.5	1908.5	2359	- 29

By solving the 7 equations by least squares I found

$$\chi = 244^\circ.7 + 40^\circ.35(t-1900.0).$$

The differences Obs — Calc. are given above.

For the period I now found 8.92 years, which could, therefore, retain provisionally the assumed value of 9 years, with which the further calculations had already been made. We have

$$-h_v = a \cos \{\chi_0 + 40^\circ (t-t_0)\}$$

$$-k_v = a \sin \{\chi_0 + 40^\circ (t-t_0)\}$$

and putting

$$-h_v = \beta \sin 40^\circ (t-t_0) + \gamma \cos 40^\circ (t-t_0)$$

$$-k_v = \beta' \sin 40^\circ (t-t_0) + \gamma' \cos 40^\circ (t-t_0).$$

we then have

$$\beta = -a \sin \chi_0 \quad \gamma = a \cos \chi_0$$

$$\beta' = a \cos \chi_0 \quad \gamma' = a \sin \chi_0.$$

I calculated each of the four coefficients independently. In this NEWCOMB'S first series was left out, on account of its smaller accuracy. I found, assuming for  $t_0$  1894.5, from both sets of values  $A$  and  $B$  obtained by the two methods of calculation.

$A$

Each series being calculated with its own  $h_c$  and  $k_c$

$$\beta = -0''.30 \quad \gamma = +0''.68 \quad \beta' = +0''.60 \quad \gamma' = +0''.16$$

$B$

The  $h_c$  and  $k_c$  being calculated by formulae  $a + bt$

$$\beta = -0''.29 \quad \gamma = +0''.63 \quad \beta' = +0''.60 \quad \gamma' = +0''.14$$

After all the results of calculation  $B$  seem to me to be the most reliable, but the differences between the two sets are very slight. We see further that the relations  $\beta' = \gamma$  and  $\beta = -\gamma'$  are very satisfactorily fulfilled and may thus assume according to calculation  $B$ :

$$a \sin \chi_0 = +0''.22$$

$$a \cos \chi_0 = +0''.62$$

from which

$$\chi_0 = 19^\circ.53$$

$$a = +0''.66$$

The value found for  $\chi_0$  must still undergo a small correction, because the annual variation was not assumed quite correctly; considering that the mean epoch of the observations is about 1886, this correction becomes  $+2^\circ.98$ .

Finally, transferring the zero-epoch to 1900.0 we find for our empirical term

$$+0''.66 \sin \{g + 244^\circ.4 + 40^\circ.35 (t-1900.0)\}.$$

The value now determined for the argument for 1900.0 thus agrees very nearly with that found above. The period of this term differs comparatively little from that of the term BrI; the difference

of  $3.43$  between the annual variation for both, however, makes the variation of the two arguments differ  $180^\circ$  in 52 years and so the two terms cannot be combined into one.

The complete formulae for the corrections, which must still be added after BROWN's inequalities have been taken into account, are therefore

$$\begin{aligned} -h &= -0''.60 + 0''.0034\{t-1900.0\} + 0''.66 \cos\{244^\circ.4 + 40^\circ.35(t-1900.0)\} \\ -k &= -0''.52 - 0''.0090\{t-1900.0\} + 0''.66 \sin\{244^\circ.4 + 40^\circ.35(t-1900.0)\} \end{aligned}$$

The two periodic terms can also be combined, as was done above.

Let us now consider the meaning of the corrections found, first as regards the non-periodic parts. We have:

$$\begin{aligned} -h_c &= + 2\delta e \\ -k_c &= - 2e\delta\pi \end{aligned}$$

in which  $\delta e$  and  $\delta\pi$  represent the corrections to the eccentricity and the longitude of the perigee adopted by HANSEN for his tables.

We find thus

$$\begin{aligned} \delta e &= - 0''.30 + 0''.0017(t-1900.0) \\ \delta\pi &= + 4''.7 + 0''.082(t-1900.0). \end{aligned}$$

The correction found for the annual variation of the eccentricity is certainly too small to be considered as real. If we assume it to be zero, we find

$$\delta e = - 0''.32.$$

The correction found for HANSEN's annual motion of the perigee may be compared with what was found by others.

The correction  $+ 0''.08$  must be applied to HANSEN's tabular value of the sidereal motion in a Julian year for 1850.0,  $146435''.23$ , which was deduced by him from the observations.

We get thus for 1850.0.

$$\text{Annual motion of } \pi = 146435''.31.$$

COWELL found from his discussion of the observations at Greenwich (Monthly Notices Jan. 1905)  $146435''.38$ , in near agreement with the result obtained here.

BROWN (Monthly Notices April 1904) gives as the result of his theoretical calculation of the motion of the perigee two values, holding for two different values of the ellipticity of the earth, viz.  $1:292.9$  and  $1:296.3$ . Extrapolating from these for the value which is at present considered the most accurate  $1:297.5$ , we find for 1850.0

$$\text{Annual motion of } \pi = 146435''.05$$

for which BROWN gives as "extreme possible error"  $\pm 0''.10$ .

Our result  $0''.26$  larger, is thus in moderate accordance with the theory.

As regards the periodic terms, it is very satisfactory that BROWN'S inequalities are so well confirmed by the observations. It is, however, remarkable that after BROWN'S thorough investigations the observations still betray an inequality with a coefficient of  $0''.66$ , which is theoretically unexplained.

Still I think that we are driven to this conclusion, and that the supposition of E. F. BAKHUYZEN (Proc. Akad. Amsterdam 6 1903, 417), when he could find no trace of the existence of BROWN'S term I (= Radau I) in the observations, that in the years considered another term must have neutralized its effect, is fully confirmed. For we now find that with equal coefficients their arguments in 1863 differed by  $180^\circ$ .

**Astronomy.** — *Investigation of the inequalities of approximately monthly period in the longitude of the moon, according to the meridian observations at Greenwich. 2<sup>nd</sup> part.* By J. E. DE VOS VAN STEENWIJK. (Communicated by Prof. E. F. VAN DE SANDE BAKHUYZEN).

In connection with my previous paper on the inequalities in the longitude of the moon, the period of which differs little from the anomalistic period of revolution, I have made some further calculations.

Even after applying the corrections which we have discussed and all the new inequalities determined by BROWN, a discordance still remained between observation and theory, which could be expressed by the following empirical term to be added to the theoretical longitude:

$$+ 0''.66 \sin \{g + 244^\circ.4 + 40^\circ.35 (t-1900.0)\}$$

I have already pointed out that it is striking that an inequality with such a comparatively large coefficient should exist, which is not explained by theory, and on this account I have tried to establish the reality of this term with greater certainty.

For this purpose first the value of this term and its influence upon  $h$  and  $k$  were calculated for each year, and my  $-h_v$  and  $-k_v$  were corrected for this. After this the mean residual discordance in  $h_v$  and  $k_v$  was determined, and in the second place for comparison the same was done, when  $h_v$  and  $k_v$  were not corrected for the empirical term. In the third place the same

calculation was made again, when  $h_e$  and  $k_e$  were neither corrected for my empirical term nor for the inequality BROWN I (the period of which differs little from that of the empirical term). In making the three calculations weight  $\frac{1}{2}$  was given to the  $h$  and  $k$  of NEWCOMB's first series, and the mean discordances given below refer to an  $h$  and  $k$  with weight unity. We found :

	$h$			$k$		
	I	II	III	I	II	III
1848—1875	$\pm 0''377$	$\pm 0''649$	$\pm 0''400$	$\pm 0''416$	$\pm 0''666$	$\pm 0''440$
1890—1910	$\pm 0.368$	$\pm 0.543$	$\pm 0.879$	$\pm 0.392$	$\pm 0.534$	$\pm 0.842$
Together	$\pm 0.373$	$\pm 0.602$	$\pm 0.667$	$\pm 0.405$	$\pm 0.608$	$\pm 0.659$

We see in the first place that the mean residual discordances in  $h$  and  $k$  agree in the three cases very well with each other, and it is shown clearly that in the period 1848—74 the term BROWN I and my empirical term counteract each other to such an extent that they could both be omitted without the mean discordance being perceptibly increased, and that therefore apparently the non-existence of BROWN I had to be inferred from the observations of these years, while in the period 1890—1910 the relation is just the opposite.

Further it is seen that the mean discordances I, remaining after the empirical term was also applied, are considerably smaller than the values II. If the former are to be attributed to accidental errors alone, they must be about equal to the mean errors in  $h$  and  $k$  deduced from the equations for each year

$$r = c + h \sin g + k \cos g$$

These mean errors were calculated for the three years 1893, 1901, and 1908, and we found :

	$\mu_h$	$\mu_k$
1893	$\pm 0''272$	$\pm 0''274$
1901	$\pm 0.321$	$\pm 0.330$
1908	$\pm 0.274$	$\pm 0.291$

We may therefore take for this mean error on the average the value  $\pm 0''30$ , while for the mean residual discordance in  $h$  and  $k$  for the years 1890—1910 we find  $\pm 0''38$ , which agreement may be considered satisfactory.

We may therefore conclude :

1. That the reality of our empirical term is established ;
2. That, when its influence, together with that of all the theoretical terms, is applied to the results for  $h$  and  $k$ , deduced from the observations, the residuals may probably be ascribed to accidental errors.

Finally I wish to make a few remarks which refer to another form in which our empirical term can be expressed.

Prof. E. VAN DE SANDE BAKHUYZEN called my attention to the remarkable fact that the period of the argument  $\chi$  which is added to  $g$  agrees, within the errors of observation, with the periodic time of the moon's perigee (the difference in annual motion is  $0^{\circ}.33$ ). As the longitude of the perigee for 1900.0 is  $334^{\circ}.3$ , our term may be put in the form (if  $l$  represents the mean longitude of the moon)

$$+ 0''66 \sin (l - 89^{\circ}.9) = - 0''66 \cos l.$$

Prof. BAKHUYZEN will give a short paper upon the possible signification of our term in connection with this transformation. The new form suggested to me to investigate in how far the term can arise from the circumstance that, following NEWCOMB, my whole investigation was based on the tabular errors in right-ascension instead of on those in longitude.

The great advantage of this method is that by it the errors of observation in right-ascension are not mixed with those in declination, but we must now pay attention to the systematic differences between the deviations  $\delta\alpha$  and  $\delta l$ , therefore also to those parts, arising from the tabular errors in latitude. NEWCOMB on pp. 12 and 16 of his "Investigation" carefully considers these differences; he finds approximately

$$\alpha = l - 2^{\circ}.5 \sin 2l - 1^{\circ}.1 \sin (2l - \theta) + 1^{\circ}.1 \sin \theta$$

in which  $\theta$  represents the longitude of the node and, as

$$\delta\alpha = \frac{d\alpha}{dl} \delta l + \frac{d\alpha}{d\theta} \delta\theta + \frac{d\alpha}{di} \delta i$$

putting

$$\delta l = \delta\alpha - P$$

we find:

$$\begin{aligned} P = & (+ 0.018\delta\theta - 0.037 \delta l) \cos (2l - \theta) \\ & - 0.037 \delta l \cos 2l \\ & + 0.018\delta\theta \cos \theta \\ & + 0.21\delta i \sin \theta \\ & - 0.21\delta i \sin (2l - \theta) \end{aligned}$$

NEWCOMB further points out that  $P$  contains no perceptible terms, whose period approaches that of  $g$ , so that their influence upon his and also upon our investigation must be small.

The value of the term  $0.018\delta\theta$  has increased since NEWCOMB's time, as  $\delta\theta$  is now about  $10''$ , but its influence may certainly still be disregarded in our investigation.

NEWCOMB did not, however, take into account the possibility of a constant error in the latitude, although he had himself previously called attention to the want of foundation of HANSEN's supposition that the centre of gravity and the centre of figure of the moon should not coincide in the direction of the radius vector.

The influence of a constant error in the latitude upon the R.A. is

$$\frac{d\alpha}{d\beta} = -\frac{\sin \epsilon}{\cos^2 \delta} \cos \lambda$$

or, as the greatest difference of  $\cos^2 \delta$  from unity, for  $\lambda = 90^\circ$  or  $270^\circ$ , is 0.16, about

$$\frac{d\alpha}{d\beta} = -0.40 \cos \lambda.$$

We see therefore that, as we may neglect here the difference between mean longitude in the orbit and ecliptical longitude our term could, as regards its form, be completely explained by a constant error in the latitude and that the correction for this would have to be  $+ 1''.65$ , more than compensating HANSEN's term  $- 1''.0$ . As BAKHUYZEN, from the declinations observed at Greenwich, after having freed them as far as possible from systematic errors, and reduced them to NEWCOMB's fundamental system, deduced a latitude-correction of only  $+ 0''.20$ , both from the observations of the limbs and from those of Misting A, while in using the uncorrected declinations the correction would have been found to be zero or negative, it appears that if I, instead of using differences  $\Delta\alpha$ , had used the errors in longitude  $\Delta\lambda$ , calculated at Greenwich, I should have found an empirical term of about the same value.

**Astronomy.** — *On the significance of the term in the Right Ascension of the moon, found by J. E. DE VOS VAN STEENWIJK.*  
By Prof. E. F. VAN DE SANDE BAKHUYZEN.

The most important result of the investigation of DE VOS VAN STEENWIJK is doubtless the fact that the observations of the moon, besides the inequalities theoretically determined by BROWN, betray the existence of a new term, apparently of an analogous form, which was not explained by the theory. The reality of this term might already be considered as established after his previous calculations; its existence and also the approximate accuracy of the coefficients were put beyond all doubt by the determination of the mean residual discordances remaining in  $h$  and  $k$  (see his second paper), after they had been corrected on the one hand only for the

constant or slowly varying parts and for the theoretical perturbations and on the other hand for the empirical term also. The mean discordance decreased, in the mean for  $h$  and  $k$ , from  $\pm 0''605$  to  $\pm 0''389$ , and the decrease was about the same for  $h$  and  $k$ , and about equally great for the earlier and the later years. It did not appear, however, to be so certain that the term deduced from the investigation of the tabular errors in *Right-ascension* really represented an inequality in the *longitude* of the moon.

Originally DE VOS VAN STEENWIJK found the term in the form

$$+ 0''.66 \sin \{g + 244^\circ.4 + 40^\circ.35 (t - 1900.0)\}$$

It soon struck me that the annual variation of the argument  $\chi$  is almost equal to the annual motion of the perigee  $40^\circ.68$ , so that, as the argument is found most accurately for the mean epoch of the observations used, 1886, the term can be written :

$$\begin{aligned} &+ 0''.66 \sin \{g + 249^\circ.0 + 40^\circ.68 (t - 1900.0)\}. \\ &= + 0''.66 \sin \{l - 85^\circ.3\} \end{aligned}$$

in which  $l$  represents the mean longitude in the orbit or approximately the ecliptical longitude.

Now it is possible :

1. That the approximate agreement of the two rates of motion is merely accidental, and that the original form found for the term is the true one, so that we might probably have to deal with a still unknown inequality caused by the planets.

2. That the transformation gives us the true formula.

Taking the first supposition, the difficulty remains, which DE VOS pointed out in his first paper, that such a considerable term should have escaped both BROWN and RADAU, and that while all terms with at all considerable co-efficients have been found nearly equal by both.

Taking the second supposition, if we look upon the term in its altered form as a perturbation-term, this would lead to a very improbable form for such a term, as it would depend upon the absolute longitude of the moon, i.e. of a difference in longitude with a fixed direction in the sidereal system or with the aequinox.

There is however a third possibility, viz. that the second form is the true one, but that we are not dealing with an inequality in the longitude, but with one in the right ascension, proceeding from the particular parts of the limb, which are used in the transit-observations, and their different distances from the centre of gravity of the moon. In DE VOS's researches, following NEWCOMB, the immediately observed errors in R.A. were used, and in the last part of his second paper he discusses the influence of this method. He shows

there that a constant error in the latitude must lead to a term in R.A. of just the form that he finds, as with fairly close approximation

$$da = -0.40 \cos \lambda d\beta$$

while the new term is pretty nearly

$$-0''.66 \cos \lambda.$$

The special form of the deviations of the limb, which would account for the result now found, would be such that the centre of figure would lie  $1''.65$  more to the north than according to our ephemerides.

If we assume, disregarding the inclination of the lunar orbit and the influence of the librations, that the moon's equator always coincides with the ecliptic, then in the transit-observations parts of the limb are used, which vary with the longitude of the moon over arcs lying between points  $23^\circ 5'$  on each side of the moon's equator. These arcs would then belong to a centre with a latitude  $1''.65$  larger than according to the ephemerides, therefore, as these include HANSEN'S constant term  $-1''.0$  a latitude  $0''.65$  larger than that according to pure theory. As further, in the course of one year, each value of the moon's longitude successively co-incides with each value of the elongation  $D$  and therefore the same number of times with observations of Limb I and Limb II, the two symmetrically lying parts of the limb must each time co-operate.

Last year, I deduced from an investigation of the declinations of the moon observed at Greenwich during the period 1883—1909, that these, after they had been freed from systematic errors as far as possible, and reduced to the fundamental system of NEWCOMB, point to a centre  $0''.8$  to the south, of the centre of gravity, that is nearly to HANSEN'S centre, while the uncorrected declinations would place the centre of figure even more to the south. I found further that the observations of the declination of Misting A lead to precisely the same results as those of the limbs, or that, when reduced to the centre of the moon with the existing data, they placed it also  $0''.8$  to the south. De Vos's results now show that the southerly centre, which satisfies arcs of  $47^\circ$  lying symmetrically with respect to the north and south pole, certainly does not satisfy the easterly and westerly arcs which are used in the observations of the rightascensions.

A centre of figure coinciding with the centre of gravity certainly brings about a better agreement. This would correspond with a correction-term  $-0''.40 \cos \lambda$ , and the question therefore arises whether this smaller co-efficient sufficiently satisfies the observations:

Before investigating this we must note another circumstance. For the years 1905—1909 the observations of Mosting A in right-ascension were also used and it is impossible to say what influence this has had. Observations of the limbs and of the crater are intermixed in each of the 20 equations deduced from each year's observations and cannot be easily separated.

I have, therefore, made a new calculation of the empirical term and simply left out the six last years. Of the seven normal places (DE Vos p. 139) I have left out the last and I took for the last but one the mean results of only 4 years 1901—1904. A new solution then gave

$$\chi = 253^{\circ}.7 + 40^{\circ}.67 (t-1900.0)$$

and we thus find an annual variation exactly equal to the annual motion of the perigee.

A new calculation of the co-efficient then gave (calculation B see DE Vos' p. 139)

$$\begin{aligned} \beta &= -0''.44 & \beta' &= +0''.67 \\ \gamma &= +0''.66 & \gamma' &= +0''.26 \end{aligned}$$

from which follows for the co-efficient itself  $\alpha = +0''.75$ , a value even greater than before. As argument for 1900.0 we now get  $\chi_0 = 251^{\circ}.6$ , thus as the mean from the two calculations  $252^{\circ}.7$ , and the term becomes

$$\begin{aligned} &+ 0''.75 \sin \{252^{\circ}.7 + 40^{\circ}.67 (t-1900.0)\} \\ &= + 0''.75 \sin (l-81^{\circ}.6) \end{aligned}$$

now deviating slightly more from the form  $-\alpha \cos l$ .

The empirical term was now again subtracted from the  $-\dot{h}_v$  and  $-\dot{k}_v$ : I with the co-efficient  $0''.75$  found here, II with the co-efficient  $0''.40$ . Calculating in both cases the mean discordance we found.

	I		II	
	$h$	$k$	$h$	$k$
1848—1874	$\pm 0''.367$	$\pm 0''.406$	$\pm 0''.463$	$\pm 0''.490$
1890—1904	$\pm 0.215$	$\pm 0.341$	$\pm 0.301$	$\pm 0.374$
Together	$\pm 0.318$	$\pm 0.382$	$\pm 0.410$	$\pm 0.450$

From these results it is clear in the first place, that for the period since 1890 the mean residual discordance is distinctly smaller than before, so that the results from the observations of the limbs and from those of the crater appear not to make a completely homogeneous whole. DE Vos himself had already observed that exactly the last years, since the crater-observations were added, gave less regular

results. In the second place the results show distinctly that the smaller co-efficient satisfies the observations less well. From all this it seems to me that the supposition that the new term is due to a deviating form of the limb gains in probability, and we must then conclude that, while the polar arcs require a centre of figure about  $0''.8$  south of the centre of gravity, the aequatorial arcs deviate in the opposite sense and require a centre of figure about  $0''.9$  to the north of the centre of gravity. This is identical with saying that the northern extremities of these arcs lie  $0''.35$  further outside, and the southern  $0''.35$  further inside relatively to the centre of gravity. If we take into account that the term has not exactly the form  $a \cos l$ , the conclusion is but little altered.

These conclusions now agree with the results found by BATTERMANN from his occultations, who deduced from them on the average a centre of figure coinciding with the centre of gravity.

Our results can be further tested by the results which HAYN, in his "*Selenographische Koordinaten*" deduced for the form of the lunar limb from his measurements in Leipzig and HARTWIG's in Strassburg and also by the results obtained by PRZYBYLLOK in his "*Das Profil der Randpartien des Mondes*". (Mitteilungen der Gr. Sternwarte zu Heidelberg, XI).

HAYN gives in his 3<sup>d</sup> paper on p. 77, for a mean libration, the mean radii for arcs of  $10^\circ$  and of  $30^\circ$  counted from the North pole along the limb of the moon (Argument  $P$ ), and I deduced analogous results from PRZYBYLLOK's *Tafel der Randkorrekturen*.

In this way I found

$P$	$\Delta r H.$	$\Delta r P.$
$60^\circ - 90^\circ$	$+ 0''.03$	$+ 0''.32$
$90 - 120$	$- 0.27$	$- 0.22$
$240 - 270$	$+ 0.09$	$+ 0.05$
$270 - 300$	$- 0.31$	$- 0.20$

Thus for parts of the limb diametrically opposed to each other HAYN finds deviations in the same sense, which does not agree with the results obtained by DE VOS. The agreement with PRZYBYLLOK is better, but not yet satisfactory.

Still I think that the explanation of the results by the form of the lunar limb is the most probable, or, at any rate, the least improbable, and certainly the investigation of DE VOS in connection with mine in 1912 confirms HAYN's remarks (l.c. p. 75) with regard to the great importance of the study of the deviations of the moon's limb, also for the determination of the moon's position.

**Physics.** — “*A quick coil galvanometer.*” By Dr. W. J. H. MOLL.  
(Communicated by Prof. W. H. JULIUS).

Galvanometers are applied for the investigation of a great variety of phenomena. The demands which the instrument is to meet, will differ according to the nature of the investigation, and therefore many different kinds have a claim to existence. If we confine ourselves to those cases where the galvanometer has to measure a direct current, and a great sensibility is required, even then the choice of the instrument that will best serve a definite purpose, is often difficult.

For some methods of investigation, in particular those in which the galvanometer is inserted in a circuit of great resistance, its own resistance will be of little importance. In those cases the string galvanometer is preferable, which is very sensitive, exceedingly quick in its indication, and not easily disturbed. For completeness' sake we must mention a galvanometer (part of the “Kardiograph”) constructed in the course of this year by SIEMENS and HALSKE, about which however no particular data have been published as yet.

In many other methods of investigation, however, the resistance of the circuit is comparatively slight, and the above mentioned galvanometers cease to be sensitive on account of their great resistance. In those cases we must choose between the needle galvanometers and the coil galvanometers.

Of these two types the needle galvanometers will only be selected for those measurements, for which the utmost sensibility is required. As a matter of fact they are greatly subject to disturbances, and it is extremely difficult to protect them, especially in cases of great sensibility.

The coil galvanometer is much simpler in its use and for most purposes sufficiently sensitive. It surpasses the needle galvanometer not only by its being less readily disturbed, but also by the ease with which the damping may be regulated and dead beat conditions attained. These two advantages account for the preference which is generally given to this apparatus.

The common coil galvanometer is, however, by no means quick; the time of its indication varies from 10 to 30 seconds for the different patterns. This drawback makes itself felt, when the investigation requires a long series of readings; the observation of rapidly varying phenomena is evidently impossible with such a slow instrument, while the string galvanometer, which is exceedingly quick, is generally not sufficiently sensitive on account of its great resistance.

Here a galvanometer is required which is at the same time sensitive *and* quick.

In what follows a method will be discussed by which quickness of indication may be reached for the sensitive coil galvanometer.

Let us call  $K$  the moment of inertia of the coil;  $D$  its directive force;  $T$  its semi-period of oscillation with open circuit;  $F$  the total area of its windings;  $H$  the intensity of the uniform magnetic field round the coil;  $W$  the resistance of the circuit, in which the galvanometer is inserted; then the sensibility  $P$  of the galvanometer, i.e. the angle of deviation (supposed small) for the unity of electro-motive force in the circuit is given by:

$$P = \frac{(HF)}{DW} \dots \dots \dots (1)$$

while

$$T = \pi \sqrt{\frac{K}{D}} \dots \dots \dots (2)$$

Since we confine ourselves to the case of aperiodicity, we have moreover, neglecting the air damping,

$$W^2 = \frac{(HF)^2}{4DK} \dots \dots \dots (3)$$

and the time of indication is approximately given by  $\tau = 3 T$ .

Six quantities occur in the three equations (1), (2), and (3), if we count  $(HF)$ , the so-called dynamic galvanometer constant, as one. We can divide them into two groups,  $P$ ,  $W$  and  $T$  being quantities, which can be measured directly, and which characterize the instrument.

The equations enable us to calculate from them  $D$ ,  $K$ , and  $(HF)$ . Thus for the most sensitive galvanometer constructed by SIEMENS and HALSKE according to JAEGER's directions:

$$T = 7,5 \quad W = 100 \text{ ohm} = 10^{11} \quad P = 1,7 \times 10^{-5 \text{ 1}}$$

are given, from which we calculate in round numbers:

$$(HF) = 280\,000 \quad D = 0,18 \quad K = 1,0.$$

For the quickest galvanometer of the same firm, designed by DIESELHORST:

$$T = 2 \quad W = 1,8 \times 10^{11} \quad P = 0,6 \times 10^{-5} .$$

from which

$$(HF) = 200\,000 \quad D = 0,19 \quad K = 0,08.$$

<sup>1)</sup> This corresponds to a deviation of 3,4 mm. for 1 microvolt on a scale at 1 meter's distance,

Not only does the above reasoning give us valuable information about a given instrument, it also leads the way in the construction of a new one, satisfying special demands. For the construction of a galvanometer which is at the same time *sensitive and quick*, we have to solve the problem how to choose  $D$ ,  $K$  and  $(HF)$  so that  $P$  be great and  $T$  small.

Here we have to consider that the six quantities are related in still other ways than expressed by the three equations. Indeed, the mode of suspending the coil, the kind of wire of which its windings consist, and its form will furnish additional relations between the six quantities, and it is the question whether a certain change of  $D$ ,  $K$  and  $(HF)$ , which would seem desirable according to the equations (1), (2), and (3), is practically feasible. The equations will only indicate the direction in which we have to seek.

The quickness of the galvanometer only depends on the directive force  $D$  and the moment of inertia  $K$  of the coil. In order to simplify the calculation we will therefore leave the dynamic galvanometer-constant  $(HF)$  out of consideration, and we do this the more readily as this quantity may be modified within a wide range independently of the five others. After the elimination of  $(HF)$  two equations remain:

$$T = \pi \sqrt{\frac{K}{D}} \quad (2) \quad P^2 = \frac{2T^3}{\pi^3 KW} \quad (4).$$

We see from this that  $T$  is diminished when  $D$  is increased, but that  $P$  is diminished in a corresponding degree. A second means of increasing the quickness, namely diminishing  $K$ , will not alter the sensibility so much, since  $K$  also occurs in the denominator of the second member of (4). A third means, however, can lead to our purpose. For a given value of  $W$ ,  $P$  remains unaltered when we leave

$$\frac{T^3}{K} = \pi^3 \frac{\sqrt{K}}{D\sqrt{D}} \text{ unchanged.}$$

Therefore by greatly decreasing  $K$ , say to one thousandth, and at the same time diminishing  $D$  to, say, one tenth,  $T$  will be reduced to one tenth, while  $P$  remains the same.

That such a change of  $K$  and  $D$  is actually feasible, may appear from the following data.

For the coil galvanometer, by means of which the rapidly varying radiation of the sun was registered during the central part of the solar eclipse of 1912<sup>1)</sup>, we have:

<sup>1)</sup> W. H. JULIUS. The total solar radiation during the annular eclipse on April 17, 1912. *Astroph. Journ.* Vol. XXXVII, p. 225.

$$T = 0,4 \quad W = 2 \times 10^{10} \quad P = 1,0 \times 10^{-5}$$

$$(HF) = 25\,000 \quad D = 0,12 \quad K = 0,002.$$

For a very sensitive instrument of the same kind :

$$T = 0,65 \quad W = 1,5 \times 10^{10} \quad P = 3 \times 10^{-5}$$

$$(HF) = 14\,000 \quad D = 0,03 \quad K = 0,0015.$$

The sensibility of this coil galvanometer with a time of indication of less than 2 seconds is *greater* than has ever been reached even in the slowest instrument. It corresponds to a deviation for 1 microvolt of 6 mm., on a scale at 1 meter distance.

For a third, very quick but less sensitive specimen :

$$T = 0,12 \quad W = 2,8 \times 10^{10} \quad P = 0,45 \times 10^{-5}$$

$$(HF) = 18\,000 \quad D = 0,14 \quad K = 0,00045.$$

$K$  may be still further diminished, but then one has to face rather great technical difficulties, and soon the moment of inertia of the mirror will play a too important rôle. For a mirror e.g. of a radius of 2 mm. and a thickness of 0,2 mm. this amounts to 0,00006.

It may seem strange that this rather obvious measure of diminishing the moment of inertia of the coil has not been made use of in the construction of the coil galvanometer since long; the reason will probably be a difficulty which arises when this principle is applied. In the usual construction of the apparatus the coil is suspended by a thin strip, which at the same time conveys the current to be measured; the current is led off by means of a metal band so slack as to have no appreciable share in the directive force of the coil. When now the moment of inertia of the coil is made very small, and consequently its weight very slight, it becomes subject to inevitable vibrations to a much higher degree, than is the case with a heavy coil. This disadvantage may, however, be obviated by not suspending the coil in the usual way, but stretching the slack band.

The reliability of the indication of a galvanometer with a coil fixed in such a way appears convincingly from the results of the above-mentioned eclipse observations published elsewhere<sup>1)</sup>.

#### *Conclusion.*

In the construction of a coil galvanometer it is desirable to take the moment of inertia of the coil *much* smaller than was usual hitherto; and not to suspend the coil, but to stretch it between two metal bands.

Galvanometers constructed according to my directions are furnished by the firm P. J. KIPP and Sons at Delft.

<sup>1)</sup> W. H. JULIUS. Loc. cit.

**Chemistry.** — “On the presence of quinine in the seed of *Cinchona Ledgeriana Moens*.” By P. VAN LEERSUM.

According to the description by MOENS<sup>1)</sup> the seeds of the genus *Cinchona* are compressed, flat, with an elongated kernel, which is completely surrounded by a membranous wing, having a toothed edge. The embryo lies in the axis of a fleshy albumen; the cotyledons are entire and egg-shaped.

The seeds vary in size and shape according to the species. Thus for instance those of *C. officinalis* are 4—7 m.m. long and 2—4 m.m. broad, those of *C. Ledgeriana* measure 4½ m.m. by 1 m.m., those of *C. succirubra* 7—10 m.m. by 2—3 m.m.

A kilogramme of the seed of *C. officinalis* consists of 1400000 seeds, for *C. succirubra* and *C. Ledgeriana* the corresponding figures are 900000 and 350000.

With due precautions, *Cinchona* seeds can be preserved for from 6 to 7 months without loss of germinating power. For this they should be perfectly ripe; they should be dried in the wind and completely freed from adherent portions of the capsule and funicle and then placed in an air-tight tin box or in a bottle with ground stopper.

The batch of seed which has contributed most to directing attention to the *Cinchona* plantations of Java is that which was bought from GEORGE LEDGER of London in 1865. G. LEDGER had obtained this seed from his brother CHARLES LEDGER, who in his turn received it from his servant MANUEL INCRA MAMANI, an Indian native of the Jungas of Bolivia.

Little is known about the chemistry of *Cinchona* seed. According to MOENS it would contain no alkaloid, but on the other hand he states that there is fat, to the extent of 6.13 % in the seed of *C. Ledgeriana*, 13.3 % in that of *C. officinalis* and 9.50 % in that of *C. succirubra*.

In the Annual Report of the Government *Cinchona* culture for 1905 I have already stated that there are alkaloids in the seed, and not only the so called amorphous alkaloid, but also cinchonine.

In order to investigate how and under what conditions the chief alkaloid i.e. quinine, is formed in *Cinchona*, it is necessary to know first whether the seed itself contains quinine.

My previous investigations of the seed had already pointed to this being the case, but there was no certainty. I found that the

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<sup>1)</sup> De Kinacultuur in Azië.

sulphuric acid solution of the alkaloids from 50 grammes of seed was fluorescent, but only so slightly, that error was not completely excluded. Moreover quinidine also fluoresces in sulphuric acid solution.

In order to obtain certainty a kilogramme of *Ledgeriana* seed was powdered and sieved (B 40). In quantities of 20 gm. the powder was mixed with 5 gm. of calcium hydroxide and then 6.5 gm. of 5% sodium hydroxide and 9.5 gm. of water were added and the mixture was stirred for about 2 hours until a suitable granular mass was obtained. This mass was extracted with benzene in a Soxhlet apparatus.

After distilling off the benzene there remained in the flask, in addition to the alkaloids and other impurities, so much of an oily liquid that it was impossible to estimate the alkaloids directly in the residue.

It was found necessary first to free the seed from the oil contained in it before an accurate estimation of the alkaloidal content could be undertaken.

A preliminary experiment showed that petroleum ether is most suitable for this purpose, since it dissolves the oil, but not the alkaloids.

The finely powdered seed was first completely extracted with petroleum ether; the mass was dried, powdered again and sieved.

Of this powder quantities of 20 gr. were thoroughly mixed with slaked lime, caustic soda, and water and the mass was then extracted with benzene as described above.

After extraction and before distilling off the benzene, 10 c.c. of  $N/20$  hydrochloric acid were added. In this way I finally obtained an almost colourless solution of the hydrochlorides of the alkaloids. After filtering through cottonwool and washing, a drop of a 0.5% solution of methylred in alcohol was added, the liquid was heated on a waterbath and then titrated back with  $N/20$  sodium hydroxide.

The average result of a few dozen fairly concordant analyses was 0.380% of total alkaloid, calculated for seed containing fat, but no water. These titrated neutral solutions were mixed and evaporated to about 50 c.c., after adding a further small quantity of  $N/20$  sodium hydroxide, so that the liquid was slightly alkaline.

After cooling, the liquid was freed from suspended impurities by filtration into a separating funnel. It was then washed, and after it had been made strongly alkaline, it was extracted several times with ether.

The ethereal solution containing all the alkaloid from a kilogramme of seed, was evaporated to dryness, and the residue was dissolved

P. VAN LEERSUM. "On the presence of quinine in the seed of *Cinchona Ledgeriana* Moens".

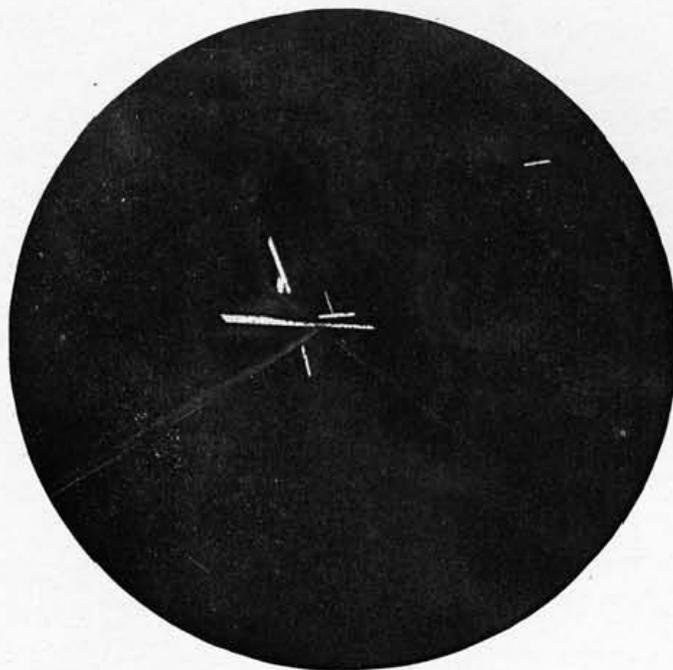


Fig. 1.

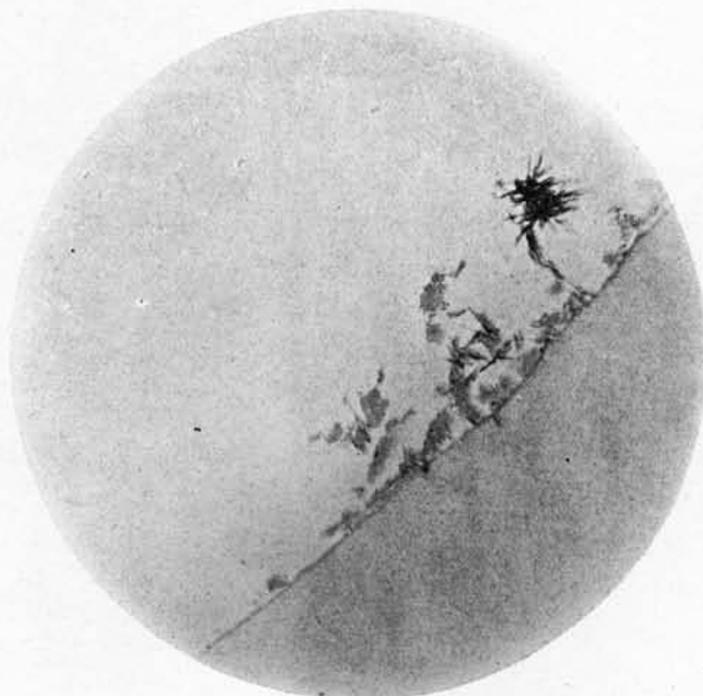


Fig. 2.

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in the minimum quantity of water, acidulated with sulphuric acid. This acid alkaloidal solution was washed repeatedly with ether until the latter removed no more colouring matter. The solution was then rendered alkaline and again shaken with ether; the ethereal solution was separated and evaporated to dryness and the residue was again treated in the way described above, in order to obtain the alkaloid finally in as pure a condition as possible.

This dry alkaloid, which had been purified several times, was now dissolved in water containing a trace of hydrochloric acid, and the faintly acid solution was evaporated to dryness in a desiccator; the residue was dissolved in a few drops of water, and after filtration the solution was placed on a microscope slide.

A platinum wire which had been moistened with a solution of sodium tartrate, was placed in the previously warmed solution and the latter was allowed to cool slowly under a double watchglass.

After some time needles separated (fig. 1).

These needles could be: quinine tartrate, cinchonidine tartrate or a mixture of the two.

In order to determine whether we were indeed concerned with quinine, the needles were washed a few times very carefully with a little water, so that they remained on the slide.

Then a trace of dilute sulphuric acid was added and a little of a mixture of equal parts of alcohol, of water, and of acetic acid coloured pale yellow by means of a potassium triiodide solution. After a short time there appeared at the edges of the preparation the very fine dichroitic leaflets of HI iodine-quinine sulphate (fig. 2), a reaction which is so characteristic of quinine, that the presence of this alkaloid in the seed of *C. ledgeriana* can no longer be doubted.

Finally I may add that the seed investigated contained 18.6% of a pale greenish yellow oil, having a specific gravity of 0.930 at 18° and a rotation of  $-26^\circ$  at 20° C. in a tube of 20 c.m.

**Physics.** — “*The red lithium line and the spectroscopic determination of atomic weights.*” By Prof. P. ZEEMAN.

In a former communication I showed that the red lithium line 6708 is a close doublet. The distance between the components was found by a rough measurement to be of the order of a quarter Ångström. I now have been able to photograph the mentioned line in the second order spectrum of a large ROWLAND grating. Using an iron-arc spectrum in the third order violet, coinciding with the

domain of the red lithium line in the second order, the distance of the components of the natural lithium doublet (6708) was now measured and found to be 0,144 Ångströms. We can be sure only of the second figure.

A reproduction of the lithium doublet is given in Fig. 1. of the Plate. Fig. 2 is considered in the communication, immediately following. It exhibits the outer components of the magnetically divided *D*-lines in the inverse effect, but it may be used now to give an idea of the closeness of the lithium doublet, the two narrow sodium lines due to the arc-light being also present. As the sodium- as well as the lithium-doublet has been photographed in the second order, the scale value can be derived from the first mentioned pair.

RYDBERG, KAYSER and RUNGE in their researches on spectrum series have emphasised that the distances between the components of pair lines in a group of chemically related elements increase with the atomic weights. With sodium, potassium, rubidium and cesium, the atomic weight is approximately proportional to the square root of the distances between the pair lines.

The ratio of the difference  $\nu_1$  between the frequencies of the components of the pair lines and the square of the atomic weight  $\mu$  should therefore be a constant. According to our observation the difference of the frequencies for the lithium doublet is 0.32.

RITZ<sup>1)</sup> came to the conclusion, a result to which my attention has been kindly drawn by Dr. LADENBURG, that for related elements the difference of the constants  $p_1$  and  $p_2$  of RITZ's spectrum formula divided by the square of the atomic weight is even more nearly constant than the ratio  $\frac{\nu_1}{\mu^2}$ .

Taking for *Li*<sup>2)</sup>  $p = -0.047510 = p_2$ , I calculate  $p_1 = -0.047521$ .

We thus find for the alkalis:

	<i>Li</i>	<i>Na</i>	<i>K</i>	<i>Rb</i>	<i>Cs</i>
$\frac{\nu_1 \cdot 10^3}{\mu^2}$ <sup>3)</sup>	6.53	32.3	37.8	32.3	31.6
$\frac{(p_2 - p_1) \cdot 10^5}{\mu^2}$	0.022	0.142	0.189	0.180	0.186

It appears that, if the data for lithium be included, there is no question about a constancy of the proposed ratios in the group of the alkalis.

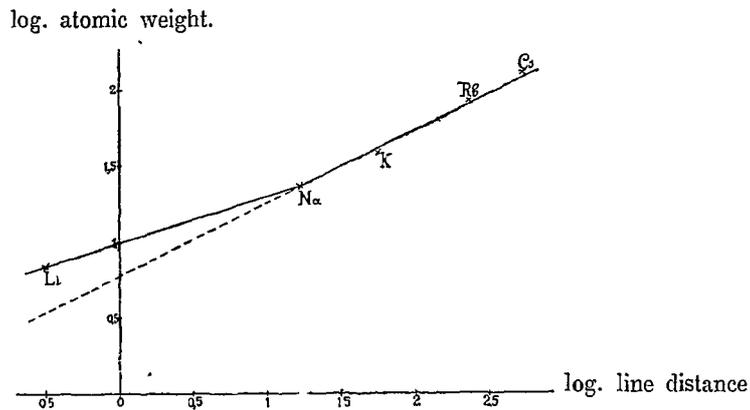
<sup>1)</sup> RITZ. Oeuvres. p. 145.

<sup>2)</sup> RITZ. l. c. p. 57.

<sup>3)</sup> The last four numbers according to RYDBERG. Rapports, etc. T. II. p. 219. Paris. 1900.

A more general form of the rule first tested, has been proposed by RUNGE<sup>1)</sup>: in every group of chemically related elements the atomic weight is proportional to a power of the distance of the lines of the doublet. Or expressed differently, when taking the logarithms of atomic weight and of distance as coordinates, the corresponding points in a group of chemically related elements are in a straight line.

Our graphical representation shows that for *Na*, *K*, *Rb*, *Cs* the mentioned rule is beautifully fulfilled, but that lithium forms an exception.



Hence we must conclude that the law connecting the frequency difference of the components of pair lines and the atomic weight is yet unknown to us.

One observation concerning the intensities of the lithium pair 6708 seems worthy of record. With very small vapour density the violet component is the most intense. With increased vapour density, a case to which Fig. 1 of the Plate relates, the ratio of the intensities is reversed and no more corresponds to that of the sodium lines. With still greater density new absorption lines appear in the vicinity of the lithium pair. They merit a separate investigation, but they are probably of the same nature as the line groups observed by WOOD<sup>2)</sup> in the neighbourhood of several lines of the principal series of sodium.

<sup>1)</sup> RUNGE and PRECHT. *Physik. Zeitschr.* 4. 285, 1903.

<sup>2)</sup> WOOD. *Phil. Mag.* 18, 530, 1909.

**Physics.** — *Magnetic resolution of spectrum lines and temperature.*

By H. R. WOLTJER and Prof. P. ZEEMAN.

An influence of the temperature of the source of light on the magnitude of magnetic separation till now has been vainly sought. There seems to be a possibility for such an influence, due to the free electrons in the source of light, if we accept RITZ's theory of magnetic resolution, at least in its original form. We thought it of interest to inquire for such an action, now that we are able to produce narrow spectrum lines of low temperature by means of the small tubes of WOOD and ZEEMAN <sup>1)</sup>. On the other hand we possess sources of light of very high temperature, viz. the oxygen-acetylene flame and the electric spark.

With these means for the magnetised source of light, Mr. H. R. WOLTJER has made an investigation concerning magnetic resolution at different temperatures. An exhaustive discussion only of the results of the measurements, which shall be published in H. R. WOLTJER's thesis for the doctorate, can fix the maximum change of the magnetic resolution. Besides, the magnitude of the resolution the *ratio* of the intensities of the divided components is of importance to theory. We have begun a separate investigation concerning this subject. In the first place the behaviour of the line  $D_2$  was investigated. Under the influence of the magnetic field it is resolved into six components, of which four vibrate at right angles to the field and therefore under the same circumstances as to polarisation. The polarising action of the grating <sup>2)</sup> and of the glass sodium tube cannot change therefore the *ratio* of the intensities of these four components. The reproduction in fig. 2 shows the outer components of the magnetised absorption sodium-lines using one of the above mentioned tubes (temperature 350° C.). The narrowness of the lines is well exhibited in the reproduction. The Figures 3 and 4 refer to experiments with a calc-spar rhomb placed before the slit of the spectroscop, and a horizontal slit near the source of light. The field of view is divided into three parts: one with the horizontal, one with the vertical vibrations and the third due to natural light <sup>3)</sup>.

The photograph reproduced in Fig. 3 was made with a gas-oxygen flame, which in later experiments (with similar results) was

<sup>1)</sup> R. W. WOOD and P. ZEEMAN, These Proceedings, Febr. 1913.

<sup>2)</sup> P. ZEEMAN, These Proceedings, October 1907.

<sup>3)</sup> Cf. P. ZEEMAN and B. WINAWER, These Proceedings, January 1910.

P. ZEEMAN. The red lithium line and the determination of atomic weights.  
H. R. WOLTJER and P. ZEEMAN. Magnetic resolution and temperature.

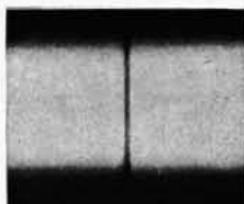


Fig. 1. Lithium doublet (6708).

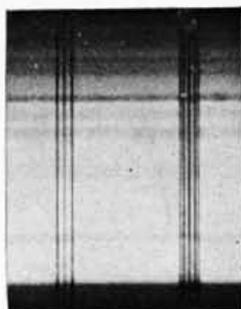


Fig. 2. Outer components of sodium lines of low temperature in magnetic field.

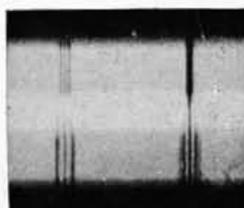


Fig. 3. Magnetised sodium lines in gas-oxygen flame.

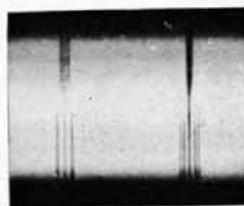


Fig. 4. Magnetised sodium lines of 300° C.

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replaced by an acetylene-oxygen flame. The temperature of the gas-oxygen flame is estimated at  $2000^{\circ}\text{C}$ , that of the acetylene-oxygen flame at  $2400^{\circ}\text{C}$ .

The temperature of the sodium tube, used for the experiment to which Fig. 4 relates, was determined at about  $300^{\circ}\text{C}$ . by means of a thermo-couple.

A comparison of the photographs 3 and 4 clearly exhibits a difference of the ratio of the intensities of the outer components. At the higher temperature the outer components appear much fainter in relation to the inner ones than at the temperature of  $300^{\circ}\text{C}$ . A closer inspection shows that in the latter case also, the inner components surpass the outer ones in intensity, but the difference is less. If the density of the sodium vapour is increased, there is a greater difference in the behaviour of inner and outer components at the higher than at the lower temperature. We have the intention to return to this point on a further occasion. It would appear that we are able by merely changing the temperature to influence the separate magnetic components and to change within certain limits their intensities.

With the electric spark the outer components are relatively feeble just as with the oxygen-acetylene flame.

It should be noticed that in the experiment to which Figures 3 and 4 relate, the temperature has been changed, but the pressure as well.

In the glass tube the pressure is of the order of some millimetres, whereas the total pressure — which according to HUMPHREYS is decisive in the phenomena of pressure-shift of spectrum lines, — in the experiment with the gas-oxygen flame is equal to one atmosphere.

In a few cases HUMPHREYS observed also a change in the relative intensities of spectrum lines. Hence there would be a possibility that the difference between figures 3 and 4 is partially due to a change of the total pressure.

The effect now under review is of a rather complicate character. Besides the DOPPLER-effect, also the density of the vapour, the change of pressure and the length of the path of the light rays must play a part. Though apparently there exists an influence of temperature on the aspect of the resolved lines under the circumstances of our experiments, it cannot be denied that the interpretation of observations concerning the amount of the separation is more easy. The complications mentioned are then eliminated.

**Chemistry.** — “On a new principle for the direct determination of osmotic pressure”. By Prof. ERNST COHEN and G. DE BRUIN.

Direct determination of osmotic pressure in very dilute solutions i. e. solutions which obey VAN 'T HOFF'S law, are of great interest both to physico-chemists and biologists. As such measurements however are attended with great difficulties, until now physical chemists have generally employed indirect methods, such as lowering of the freezing point, elevation of the boiling point etc. Considering that in a dilute solution in water a lowering of the freezing point of  $\frac{1}{1000}$  of a degree corresponds to an osmotic pressure of 124 mm. water, the superior accuracy of the direct determination becomes evident. We describe here a principle which avoids the above mentioned difficulties. The vessel *B* in the figure is to receive a dilute solution in water (for instance of cane-sugar). Its bottom is formed by a membrane which is semi-permeable with respect to this solution.

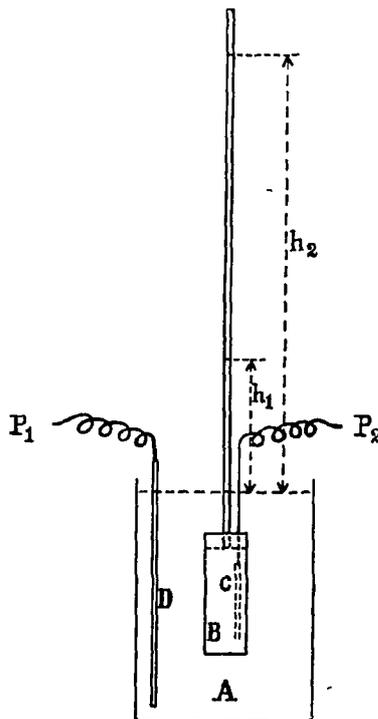
Copper ferrocyanide may be used for the purpose. The vessel *A* contains water. The top of *B* is tightly closed with a stopper through which is passed a fine capillary tube and a wire which carries the half of a reversible electrode. A copperplate will serve. The other part of the electrode is put into the water in *A*.

If *B* is new immersed in the water in *A* the liquid rises, as is well known, in the capillary. When it has reached a certain height, say  $h_1$ , which is noted on a millimetrescale, the rise of the liquid is stopped by introducing between the electrodes *C* and *D* (at  $P_2$  and  $P_1$ ) a certain potential-difference ( $E_1$ ). According to the researches of G. WIEDEMANN and those of VON HELMHOLTZ<sup>1)</sup>, we can write then:

$$P - h_1 = k E_1 \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where  $P$  is the osmotic pressure to be measured and  $k$  is a constant.

<sup>1)</sup> Comp. G. WIEDEMANN, Die Lehre von der Elektrizität; 1, 993 seq. Braunschweig 1893 CHWOLSON, Lehrbuch der Physik. 4, (2) 583 Braunschweig 1903.



If we cut out now the potential-difference  $E_1$  the liquid will rise again in consequence of osmosis. When it has reached the height  $h_2$ , we stop it again by introducing a new potential difference ( $E_2$ ) between  $P_1$  and  $P_2$ .

Now the equation holds:

$$P - h_2 = k E_2. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

From (1) and (2) it follows:

$$P = h_1 + (h_1 - h_2) \frac{E_1}{E_2 - E_1}$$

so that the osmotic pressure to be measured is known.

The great difficulties which arise when a semi-permeable membrane is used for direct determination of osmotic pressure may thus be avoided. These difficulties are.

1<sup>st</sup>. The long time needed to reach equilibrium. During this time diffusion takes place with consequent change in the concentration of the solution. In the above method the measurement is made at the beginning when the rise is greatest and is completed in a short time so that diffusion is avoided.

2<sup>nd</sup>. That the semi-permeable wall is pressed on one side until equilibrium is reached. Here, on the contrary, osmotic pressure is compensated by the electro-endosmotic pressure; consequently the wall is not pressed.

3<sup>rd</sup>. By the entrance of solvent the concentration within the cell changes. Here, on the contrary, this change of concentration may be avoided by making  $h_1$  and  $h_2$  and also the internal diameter of the capillary tube small.

One might inquire whether the laws of electro-endosmosis which play a role in the principle described, are valid when electro-endosmosis takes place through a semi-permeable membrane. It will be shown later that it is possible to construct the apparatus in such a way that the principle holds even if this question must be answered in the negative.

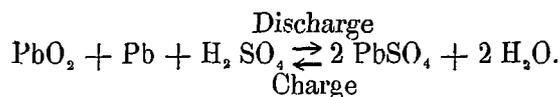
Utrecht, June 1913.

VAN 'T HOFF-Laboratory.

**Chemistry.** — “*The influence of pressure on the E. M. F. of the lead-accumulator*”. By Prof. ERNST COHEN and G. DE BRUIN.

According to chemical and thermodynamical investigations which have been carried out recently<sup>1)</sup> the reactions which take place in the lead-accumulator when it is discharged (charged) can be represented by the equation:

<sup>1)</sup> DOLEZALSK, die Theorie des Bleiakкумуляtors”, Halle 1901.



By reference to this equation it is now possible to calculate a priori the influence of pressure on the E. M. F. of accumulators of this kind.

This influence has been determined experimentally in the VAN 'T HOFF-Laboratory by Dr. G. TIMOFEJEV, who will shortly publish his results.

The connexion between the influence of pressure on the E. M. F. of a reversible galvanic cell (such as the accumulator is) and the changes of volume which occur when the quantity of electricity  $d\varepsilon$  passes through it, are given by the equation<sup>1)</sup>

$$-\left(\frac{dE}{dp}\right)_{T,v} = \left(\frac{dv}{d\varepsilon}\right)_{T,p},$$

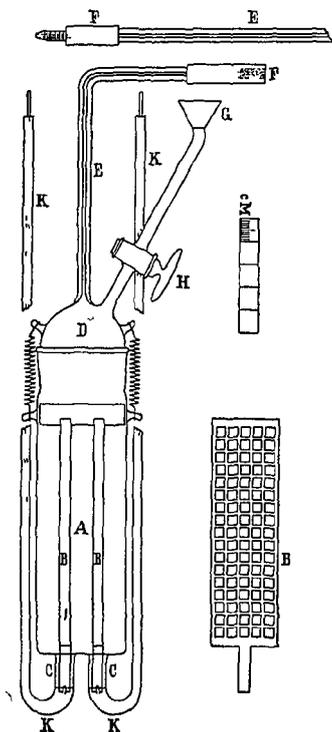
where  $E$  is the E. M. F. of the cell at the pressure  $p$  and  $dv$  the change of volume mentioned.

This change can be calculated if the spec. volume of the systems which are present before and after the passage of the quantity of electricity  $d\varepsilon$  are known, but it can also be determined experimentally.

While Dr. TIMOFEJEV followed the first plan, we have employed the second. A full description of our experiments will be published

before long in the *Zeitschrift für physikalische Chemie*.

Two plates of pure lead (3 cm. broad, 10 cm. long and 5 mm. thick) were perforated as shown in the diagram *B*. These were placed in a glass-dilatometer (of approximately 150 cc. content) and fixed with compound-glass in the holes *CC*. The upper ends of the plates were fastened in a piece of ebonite in order to avoid any contact. The glass cover *D* was held in its place by means of two spiral springs. The apparatus was filled with diluted sulphuric acid through the funnel *GH*. The fluid was pressed into the horizontal part of a capillary tube *EF* by means of an india-rubber bulb. The stopcock *H* was then closed. The capillary tube was placed on a milli-



<sup>1)</sup> ERNST COHEN and L. R. SINNIGE, *Zeitschr. für physik. Chem.* **67**, 1 (1909).

meterscale. *F* is a connexion-tube made of gold or platinum. It is necessary to use one of these metals in order to avoid an evolution of gas, as the metal is in contact with the acid. Even the minutest trace of gas will spoil the measurements.

After having repeatedly charged and discharged the plates (this was continuously done for 4 weeks) it was necessary to evacuate the apparatus several times after having filled it with the acid. Only in this way we were able to secure that the accumulator remains free of gas during its discharge by a weak current.

After these manipulations the apparatus was ready for use.

As the whole forms a very sensitive thermometer the temperature at the beginning and the end of the experiment must be absolutely the same. It was therefore placed in a thermostat which was heated electrically and whose temperature was kept very carefully at 15°.00 within 0° 005.

The procedure was now as follows. The accumulator was inserted in a circuit which contained a rheostat, a milliammeter and two silver-coulometers. After the temperature and the position of the meniscus in the capillary tube had been noted, the current was turned on and the apparatus was kept at work for 20 hours. During this time the meniscus slowly moved forward, indicating an increase of volume. After turning off the current the coulometers were carefully washed, dried and weighed. In this way the quantity of electricity which had passed the cell was known.

In order to determine the increase of volume which accompanied the reaction, the volume of that portion of the capillary tube through which the meniscus had moved, was ascertained by filling it with mercury and weighing the metal. In this way the following data were obtained:

#### Experiment I.

Displacement of the meniscus 40.6 mm. = 14.92 mm<sup>3</sup>.

Silver deposit in grams:

Coulometer 1.	Coulometer 2.
0,4304	0,4304

Increase of volume per gramaequivalent ( $Ag = 107.93$ )

3.74 cc.

#### Experiment II.

Displacement of the meniscus 35.3 mm. = 12.98 mm<sup>3</sup>.

Silver deposit in grams.

Coulometer 1.	Coulometer 2.
0,4098	0,4095

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Increase of volume per gramaequivalent:

3.42 cc.

Experiment III.

Displacement of the meniscus 39.6 mm = 14.53 mm<sup>3</sup>.

Silver deposit in grams.

Coulometer 1.                      - Coulometer 2.

0.4073

0.4079

Increase of volume per gramaequivalent:

3.84 cc.

As the experiments were executed with equal care, we take the mean of our results viz. **3.67** cc.

Dr. TIMOFEEJEW found in the way indicated **3.54** cc.

The agreement is satisfactory when we consider that PbO<sub>2</sub>, the density of which has so great an influence on the result, cannot be obtained in a pure state as we shall show in our paper in the "Zeitschrift für physikalische Chemie."

We wish to thank Mr. W. D. HELDERMAN, who very kindly helped us in one of our experiments.

*Utrecht, VAN 'T HOFF-Laboratory, June 1913.*

**Physiology.** — "*Influence of alcohol upon the respiratory exchange during rest and during muscular exercise*". By Dr. C. J. C. v. HOOGENHUYZE and J. NIEUWENHUYSE (Communicated by Prof. C. EIJKMAN).

In an earlier publication <sup>1)</sup> we have demonstrated the influence of the temperature of the surroundings upon the respiratory exchange during muscular exercise, our evidence showing that the latter occurs more economically at a high than at a low temperature.

We have now set ourselves the problem how far under these various circumstances the use of alcohol acts upon the respiratory exchange.

For this the first essential was to find out whether the use of alcohol affects the metabolism during rest.

Experiments on this subject have been published by GEPPERT <sup>2)</sup>

<sup>1)</sup> C. J. C. VAN HOOGENHUYZE and J. NIEUWENHUYSE: Influence of the seasons on respiratory exchange during rest and during muscular exercise. Proceedings Oct. 26, 1912.

<sup>2)</sup> GEPPERT Einwirkung des Alkohols auf den Gaswechsel des Menschen. Archiv. f. Exper Path und Ther. Bd XXII p. 367, 1887.

and by N. ZUNTZ and BERDEZ<sup>1)</sup> indicating that a moderate dose of alcohol (30—75 cc) did not or hardly at all change the consumption of oxygen and that accordingly the carbon-dioxide elimination had diminished, because with like oxygen consumption alcohol produces a smaller amount of carbon dioxide than other food stuffs.

In our researches we experimented on ourselves. We are neither of us teetotalers, nor do we indulge in alcohol regularly.

In our rest-experiments we proceeded as follows: At 9 o'clock in the morning the subject reclined in an easy chair. A determination with the ZUNTZ—GEPPERT apparatus was made of the oxygen-intake and the carbon-dioxide output. The subject then took at one time 60 cc of 96% alcohol diluted with 90 cc of water. After resting quietly for 10 minutes he breathed through the valves for another 10 minutes; samples of air were then collected for analysis in the burets. This required about 6 minutes, so that in the first alcohol-experiment it took place 20—26 minutes after the alcohol was taken. An hour afterwards another test was made; likewise a third at 3 o'clock in the afternoon.

In either case the subject breathed through the valves for 10 minutes before the air for analysis was collected.

In order to compare the results arrived at, alcohol and non-alcohol experiments followed each other alternately, both categories being carried out in precisely the same way, alcohol being exchanged for an equal amount of water.

We subjoin the averages of experiments on J. N. during five alcohol days:

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient.
a. Before taking alcohol (9 o'clock a. m.)	215.1 {max. 227.9 min. 201.2}	248.2 {max. 255.4 min. 236.6}	0.867 {max. 0.892 min. 0.826}
b. 20 min. after taking alcohol.	196.8 {max. 201.4 min. 190.0}	251.5 {max. 260.4 min. 244.6}	0.782 {max. 0.809 min. 0.765}
c. 1 hour after b.	187.9 {max. 200.7 min. 177.0}	251.5 {max. 258.8 min. 236.8}	0.747 {max. 0.781 min. 0.687}
d. 3 o'clock p. m.	214.3 {max. 232.7 min. 197.6}	250.2 {max. 267.5 min. 234.0}	0.858 {max. 0.933 min. 0.791}

The means of 4 non-alcohol-days being the following:

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient.
b' 9½ o'clock a. m.	225.6 {max. 235.7 min. 214.9}	251.7 {max. 258.4 min. 248.4}	0.896 {max. 0.943 min. 0.851}
c' 1 hour after b'	211.1 {max. 218.2 min. 198.7}	252.3 {max. 264.2 min. 239.4}	0.839 {max. 0.898 min. 0.752}
d' 3 o'clock p. m.	224.7 {max. 239.3 min. 208.1}	247.2 {max. 250.7 min. 242.2}	0.909 {max. 0.988 min. 0.831}

<sup>1)</sup> R. ZUNTZ und BERDEZ. Fortschritte der Medicin 1887. Heft 1. Beitrag zur Kenntnis der Einwirkung des Weingeistes auf den Respirationsprocess des Menschen.

With v. H. the averages of 5 alcohol-days were the following:

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient.
a. Before taking alcohol (9 o'clock a. m.)	266.0 {max. 284.2 min. 253.2}	293.2 {max. 303.8 min. 283.9}	0.908 {max. 0.987 min. 0.862}
b. 20 min. after taking alcohol.	210.5 {max. 235.8 min. 170.5}	292.0 {max. 306.2 min. 279.9}	0.720 {max. 0.780 min. 0.606}
c. 1 hour after b	212.4 {max. 234.7 min. 196.3}	286.1 {max. 295.4 min. 280.1}	0.742 {max. 0.795 min. 0.690}
d. 3 o'clock p. m.	259.0 {max. 291.6 min. 225.2}	330.5 {max. 347.3 min. 310.2}	0.782 {max. 0.873 min. 0.726}

His averages on 4 non-alcohol-days were:

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient.
b' 9 1/2 a. m.	264.2 {max. 304.8 min. 238.5}	290.9 {max. 309.7 min. 283.7}	0.906 {max. 0.985 min. 0.859}
c' 1 hour after b'	222.4 {max. 250.0 min. 205.3}	283.4 {max. 308.0 min. 270.8}	0.785 {max. 0.811 min. 0.758}
d' 3 o'clock p. m.	260.4 {max. 291.6 min. 237.0}	303.1 {max. 318.4 min. 293.4}	0.843 {max. 0.916 min. 0.785}

The O<sub>2</sub>-absorption and the CO<sub>2</sub>-elimination are here expressed in cc. per min., reduced to 0° C. and a barometric pressure of 760 mm.

We see then that both on days with and without alcohol the amount of carbon dioxide given off lowers in the morning, still more so in the alcohol experiments whereas with N. the amount of oxygen remains constant all day, with v. H. this is the case only in the morning. In the afternoon his oxygen value is higher on alcohol-days than on the non-alcohol-days.

It is therefore permissible to conclude that in agreement with ATWATER and BENEDICT's<sup>1)</sup> researches the alcohol is not only oxidized (fall of the respiratory quotient CO<sub>2</sub>/O<sub>2</sub>) but also protects other material from consumption in isodynamic quantity, anyhow for some hours after the taking in of alcohol, since the amount of oxygen consumed remains constant. With v. H. however the oxygen values are invariably a little higher in the afternoon on alcohol-days than in the control experiments. It is extremely difficult to account for this. If from the low respiratory quotient we should infer that the alcohol has not been entirely oxidized (with N. also the respiratory quotient was in the afternoon somewhat lower than the one before the taking in of the alcohol and that on the non-alcohol days) we might assume that after the lunch (which in v. H.'s case was more substantial than the breakfast, though each in itself was about the same every day) the metabolism is increased even more through the influence of the alcohol than under the influence of the meal alone. This tallies with our experience that in non-alcohol experiments also v. H.'s oxygen values were higher in the afternoon than in the morning.

<sup>1)</sup> ATWATER and BENEDICT. 'Memoirs of the National Academy of Sciences 1902.

In N.'s case there was no such variation. His meals were about the same.

After taking the alcohol in the morning the only effect experienced by either subject consisted in their being rather more cheerful than usual; in the afternoon, however, they felt somewhat languid and drowsy.

We now passed on to our inquiry into the effect of alcohol during muscular work.

ATWATER and BENEDICT, who administer 72 gr. of alcohol a day to their subject in 6 portions at different intervals, come to the conclusion that the utilization of the energy of the whole ration was slightly less economical with the alcohol than with the ordinary diet, especially when the subjects were at hard muscular work, but the difference in favour of the ordinary food was very small indeed, hardly enough to be of practical consequence. From this it follows that the energy of the alcohol was utilized very nearly or quite as well as that of the other fuel ingredients which it replaced.

CHAUVEAU<sup>1)</sup>, who gave a dog 48 gr. (= 60 cc) of alcohol, so that the animal got drowsy and consequently did less work, found a decrease in the body-weight when compared with that of a control-experiment, in which an isodynamic amount of sugar substituted the alcohol. Though this evidence has been frequently quoted we cannot appreciate its weight, as also other factors may be responsible for the decrease, e. g. the loss of water through the diuretic action or the alcohol. Besides CHAUVEAU detects a considerable fall in the CO<sub>2</sub>-elimination and the O<sub>2</sub>-absorption (15,3 %) during the exercise under the influence of alcohol. We do not understand why he ignores this altogether and only draws his conclusions from the variation of the respiratory quotient. These conclusions are open to objection but no attempt will here be made to refute them, considering that the dose of alcohol administered to the dog was so disproportional to his body-weight (about 20 K.G.) that no practical results could be obtained.

DURIG<sup>2)</sup> who made the same walking-tour in the mountains with and without alcohol and compared the results, did not begin his respiration tests before the quantity of alcohol (30—40 cc of 96 %) had presumably been oxidized (i. e. about two hours after taking it) or when only the last small portions of it were undergoing the process. He comes to the conclusion that, though the alcohol is oxidized during the exercise and although part of its energy benefits the body

<sup>1)</sup> CHAUVEAU, Comptes rendus de l'Ac. d. Sc. Paris, 1901, Tme 132.

<sup>2)</sup> DURIG. Beitrage zur Physiologie des Menschen im Hochgebirge III. Pfluger's Archiv 1906 Bd 113 p. 341.

and is utilized in the exercise, the capacity for performing a definite sort of work is reduced under the influence of alcohol and a rise in the metabolism takes place. Whereas after taking alcohol the walk took up 20 proc. more time only about 7 proc. of energy was gained per time-unit, as calculated from the oxygen intake.

In our work experiments we used the bicycle with adjustable and registrable resistance described in detail in our previous paper<sup>1)</sup>. They were executed as follows: at 9 o'clock a. m. a determination was made, the subject sitting quietly on the bicycle; subsequently while breathing freely, he began to pedal for twenty minutes, the brakeband being tightened in order to fatigue him before the experiment proper. The work done in this way amounted to 570 K.G.M. per minute. Then, on the so-called alcohol-days, 60 cc of 96 % alcohol diluted to 150 cc was taken at one time and immediately after the pedalling was begun, while the subject was breathing freely for 15 minutes and thereafter for five minutes through the valves. Now the resistance was such that the amount of work was the same as in our earlier experiments, viz. 380 K.G.M. per minute. After this the exhaled air was collected for the analysis while the subject went on pedalling.

One hour later the subject resumed the exercise, breathing freely for 15 minutes and through the valves for five minutes, the quantity of labour performed being 380 K. G. M. per minute. Subsequently the air was again collected for the analysis while the pedalling was continued. The same process was gone through at 3 p. m.

To control our results we carried out precisely the same experiments on other days without alcohol. The same person was subjected to an alcohol test only every four or five days, so that getting used to the influence of alcohol was out of the question.

Our individual experience was that, especially close upon the taking of the alcohol the work was done with greater ease and pleasure; but already the second time, i. e. about 1½ hour later the pleasure subsided, while in the afternoon the work was even a little more trying than before.

Alternately four sets of experiments with alcohol were performed and four without. The temperature at which the following tests were made varied from 8° to 15° centigrade.

The determination before the pedalling was made with a view to noting any possible anomaly in the subject's respiration. The gas-exchange proved to be rather constant and the fluctuations comparatively slight.

<sup>1)</sup> G. J. G. v. HOOGENHUYZE and J. NIEUWENHUYSE l. c.

J. N.: with alcohol:			
	CO <sub>2</sub>	O <sub>2</sub>	resp. quotient
a. during rest (before alcohol)	201.8 {max. 209.6 min. 186.9}	245.2 {max. 252.7 min. 230.4}	0.824 {max. 0.880 min. 0.756}
b. 20 min after alcohol (pedalling)	634.4 {max. 657.0 min. 614.1}	721.1 {max. 740.6 min. 696.0}	0.879 {max. 0.897 min. 0.844}
c. 1 hr. after b (pedalling)	659.6 {max. 697.6 min. 603.7}	780.9 {max. 830.8 min. 785.4}	0.835 {max. 0.850 min. 0.840}
d. 3 o'clock p. m. (pedalling)	723.5 {max. 775.7 min. 669.5}	813.1 {max. 824.9 min. 790.4}	0.890 {max. 0.940 min. 0.827}
without alcohol:			
	CO <sub>2</sub>	O <sub>2</sub>	resp. quotient
a' during rest	205.1 {max. 215.2 min. 187.7}	254.5 {max. 258.1 min. 248.3}	0.805 {max. 0.833 min. 0.756}
b' 20 min. after drinking water (pedalling)	706.1 {max. 739.6 min. 685.0}	803.1 {max. 836.6 min. 780.3}	0.879 {max. 0.884 min. 0.876}
c' 1 hr. after b' (pedalling)	702.1 {max. 723.6 min. 664.9}	805.9 {max. 869.6 min. 778.6}	0.873 {max. 0.910 min. 0.825}
d' 3 o'clock p. m. (pedalling)	710.0 {max. 725.1 min. 694.9}	801.6 {max. 817.4 min. 785.9}	0.886 {max. 0.923 min. 0.850}
v. H. with alcohol:			
	CO <sub>2</sub>	O <sub>2</sub>	resp. quotient
a. during rest (before alcohol)	255.2 {max. 264.0 min. 245.2}	301.4 {max. 326.0 min. 290.0}	0.847 {max. 0.870 min. 0.810}
b. 20 min. after alcohol (pedalling)	631.7 {max. 696.6 min. 599.8}	787.6 {max. 805.0 min. 773.1}	0.813 {max. 0.865 min. 0.763}
c. 1 hr. after b (pedalling)	721.9 {max. 789.3 min. 664.0}	923.0 {max. 941.7 min. 904.6}	0.783 {max. 0.840 min. 0.705}
d. 3 o'clock p. m. (pedalling)	804.6 {max. 844.5 min. 751.3}	944.1 {max. 1001.0 min. 901.0}	0.852 {max. 0.879 min. 0.834}
without alcohol:			
	CO <sub>2</sub>	O <sub>2</sub>	resp. quotient
a' during rest	243.5 {max. 257.5 min. 228.7}	297.2 {max. 303.5 min. 285.6}	0.821 {max. 0.891 min. 0.754}
b' 20 min. after drinking water (pedalling)	710.0 {max. 801.3 min. 642.7}	837.7 {max. 885.9 min. 811.9}	0.845 {max. 0.904 min. 0.792}
c' 1 hr. after b' (pedalling)	698.9 {max. 744.0 min. 676.2}	856.1 {max. 908.1 min. 818.6}	0.817 {max. 0.858 min. 0.767}
d' 3 o'clock p. m. (pedalling)	749.7 {max. 767.9 min. 735.2}	894.3 {max. 914.8 min. 880.2}	0.839 {max. 0.865 min. 0.816}

It appears from these data that the instantaneous effect of alcohol is that both the carbon dioxide values and the oxygen values are lower than those on non-alcohol days. The rise of the O<sub>2</sub>-consumption entailed by the muscular exercise in the case of N. is at the beginning of the period about 13.6% less on alcohol days than on non-alcohol days, although the physical exertion is the same, one hour later the difference is still 2.8%. With v. H. this difference is 10% at the beginning. One hour later the average oxygen consumption is higher than in the control-experiments (O<sub>2</sub> 11.2%).

In the afternoon also both numbers are in the case of v. H. higher on the alcohol days than on the other (O<sub>2</sub> 7.6%). Similarly with N., but his variations are very small, indeed.

Whereas with N. there is a lack of uniformity in the respiratory quotient, a gradual decrease is to be noted on v. H.'s alcohol days; in the afternoon however the original value returns.

Since the experimental evidence here reported goes to show that alcohol exalts the economy of muscular activity, at least at the outset, and since, as stated heretofore, it appeared from our previously published experiments that a high temperature renders muscular work less economical, we have endeavoured to ascertain whether this unfavourable influence could perhaps be arrested or lessened by alcohol, in other words we have tried to solve the question as to whether alcohol has any action on respiratory exchange during muscular exercise and at a high temperature.

These experiments were in every respect conducted as described above. Particular attention was given to keeping the room-temperature well above the limit found by us heretofore (21.5°) and also to keeping the relative humidity approximately constant and corresponding to that of the lower temperatures of from 50°—60°.

The following averages were found:

N. at a mean temperature of 28° C.

*with alcohol:*

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient
a. during rest (before alcohol)	200.6 {max. 219.1 min. 190.2}	261.3 {max. 267.4 min. 252.0}	0.767 {max. 0.819 min. 0.719}
b. 20 min. after alcohol (pedalling)	723.0 {max. 761.0 min. 664.6}	881.5 {max. 910.1 min. 830.2}	0.820 {max. 0.849 min. 0.786}
c. 1 hr. after b	" 781.5 {max. 830.5 min. 705.0}	920.2 {max. 979.0 min. 847.0}	0.849 {max. 0.872 min. 0.832}
d. 3 o'clock p. m.	" 900.4 {max. 923.2 min. 868.2}	992.3 {max. 1040.0 min. 955.4}	0.908 {max. 0.925 min. 0.874}

*without alcohol:*

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient
a' during rest	202.9 {max. 216.4 min. 184.5}	266.6 {max. 281.8 min. 256.3}	0.762 {max. 0.818 min. 0.720}
b' 20 min. after drinking water (pedalling)	868.0 {max. 890.0 min. 847.2}	941.7 {max. 972.1 min. 890.6}	0.923 {max. 0.981 min. 0.886}
c' 1 hr. after b'	" 845.5 {max. 869.6 min. 810.6}	966.0 {max. 1002.0 min. 932.1}	0.876 {max. 0.882 min. 0.868}
d' 3 o'clock p. m.	" 923.5 {max. 951.5 min. 887.6}	1022.5 {max. 1117.0 min. 984.2}	0.905 {max. 0.934 min. 0.854}

v. H. at a mean temperature of 28° C.,

*with alcohol:*

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient
a. during rest (before alcohol)	264.3 {max. 273.0 min. 256.4}	315.2 {max. 336.7 min. 304.4}	0.839 {max. 0.874 min. 0.811}
b. 20 min. after alcohol (pedalling)	800.5 {max. 907.8 min. 719.9}	995.9 {max. 1075.0 min. 903.8}	0.803 {max. 0.868 min. 0.763}
c. 1 hr. after b	" 842.8 {max. 943.6 min. 739.2}	1056.9 {max. 1168.0 min. 973.8}	0.799 {max. 0.892 min. 0.741}
d. 3 o'clock p. m.	" 965.9 {max. 1081.0 min. 829.6}	1102.9 {max. 1241.0 min. 998.6}	0.876 {max. 0.927 min. 0.830}

*without alcohol:*

	CO <sub>2</sub>	O <sub>2</sub>	Respiratory Quotient
a' during rest	251.6 {max. 286.1 min. 236.7}	308.2 {max. 319.5 min. 294.7}	0.816 {max. 0.905 min. 0.760}
b' 20 min. after water (pedalling)	878.3 {max. 957.4 min. 745.8}	1048.9 {max. 1134.0 min. 924.7}	0.837 {max. 0.881 min. 0.804}
c' 1 hr. after b'	884.8 {max. 987.0 min. 794.7}	1060.6 {max. 1110.0 min. 972.5}	0.833 {max. 0.889 min. 0.786}
d' 3 o'clock p. m.	948.3 {max. 1052.4 min. 885.3}	1094.9 {max. 1174.0 min. 999.9}	0.868 {max. 0.938 min. 0.806}

These figures go to show again that at this high temperature alcohol had a similar though less marked influence than at low temperatures, since, half an hour after taking the alcohol, with either subject the values of the carbon dioxide output and of the oxygen intake are smaller than in the control-experiments (with N. a difference of 8% O<sub>2</sub>, with v. H., 8.1%); after 1½ hour, however, v. H. shows no difference and N. a smaller one (5.8%); in the afternoon again we observe rather the reverse, though the differences are insignificant.

In comparing the data reported in this paper they will be found to lend support to our previous experience, viz. that muscular work is done less economically at a higher than at a lower temperature. Furthermore we shall see that in both cases alcohol, shortly after being taken in, has a restraining influence upon the respiratory exchange, in other words the muscular work is performed more economically. However, this influence gradually weakens (with one subject sooner than with another) and ultimately even alters more or less to the opposite. The fact that with the one subject. (N.) the favourable influence lasted longer than with the other (v. H.) may be attributed to an equal dose of alcohol (60 c.c. of 96%) being taken in by either, while their bodyweights differ considerably. N. weighs without clothing 70½ K.G., v. H. 87½ K.G.

Our results do not bear out DURIG's experience in every respect. Probably this is mainly due to the circumstance that he started his experiments when in all likelihood the alcohol had been entirely oxidized, in consequence of which the favourable action at the beginning of the period, as detected by us, escaped his notice. Neither did we find that the action at the end of the period was as unfavourable as was implied by DURIG's results.

In our opinion the weak point in DURIG's experiments is that the work performed in the time unit had not, as in our experiments, been carefully and equally apportioned, but had virtually been left to chance. In consequence of this the alcohol tests always lasted much longer than the non-alcohol tests. Therefore his tables of results with

and without alcohol can hardly be compared the one with the other.

To ATWATER and BENEDICT'S experiments it must be objected (as DURIG has also pointed out) that their determinations covered lengthy periods at the close of which a favourable influence may have been neutralized by a subsequent unfavourable action, so that the totals do not vary much and are not typical of the real process.

*Our conclusion is that directly or indirectly alcohol not only produces energy for muscular exercise, but also that after the taking in of alcohol the latter occurs more economically at the outset, even under the unfavourable condition of a high temperature of the surroundings. This favourable influence of the alcohol gradually decreases and ultimately alters to the opposite in one of the subjects.*

Utrecht.

Institute of Hygiene.

**Physiology.** — *“On fibrin in sol and gel state. Likewise a contribution to our knowledge of the blood-coagulation problem.”* By E. HEKMA. (Communicated by Prof. HAMBURGER).

(Communicated in the meeting of April 25, 1913).

The coagulation of blood is based, as we know, upon the transition of a coagulable albuminous substance, found in circulating blood and called fibrinogen, into a solid substance, fibrin.

Fibrin forms threads, fibrils, these fibrils may form a network which can enclose the blood-corpuscles. Hence, when the blood, which flows from a wound coagulates, a plug is formed which can close the wound, whilst if for instance the blood, spouting from an opened blood-vessel, is left to itself in a glass, the fibrin-network with the enclosed blood-corpuscles forms the so-called blood-clot. If, however, the blood, flowing from a blood-vessel is not left to itself, but beaten up, then the fibrinogen is turned into fibrin in the form of a compact, white mass of fibrils. This fibrin, however, should not be looked upon as pure fibrin, that is to say as the coagulated substratum of fibrinogen. For besides the latter substance, which forms its main component part, blood-platelets and likewise red blood-corpuscles and leucocytes or rests of them, not to mention other substances, pass into the fibrin.

The study of the problem relating to the nature of blood-coagulation, in other words the formation of fibrin is mainly occupied with two questions. First with the question: what relation exists between fibrinogen and fibrin, and secondly: what agents cause fibrinogen to pass into fibrin.

Until now next to nothing was known of the former question, whilst the latter has given rise to a great many investigations which have resulted in more or less divergent theories, without a definite solution of the problem being arrived at. The latter circumstance is naturally connected with the former; as long as the nature of the relation between fibrinogen and fibrin, the base so to speak of the problem relating to blood-coagulation, was unknown, a solution of this problem could hardly be expected.

As I believe that my investigations bearing on this subject have brought to light the nature of the relation between fibrinogen and fibrin, I beg leave to give the following short account of the researches which have led to this result.

Beforehand it should be observed that originally it was by no means my intention to occupy myself with researches in this direction. It was rather some observations, made in the course of experiments, undertaken for another purpose, which suggested to me a series of investigations relating to fibrin, with a view to the problem of blood-coagulation. I had observed, for instance, that an addition of an acid, to a solution of fibrin in strongly diluted NaOH caused a precipitate, which, after being left to itself for some time, was found to have passed into a fibrous coagulum. This observation, which naturally struck me very much, was first made with phosphoric acid and afterwards also with other acids<sup>1)</sup>.

When subsequently it was investigated more closely under what experimental conditions coagulation in fibrin-NaOH solution took place when an acid was added, it appeared:

1. that by adding drops of HCl of a rather high concentration, to a fibrin-NaOH-solution, an acid coagulum in an alkaline medium could be obtained, which coagulum disappeared again when it was shaken and could be produced again by the addition of more HCl, as long as the fluid gave a distinctly alkaline reaction.

2. That by an addition of so much HCl, either gradually or at once, that the solution was about neutral a permanent coagulum could be obtained.

3. That likewise a permanent coagulum was obtained by an addition of so much HCl that the medium became strongly acid.

4. That an addition of so much HCl that a feebly but distinctly

<sup>1)</sup> The fibrin-NaOH-solution had been obtained by exposing ordinary fibrin to a strongly diluted NaOH-solution (e.g. 0.3%). The fibrin swells in it strongly, the swollen mass gradually passes into a liquid state and finally forms a thin liquid solution. Such a solution, after being filtered, was used for the experiments.

acid reaction of the medium set in, caused a coagulum, formed in a neutral medium, to disappear again.

5. That the coagulum, mentioned sub 1—4, consisted of a spongy mass of fibres.

From these experiments it might be concluded that a solution of ordinary fibrin in strongly diluted NaOH, contained a substance that could be obtained as a flake-like precipitate by an addition of HCl, which precipitate was found to agglutinate in fibres *a.* at an alkaline, *b.* at a neutral, *c.* at a rather strongly acid reaction of the medium; these fibres, in their turn, formed a net- or spongework, a real coagulum, which coagulum could be dissolved in strongly diluted NaOH and in strongly diluted acid.

Further it appeared that this coagulum, formed at a neutral reaction, not only dissolved again in a dil. NaOH-sol., but also that in this solution a new coagulum could be obtained by neutralizing this solution, and also by acidifying it rather strongly. And conversely, if the coagulum was dissolved in strongly diluted acid, a coagulum could be obtained from this solution by neutralizing it with NaOH.

It followed that we had to deal with a coagulating substance, derived from fibrin, which could be made to pass from a sol-state into a gel-state and back again.

Now the question suggested itself what remarkable substance this might be.

Must it be assumed that the fibrin, when dissolved in NaOH, had been decomposed, forming meanwhile a coagulable substance hitherto unknown, a substance derived from fibrin itself or from one of its accompanying substances such as: blood-platelets, red and white bloodcorpuscles?

Or might it be that the fibrin when dissolved in NaOH, had *not* been decomposed, but had passed into a colloid solution, that therefore we might have to do here with fibrin in a sol-state, with an alkali-hydro-sol of fibrin, from which state it might be brought again into a gel-state by an action of acid, with or without the help of a fibrin-ferment?

It will be readily understood that I hesitated in making the latter supposition. First because it was diametrically opposed to the generally received opinion that fibrin must be looked upon as an irreversible gel. And secondly it seemed strange that fibrin coagulation should take place in a strongly acid as well as in a neutral and alkaline medium.

Yet the new problems which had presented themselves so unexpectedly, were fully deserving of attention. Not only from a general, biological or a colloid-chemical point of view, but also because it was clear that the solution of these questions might open new views on the important problem of the nature of blood-coagulation, and perhaps also on that of thrombus-formation.

These questions were therefore submitted to a further investigation.

In this investigation it had to be determined in the first place which part of the fibrin produced the coagulating substance, either the fibrin proper, as I began to suspect, or the attendant substances.

Therefore *pure fibrin* free from blood-corpuscles was experimented on. This pure fibrin was obtained from bloodplasma which was kept fluid by receiving the blood in an equal volume Na-fluoride-solution of 1—2 %, or in a citrate-NaCl-solution.

The blood taken from cow or horse, and kept fluid in this manner, was centrifugated until the fluid at the top had become clear, when the red and white blood-corpuscles and the blood-platelets were obtained as a sediment.

This clear fluid, which contained "fibrinogen", the parent substance of fibrin, was removed with a pipette and left to itself. After some time, (from a few to 48 hours) a spontaneous coagulum had been formed.

The coagulum thus obtained, was filtered off and the filtrate was again left to itself. After a shorter or longer period a new coagulum was found in the filtrate. This process of partial coagulation was repeated 3 or 4 times, the coagulum obtained from the last filtrate being used for the experiments. This somewhat lengthy method was followed in order to have the greatest possible certainty that all blood-corpuscles, including the blood-platelets, had been removed, so that the fibrin was obtained in as pure a state as possible.

The somewhat coloured coagulum thus obtained, grew white when washed with water, and consisted of a mass of elastic fibres.

It soon appeared that this pure fibrin dissolved readily in strongly diluted NaOH, Na<sub>2</sub>CO<sub>3</sub> and in strongly diluted acids, which solution was preceded by a short stage when the fibres were visibly swollen. The swollen fibres were absolutely transparent, as clear as glass, not turbidly transparent as I had observed in the case of ordinary fibrin.

I shall first describe some experiments, made with solutions of this pure fibrin in diluted acids, for instance in 0,1 % orthophosphoric acid.

These and the following experiments were always carried out at room-temperature.

If to this fibrin-orthophosphoric acid-solution-strongly diluted NaOH was added, so that the fluid became about neutral, a very thin haze was formed, which after some time was found to consist of very fine threads which were dissolved again by the addition of some more NaOH. If, however, the latter solution was neutralized again by diluted acid, the coagulum of fibres appeared again; we evidently had to do here with a reversible process. The fibres were also formed if to the fibrin-orthophosphoric-acid-solution di- or trisodiumphosphate were added, both, alkaline solutions as we know.

If now the coagulum caused by  $\text{Na}_2\text{HPO}_4$  or by  $\text{Na}_3\text{PO}_4$  in a fibrin  $\text{H}_3\text{PO}_4$  solution was thoroughly washed in water and exposed again to strongly diluted  $\text{H}_3\text{PO}_4$ , the coagulum was dissolved again, whilst an addition of  $\text{Na}_2\text{HPO}_4$  or  $\text{Na}_3\text{PO}_4$  again effected a coagulum.

Secondly some results may be mentioned, obtained in experiments with solutions of pure fibrin in strongly diluted NaOH.

Neutralization with diluted  $\text{H}_3\text{PO}_4$  first caused a hazy precipitate which turned into fibres. With various other acids the same results were obtained. An addition of somewhat too much acid, so that the fluid became distinctly acid caused the coagulum to pass into solution again; it could, however, be produced again by neutralizing this solution.

If to a solution of pure fibrin in 0.1 % NaOH drops of  $\text{NaH}_2\text{PO}_4$ , which as we know gives an acid reaction, were added, a precipitate was formed which, often after a few minutes already, passed into a network of fibrils.

Here too it could be observed that whilst at first the fibrous substance was distributed over the whole fluid, after some time the coagulum settled upon one of the sides of the test-tube, whence we may conclude that the coagulum must possess the power of retraction.

If this coagulum, after being washed with water, was exposed to a 0.1 % NaOH-solution it was dissolved again, while the addition of an acid or of an acid phosphate of Na brought out again a very fine coagulum of fibres, often after only a few minutes.

Acid *phosphate of Ca* was found to effect coagulation in fibrin NaOH-solutions under the same circumstances as acid phosphate of Na. To a certain extent there was a difference, however, as the coagulum, obtained by acid phosphate of Ca, even after being washed thoroughly, did not dissolve so easily in dil. NaOH as the coagulum caused by acid Na-phosphate.

It seemed interesting to find out if a weak acid such as  $\text{CO}_2$  would act in a similar way on fibrin-NaOH-solutions, as the other acids and acid salts, mentioned above. And it appeared indeed that

an addition of an equal volume of water, containing  $\text{CO}_2$ , to a fibrin-NaOH-solution, brought about turbidity and a subsequent coagulum of fibres. As a rule I saw already after some minutes that flakes were formed round the beads of  $\text{CO}_2$ , which had adhered to the side of the test-tube. These flakes formed the starting-point for further thread-formations. The beads of  $\text{CO}_2$ , being weak acid-centres with a great surface, became the starting-point of the coagulation, a mechanical factor playing undoubtedly a certain part since on the precipitate or coagulum, formed at the surface of a  $\text{CO}_2$ -bead, other precipitated colloid particles could settle.

Besides with fibrin-solutions in diluted NaOH, experiments were also carried out with solutions of pure fibrin in strongly diluted  $\text{Na}_2\text{CO}_3$ -solutions. Fibrin was found to dissolve very well in diluted  $\text{Na}_2\text{CO}_3$ -solutions, whilst on the other hand it was insoluble, or almost so, in solutions of  $\text{NaHCO}_3$ .

The results, obtained with solutions of fibrin in diluted  $\text{Na}_2\text{CO}_3$ , were entirely analogous to those obtained with fibrin-NaOH-solutions, as appears from the following example, which may also serve to prove that a  $\text{CaCO}_3$ -solution could effect coagulation in fibrin- $\text{Na}_2\text{CO}_3$ -solutions, which was indeed also the case, though it was not mentioned before, in fibrin-NaOH-solutions.

Pure fibrin was put in a 0.2 %  $\text{Na}_2\text{CO}_3$  solution in which it dissolved rather easily.

To 10 cc. of this fluid were added:

1. 10 cc water containing  $\text{CO}_2$ .
2. 10 cc water containing  $\text{CO}_2$  + 1 cc of a 0.4%  $\text{CaCl}_2$ -solution.
3. 10 cc of a 0.4%  $\text{CaCl}_2$  solution.

The result was as follows:

	Fluid.	Reagent.	Result.
1	Pure fibrin in 0.2 % $\text{Na}_2\text{CO}_3$ -sbl. 10 cc.	10 cc. of water containing $\text{CO}_2$	Coagula in flakes and fibrils which include beads of $\text{CO}_2$
2	the same 10 cc.	10 cc. of water containing $\text{CO}_2$ + 1 cc. of $\text{CaCl}_2$ sol. 0.4%	the same
3	the same 10 cc.	0.4 % $\text{CaCl}_2$ sol. 10 cc.	Seemingly jellylike coagulum; the test-tube could be turned upside down. When shaken the coagulum divides into fluid and a mass of fibrils.

The coagula obtained in 1, 2, and 3 were then put into a 0.1 %

NaOH-solution in which 1 dissolved quickly, 2 slowly, and 3 very slowly. It seemed as if  $\text{CaCl}_2$ , or Ca changed the coagulating substance in such a manner that it was difficult to dissolve it in strongly diluted NaOH. With regard to  $\text{CaCl}_2$  it appeared, therefore, that a fibrin-NaOH-solution (and also a fibrin- $\text{Na}_2\text{CO}_3$ -solution) had the same properties as are known of fibrinogen-solutions.

From the foregoing experiments it follows therefore:

That, like impure fibrin, also pure fibrin, free from blood-corpuscles, could be dissolved by strongly diluted NaOH or  $\text{Na}_2\text{CO}_3$ , and by diluted acids. That the fibrin-solutions in alkali contained a substance which, under the action of acids (also of  $\text{CO}_2$ ) and likewise of  $\text{CaCl}_2$  sol., could be obtained as a fibrous coagulum, whilst solutions of strongly diluted acids could be made to coagulate by diluted alkali.

Whilst, however, the impure fibrin could be dissolved by dil. alkali or acid, only after several days, the pure fibrin was discovered to pass into solution in a much shorter time, often after only a few minutes.

*Without entering into the question if it would appear afterwards whether a coagulating substance might be obtained from attendant substances of impure fibrin more particularly from its blood-corpuscles or their component parts, these experiments justified the conclusion that at any rate pure fibrin, the coagulated substratum of fibrinogen, when dissolved in diluted acid or alkali, supplied a substance which could again be made to coagulate.*

Meanwhile, I had grown more and more convinced in the course of these experiments, that I had not got to deal with a new coagulable substance, formed from fibrin when it was dissolved, but with fibrin itself in sol- and gel-state.

And as the coagulation of fibrin is generally attributed somehow to the action of a ferment (fibrin-ferment), it stands to reason that repeatedly the question suggested itself if the coagulation in the fibrin-solution, under the action of acids or alkali or  $\text{CaCl}_2$ , would have to be attributed to an action of these substances only, or if it might also be due to a ferment-action.

*It was found that the latter, not unimportant question had to be answered in the negative, at least if it may be assumed that such a ferment would be destroyed by being boiled.*

For coagulation could be effected in fibrin-alkali- and also in fibrin-acid solutions, even after they had been boiled, under exactly the same circumstances as in the case of the unboiled solutions.

The results, hitherto obtained, gave rise to the following provisional conclusions:

I. That in the solution of fibrin in strongly diluted NaOH or  $\text{Na}_2\text{CO}_3$  or in strongly diluted acid, we have not a new coagulable substance derived from fibrin, but a transition of the gel-fibrin into the sol-state.

II. That under certain experimental conditions, fibrin from its sol-state, can be made to pass again into its gel-state whilst forming an elastic coagulum, the cooperation of a ferment being found to be unnecessary.

III. That, therefore, fibrin must be looked upon as a reversible gel, the sol-state of which can be compared, or is identical, with blood-fibrinogen in solution.

If these results might indeed be looked upon as conclusive, they would evidently furnish an entirely new foundation for the solution of the problem relating to the nature of blood-coagulation.

These preliminary conclusions, however, and more especially the third would have to be confirmed by further proofs if they were to be accepted without reserve. It seemed to me that one would be justified in considering the formulated conclusions proved, and more especially III, if it could be shown :

1. That in fibrinogen-solutions, more especially in natural fibrinogen solutions, coagulation could be effected under the same conditions as it had been effected until now, either in fibrin-alkali- or in fibrin-acid-solutions.

2. That fibrin-alkali- or fibrin-acid-solutions could be made to coagulate not only by acid or alkali, but also by those factors by which "fibrinogen-solutions" generally coagulate.

3. That saturated salt-solutions, such as NaCl or NaFl-solutions, act upon fibrin-alkali- or fibrin-acid-solutions in the same way as upon plasma which has been kept fluid or upon fibrinogen-solutions.

Ad 1. To investigate the first condition centrifugated plasma, kept fluid by a NaFl or citrate NaCl-solution, was made use of, and likewise of a transudate which did not coagulate spontaneously and was almost free from blood-corpuscles, which transudate had been obtained from a patient suffering from ascites. It appeared now that these fluids did not coagulate when strongly diluted NaOH was added. On the contrary, an addition of only slight quantities of NaOH-solution retarded the spontaneous coagulation of the fluid plasma, and if somewhat more of the diluted alkali-solution were added, spontaneous coagulation did not take place at all.

The results obtained with diluted acids and acid salts were entirely different. By an addition of a trace of acid, coagulation took place

within 15 minutes as a network or rather a spongy mass of fibres, in a NaFl or citrate NaCl plasma in which no spontaneous coagulation took place within 24 hours. The same thing was found to be the case with the ascites-fluid, a transudate which did not coagulate spontaneously. This result was obtained with all sorts of acids, also with  $\text{CO}_2$ . The coagula obtained, could be dissolved again in alkalies or acids whilst in these solutions coagulation could be effected again by neutralization of the dissolving fluid.

*Plasm which was kept fluid, and likewise a transudate which did not coagulate spontaneously, were, therefore, found to present a great resemblance with fibrin-alkali-solutions and NOT with fibrin-acid-solutions.*

Ad 2. The second condition viz. that fibrin-alkali or fibrin-acid solutions must be coagulated by those factors which coagulated fibrinogen-solutions, was also satisfied. What is the characteristic of a fibrinogen-solution? That by the action of blood-serum or by organic extracts, as containing "fibrinferment", it coagulates and passes into fibrin.

Now solutions of pure fibrin in strongly diluted NaOH also had this property. If for instance to a solution of pure fibrin in NaOH 0.05 %, an equal volume of serum was added, a coagulum was formed within a few minutes in the shape of a spongy mass, whilst within 15 minutes a jellylike coagulum seemed to have been formed so that the test-tube could be held upside down, without more than a few drops of fluid running out. This seemingly jelly-like coagulum turned out to be a very dense fibrous, spongy mass, for when it was shaken well it separated into fluid and a small clump of fibrils.

A test with the ascites-fluid, which might be looked upon as a natural fibrinogen-solution, revealed that its action on serum was identical with that of the fibrin NaOH-solution; here too a jelly-like coagulum was formed, which was in fact a fibrous, spongy mass, filled with fluid. Evidently in both cases the fibrous mass which, on the coagulum being shaken, was found to have such a small volume, was yet capable of enclosing all the fluid, so that the coagulum had the appearance of being a homogeneous jelly. Similar coagula were obtained by the addition of serum, in fibrin NaOH-solutions, the fibrin of which was supplied by the blood of horses as well as cows. Nor was the action of the serum at all a specific one, for cow- as well as horse-serum effected coagulation in solutions of cow-fibrin.

Besides, this appeared already from the fact that cow's as well as horse's serum effected coagulation in a human ascites-fluid as I observed before.

Like serum, watery organic extracts, for instance a watery extract of calf's thymus-gland, were found to effect coagulation in fibrin NaOH-solutions and in ascites-fluid.

Ad 3. Thirdly fibrin-NaOH-solutions would have to act upon saturated NaCl- and NaFl-solutions in the same way as fibrinogen-solutions, such as plasm which is kept fluid or transudates.

By the addition of an equal volume of saturated NaCl-sol. to fibrin-NaOH-solution, flakes and jelly-like strings were obtained, just as when an equal volume of saturated NaCl-solution was added to plasm which was kept fluid or to ascites-fluid. A saturated NaFl-solution immediately effected coagulation as a rule, and that in all 3 fluids. The agreement in both respects between fibrin-NaOH-solutions on the one hand, and plasm which is kept fluid and ascites-fluid, on the other, was, therefore, a striking one.

The result of these series of experiments removed all doubts as to the accuracy of the foregoing provisional conclusions. *I felt absolutely certain now that fibrin can be brought from a gel-state into a sol-state and vice versa. And moreover that the sol-state, caused by the solution of fibrin in strongly diluted alkali and not the one obtained by the solution of fibrin in diluted acid, must be considered identical with "fibrinogen" as found in blood and body-fluids.*

How are we to conceive the transition of fibrin from the gel-state into the sol-state under the action of diluted alkali or acid, and also the return from the sol-state to the gel-state under the influence of this action?

The following experiments and considerations may supply an answer to this question. The ordinary impure fibrin, as formed when blood is beaten up and likewise pure fibrin, formed at spontaneous coagulation of plasm which is kept fluid, contains a certain amount of water, is swollen to a certain extent. By drying the washed-out fibrin, for instance by exposing it to the air, this water evaporates. The dried fibrin is brittle, hard and not elastic. If, however, the dried fibrin is placed in water, it swells again, whilst its elasticity returns.

Also if a dried fibril was *boiled* in water it began to swell, and became elastic as at first. This swelling caused by water is, however, a very restricted one. But if the ordinary, moist fibrin or the air-dry fibrin are exposed to water, to which alkali or acid have been added, the fibrin swells much more than by water only; undoubtedly we have to deal here with a swelling-process, introduced by water.

If in these experiments much fibrin is taken in proportion to alkali or acid-solution then it will be observed that the fluid is entirely imbibed by the fibrils. Every fibre is seen to swell strongly, has become jelly-like, and more or less transparent. (We mean here the ordinary, raw fibrin; pure fibrin gives less striking results because it is dissolved very quickly by alkali and acid, so that the swelling-stage is only very short).

The separate coarser fibrils are at first still plainly visible in the swollen mass as jelly-like strings.

If a coarse fibril, swollen by dil. alkali, e.g. NaOH 0.2%, is placed in dil. acid so that the fluid becomes about neutral, then the swollen fibril gradually resumes its original form and qualities; it becomes elastic again as before. If the fibril is not placed in diluted, but in concentrated acid, the swollen fibril resumes its shape and qualities much sooner. This is also the case if the swollen fibril is put into solution of acid phosphate of sodium or a solution of acid phosphate of calcium. Hence we have to deal here with a reversible process. But not only by acids and acid salts the fibre, swollen by alkali, may be brought again into its original state, it may also be effected by a 1% CaCl<sub>2</sub>-sol. or by a saturated sol. of NaCl or NaF, or by any other saturated salt-solution, such as MgSO<sub>4</sub> or (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>. And it also appeared that a fibril, swollen by alkali, also gradually resumes its original form and qualities, if it is placed in an excess of water, and more quickly by shaking it with much water. It is a remarkable fact that the swollen fibril retains these qualities also when *the swollen fibril is boiled first*, at least if the alkali is in a weak concentration and has not acted too long. Also after being boiled the fibril, swollen by 0.20% NaOH, returns to its original state as regards shape and qualities, when exposed to acid, salt, or an excess of water.

It follows that the process which takes place when fibrin is swollen by diluted alkali, must be of a very superficial kind, and that ordinary chemical process, or change is out of the question.

Between fibrin on the one hand and alkali on the other, only an extremely loose compound, an *adsorption-compound* can have been formed.

The logical conclusion is that all component parts of the swollen coarse fibril, first the smaller fibres, next the smallest fibres, and lastly the minutest parts of which these smallest fibres consist, have formed an adsorption-compound with the alkali, and are consequently swollen.

But it must also be inferred that the component parts and parti-

cles have not changed their places with regard to each other, as long as the coarse fibril, swollen under the influence of alkali, entirely resumes its former shape and qualities when exposed to acid, salt or water.

If the fibrin mass, swollen by alkali or acid, has absorbed all the fluid, and is left to itself, then, after some days, the swollen mass (we mean here ordinary impure fibrin) first passes into a thick and then into a thin, colloid solution. It appears to me that we must look upon this process as a continuation of the swelling-process, mentioned before. The colloid-particles retaining in the swollen fibril their coherence, their place with regard to each other, are driven apart by the continual swelling and at last pass into a colloid solution, into a sol-state.

If this view is correct, this colloid solution, this alkali-hydro-sol if I may call it thus, must have the same qualities as the swollen fibril, and we saw already that this is indeed the case.

For we saw that flakes are formed in a fibrin-NaOH-solution by neutralization, by stronger acids, and by the action of salts under the successive formation of a coagulum of fibres, of an elastic gel, which may either remain somewhat swollen, as is the case when it is treated with a saturated NaCl-solution, or a coagulum with little or no swelling, a retracting, fibrous or spongy mass may be formed as was observed under the action of acids and acid salts, of CaCl<sub>2</sub>-sol, and of a saturated NaFl-sol.

The solution of fibrin in strongly diluted alkali gives rise, as we saw, to an alkali-adsorption compound. And since bloodplasm kept fluid, and also a transudate, were acted upon in a similar manner by acids and salts, as a solution of fibrin in strongly diluted NaOH, both as regards the formation of flakes and the succeeding agglutination in the form of fibrils, in other words the coagulation, it may confidently be assumed that *fibrinogen, as found in transudates, in bloodplasm kept fluid, and hence also in blood, may be looked upon as an alkali-adsorption compound of fibrin.* In other words fibrinogen as found in blood must be looked upon as an alkali-hydrosol of fibrin, as fibrin in a colloid solution in which the fibrin-particles are found in an exceedingly fine state of division, owing to the adsorbed ions of OH.

It seems to me that hereby the nature of the relation between fibrinogen and fibrin it has been determined, but likewise that it has been shown that blood contains a source of alkali in an extremely loose compound, in the form of fibrinogen. A compound so loose that it must be judged capable of giving up at any moment its

alkali to acid substances, under the formation of fibril-flakes, and, under favourable circumstances, coagulation of the colloid fibrin. Perhaps we have to deal here with a fact, the importance of which to physiology and pathology goes far beyond the problem of blood-coagulation, I do not however, wish to enter into this question in this paper; I shall restrict myself to emphasize the possible significance of this fact, as a foundation for the solution of the problem concerning the nature of blood-coagulation.

It has been demonstrated that the transition of fibrin from the sol-state into the gel-state may be brought about by the following factors:

- a.* by acids in weak concentration, or by neutralization;
- b.* by acid salts, also at an acid reaction of the medium;
- c.* by acids in strong concentration;
- d.* by saturated salt-solutions;
- e.* by calcium-chloride solutions.

This formation of flakes in fibrinogen-solutions is only a special case of a quality, characteristic of colloids and albumens in general, at least as regards the factors mentioned sub *a*, *c*, and *d*. The colloid fibrin, however, is distinguished from other albumens, except casein, in being able to agglutinate in fibres under favourable circumstances, to form an elastic gel, a real coagulum such as is formed when blood coagulates.

Will our knowledge of the relation between fibrinogen and fibrin on the one hand, and of the factors which cause fibrin to pass from the sol-state into the gel-state, on the other, enable us to give a satisfactory explanation of the phenomenon of natural blood-coagulation?

This would indeed seem to be the case if only it could be demonstrated that in blood, substances are found or can be formed, whose action would be identical with that of one or more of the factors mentioned above.

For this purpose it might be investigated if acid salts are formed in the blood, or a hypothesis might be formed as to the importance of  $\text{CO}_2$  in this respect, after the manner of some other investigators.

All this seems superfluous, however. Keeping in view the data to be found in the literature on the problem of blood-coagulation, it stands to reason that we should think in the first place of the *nucleoproteids* and of *calcium*. The nucleoproteids, substances derived from decomposed nucleated cells, possess as we know properties of an acid, while more especially PEKELHARING and his school have established beyond doubt that these substances can effect blood-coagulation.

The nucleoprotéids might, therefore, be ranked with acids in general, both on account of their acid-qualities and on account of their coagulating qualities, if not PEKELKARING were of opinion that the nucleoproteids, together with calcium, produce a ferment, which ferment would have to be looked upon as the cause of blood-coagulation, while likewise most other investigators attribute the coagulation of blood to a fibrin-ferment.

Since, however, it has appeared from my investigations that the relation between fibrinogen and fibrin is of such an extremely simple kind, it seems strange that the transition of the former substance into the latter, which process is in fact nothing but a withdrawal of ions of OH from fibrinogen, should require a fermentation. The more so since, as we observed before, the action of the nucleoproteids might be readily explained by the acidity of these substances.

The conception that the nucleoproteids owe their coagulating properties to their acidity, would at once explain why nucleoproteids of such different origin, and also nucleohistons and nucleoalbumens all have the power of effecting coagulation, the reason being that all these substances act as acids.

Judging myself entitled on the ground of the investigation, of which a short summary has been given in the preceding pages, to the conclusion:

*That fibrinogen, as found in the blood, must be looked upon as an alkali-adsorption compound of fibrin, in other words, as fibrin which, under the influence of adsorbed ions of OH, is in a finely divided and swollen state, in a sol state; that consequently the transition of fibrinogen into fibrin, that is to say the coagulation of blood, must be based upon a withdrawal of ions of OH from fibrinogen, I think I may add the supposition that the natural blood-coagulation must be the result of the withdrawal of ions of OH from fibrinogen by nucleoproteids in consequence of their acidity.*

If this supposition is found to be correct, further investigations will have to teach if nucleoproteids act as such, or if their coagulating capacity is due to the formation of nucleinic acid or phosphoric acid; and also what part is possibly played by calcium in this process. Moreover it will have to be explained how this acid-action of the nucleoproteids can have impressed various investigators as being a ferment-action.

Groningen, April 1913.

*Physiological Laboratory.*

**Anatomy.** — “*On the visual centra in the brain of an anophthalmos.*”

By Dr. C. T. VAN VALKENBURG and Dr. L. H. J. MESTROM.  
(Communicated by Prof. C. WINKLER.)

Through the Director of the lunatic-asylum Maasoord, Dr. Vos, the Central Institute for Brain-Research came into possession of the brain of a female anophthalmos, who had died at *fullgrown age*. She was moreover an idiot.

The number of investigations of the central nervous system in cases of congenital anophthalmia is a very modest one. It is also — even with regard to the central visual system — not complete. Moreover very general conclusions were sometimes drawn from the partial investigation of one single case (BOLTON). We are consequently of opinion that the communication of the discoveries made in a new case, are not unwelcome. We give a very short account of them in this paper.

1. *Corpus quadrigeminum anticum* on both sides flatter than normally;

2. *Pulvinar thalami optici* in sagittal direction shorter than normally;

3. *Corpus geniculatum externum* almost entirely without the basal prominence;

4. *Occipital lobe*: Besides the remains of a chronical leptomeningitis (existing still more distinctly in other parts of the cerebrum) both lobi occipitales show a somewhat too feeble development. Though the cerebellum is, in sagittal direction, entirely covered, one sees the central part of the dorsal surface of the cerebellum lying more bare than normally, in consequence of the caudal distention of the two cerebral hemispheres. The latter are slightly tapering. The mediobasal parietes of the occipital lobi are likewise shorter than usual. The configuration of the sulci and gyri there falls inside the line of demarcation of the physiological variation. The sulcus calcarinus to the left bends round the rim of the occipital pole, to the right it finishes at a short distance in front of this pole T-shaped. On the convex side one finds, on both sides, remnants of a sulcus lunatus.

*Microscopical examination.* All the above-mentioned visual centra to the left were examined by Pal-preparations and sections coloured according to VAN GIESON. The right ones were coloured according to NISSL (paraffine enclosure, toluidine-blue) the calcarine-region partially. The results are as follows:

1. *Corpus quadrigeminum anticum.* On account of the absence of the visual fibres of the tractus opticus this ganglion is poorly

medullated. This poverty regards the superficial (stratum zonale, certainly not in a considerable degree, possibly not at all. This is in accordance with what CAJAL <sup>1)</sup> ascertained for embryonal preparations, and what one of us concluded from a pathological case <sup>2)</sup>, in contradiction with the current view regarding this subject. The following stratum of medulla (stratum opticum) is on the contrary less rich in fibres; these originate thus for the greater part in the nervus, resp. tractus opticus. In cellpreparations (v. GIBSON, NISSL) no distinct difference from normal sections can be ascertained.

2. *Pulvinar thalami optici*. The nucleus, as a whole, is decidedly smaller. It is however very difficult to indicate what anatomical category of fibres has disappeared. The long radiary fibres are beautifully developed, they run distinctly into the capsula interna retrolenticularis, and consequently most likely belong to the projection-system of the cerebral cortex. The cells have a healthy appearance in the central part of the nucleus and in the medial part. In the lateroventral part the cells have possibly drawn a little too closely together, and there is too rich a collection of glia-elements. We have *not* been able to *demonstrate* a loss of cells.

3. *Corpus geniculatum externum*. The section was made almost parallel to the entering tractus opticus. On account of the absence of the ventral prominence hardly any vestige of a "hilus" can be observed. Of course there is no question of a medullated tractus- resp. retina-part; in so far as this part is grey in normal preparations one can observe in this anophthalmos a considerable diminution of volume. The frontal part of the ganglion misses thus the scattered thick bundles of medullated fibres, which are seen lying as little blocks amidst the finer network of fibres, the ventral part misses the infiltrating fibres. The medullated lamellae are distinctly arranged in the usual way. They contain however a little fewer fibres than are found in the healthy ganglion. As, also in normal preparations, we cannot find in the retina- resp. tractus-part the "kleinste Elemente" of VON MANOKOW, there is no occasion to ask if they have disappeared. One sees indeed glia-cells in normal numbers, as it appears, and more closely together than with a healthy person. In the ganglion itself one finds both the nucleus principalis (Hauptkern) and the nucleus magnocellularis (ventraler Kranz grosser Elemente) resp. after

<sup>1)</sup> S. R., y CAJAL. Textura del sistema nervioso, 1904. II, I. p. 477.

<sup>2)</sup> v. VALKENBURG. Contribution à l'étude d. l. substance blanche temporo-occipitale de l'homme, Psych. e. Neurol. Bladen. 1911.

the nomenclature of MALONE<sup>1)</sup> and MONAKOW<sup>2)</sup>. The cells of the former are perhaps somewhat smaller than normal, those of the latter are of the usual size. Neither of the two kinds of cells have a pathological appearance. They are lying only clearly too closely together. The result of this compression is a diminution of the whole ganglion to about  $\frac{2}{3}$  or less than its usual size. The medullated fibres lying dorsally and laterally from the C. g.e. (triangular area of Wernicke and lateral medulla) have an entirely normal appearance, they are only reduced in accordance with the diminution of the ganglion.

4. *Occipital lobe.* This lobe was cut — to the left — from the transversal surface through the confluence of sulcus calcarinus and sulcus parieto-occipitalis backward. The sagittal strata round the posterior shell of the ventricle are extant, of normal colour, too narrow and elongated; there is a tolerable expansion of the ventricle. The latter reveals itself also in so far that the cerebral ventricle is fissure-shaped continued in a medial direction, ventral from the inferior lip of the sulcus calcarinus. The calcar avis is well-developed. At about the middle of the sulc. calcarinus — behind the place of confluence with the sulc. parieto-occipitalis — there appears to exist a transition-convolution (cuneolingual fold) the cortex of which has not the typical characteristic of the calcarina-limitation: the strip of VICQ D'AZYR. As to this strip, which has given a name to the designated part of the cortex (area striata) it extends on all sections over a part, distally over the entire limitation of the calcarina and reaches exactly the occipital pole. The annexed figures show, in normal size, its extension. The interruption through the cuneolingual transition-convolution mentioned above lies between figures 2 and 3. One sees moreover from the reproductions, that the sulcus calcarinus, especially in its distal part, has very little depth. In connection herewith the length of VICQ D'AZYR's strip is on each section considerably smaller than normally.

This added to the abbreviation of the lob. occipitales proves thus a considerable diminution of its extensity:

We found the fibre percentage of the cortex, both round the sulcus calcarinus and the rest of the occipital part, normal.

The cells of the cortex do not show any deviation in the area striata, neither individually nor in their arrangement to strata.

<sup>1)</sup> MALONE: Ueber die Kerne des menschlichen Diencephalon. Abhdl. d. k. preuss. Akad. d. Wiss. Physik.-Math. Klasse, 1910.

<sup>2)</sup> v. MONAKOW: Gehirnpathologie.

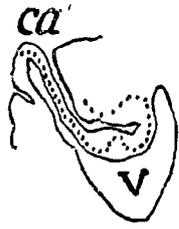


Fig. 1. Immediately behind the meeting of Sulcus calcarinus and sulc. parieto-occipitalis.



Fig. 2. 6 mm. behind fig. 1.



Fig. 3. 1 1/3 cm behind fig. 2.



Fig. 4. 6 1/2 mm. behind fig. 3.

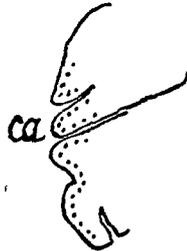


Fig. 5. 3 mm. behind fig. 4.



Fig. 6. 4 mm. behind fig. 5; occipital pole.

V = Ventricle (posterior shell).  
Ca = Sulcus calcarinus.

We remarked however that in the immediate neighbourhood of the area striata (area 17 BRODMANN) the cortical area (18 BRODMANN) shows a less beautiful development in its large supragranular pyramids than one sees normally. Also in comparison with corresponding sections through this region of an idiot that was not blind, this difference continues to exist.

If we summarise our discoveries, it appears that the primary-optical centra show the deviations that are typical for the consequences of the early enucleation of the two eye-globes on both sides. Moreover that part of these nuclei that is connected with the cerebral cortex, though it may be ever so reduced, has not changed its nature. Entirely in keeping with what might be expected on these grounds, the nucleocortical connection — on account of the minuteness of the composing fibre-elements — though it has diminished, in volume, is very distinctly extant. It is exactly the same with the regio calcarina, if not exclusively (according to our view) yet very predominantly (WINKLER)<sup>1)</sup> the boundary, of the geniculo-cortical

<sup>1)</sup> WINKLER: Over gelocaliseerde atrofie i. h. corp. geniculatum. Versl. K. Ak. v. Wetensch. 1912, bldz. 714.

fibres. In extensity it is reduced in every direction, but the construction is entirely normal.

This discovery is directly opposite to that of BOLTON<sup>1)</sup>, who states for special strata a considerable diminution and moreover admits for anophthalmia a shortening of the area striata in a sagittal direction to half its length. In his one case (p. 203) the area striata did not extend farther than half way the sulc. calcarinus, in so far as it limits the cuneus ventrally. As one sees from the reproductions of our anophthalmos by no means answers this condition; the photographs of the Nissl-preparations prove for the cell-percentage likewise what we communicated above. The latter, besides being contrary to BOLTON's statements, is likewise at variance with LEONOWA's<sup>2)</sup> discoveries in this respect. This author, who disposed of more cases examined however only very young children aged at the utmost 2 months. In our opinion greater conclusive value should be ascribed to our case.

We cannot decidedly ascertain the signification that must be attached to the comparatively less beautiful and complete development of the large supra-granular cells in area 18. It is well-known that English investigators (CAMPBELL, MOTT, BOLTON) are accustomed to distinguish this cortical area specially as the visuo-psychic area. Though — in our opinion on good grounds — one may only hesitatingly apply such a localising nomenclature to special parts of the cortex, it cannot but be admitted that field 18 is very nearly concerned with the optical impressions which, at any rate, are received in its immediate vicinity — field 17 —.

In this train of thought it would be explicable, that elements which under normal conditions take part in retaining or modifying etc. optical, eventually modified stimuli but cannot perform the principal part of their activity on account of the existence of anophthalmia, show the vestiges of it in their construction. The fact that exactly *these* seem to suffer most under the perpetual optical inactivity of the organism should then be attributed either to their great vulnerability (connected perhaps with their tardy embryogenetic maturity) or to the fact that, exactly by their size, histological modifications are sooner visible. It is at all events a fact that, as we mentioned above, we could not discover any pathological properties in the cells of area 17 itself.

<sup>1)</sup> BOLTON: The exact histological localisation of the visual area of the human cerebral cortex. Philos. Transact. R. S. of London, Series B. vol. 193, p.p. 165—222.

<sup>2)</sup> LEONOWA: Beitr. z. Kenntniss der secund. Veränder. der prim. opt. Centren u. Bahnen u. s. w. Arch. f. Psych. Bd. 23, S. 53, 1896.

**Chemistry.** — “*The passivity of metals in the light of the theory of allotropy.*” By Prof. A. SMITS (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of January 25, 1913).

It struck me already some time ago that the above-mentioned phenomenon, which has not been satisfactorily accounted for as yet, might be explained in a plausible way in the light of the theory of allotropy. We need namely only assume that, as the said theory requires, the metals are built up as a rule of different kinds of molecules, which in general have a different reactive power, so that one kind of molecules will act more readily than another. In this case the internal equilibrium in the surface of the metal will be disturbed by chemical action, and it will now depend on the rapidity with which the internal equilibrium will be restored whether or no anything particular occurs.

Let us take iron as an example, whose curve of heating of the solid substance betrays the presence of different kinds of molecules<sup>1)</sup>, and let us immerse this in strong nitric acid. We then notice the following fact:

One kind of molecules is quickly dissolved, the other is not.

If it is now assumed that the oxygen split off by the nitric acid, which is possibly partially dissolved in the iron, acts as a negative catalyst for the setting in of the internal equilibrium, only the non-dissoluble kind of molecule will be left in the surface layer of the iron. If the iron plate is now taken out of the nitric acid, and rinsed with water, it appears that the iron no longer yields all kinds of known iron reactions. The strong metastable state in the surface can now however be suddenly disturbed by a blow, by the application of a magnetic field, by contact with positive catalysts, and in other ways; the inactive molecules are then again changed into the active ones, and the ordinary iron reactions have been restored. This may be demonstrated in all kinds of interesting ways. The periodic abrupt variations of the potential in the case of electrolysis of acids with iron as anode<sup>2)</sup>, may be explained in a similar way. This will, I hope, be soon-discussed in a following communication.

There are views among the earlier hypotheses, which show some relationship with the explanation given here, but on account of the

<sup>1)</sup> Cf. BENEDICKS “On allotropy in general and that of iron in particular. Journal of the Iron and Steel Institute” N<sup>o</sup>. 11, 1912 p. 242.

<sup>2)</sup> Adler. Z. f. phys. Chem. 80, 385 (1912).

exceeding vagueness of the conceptions of the nature of the solid state, and the absence of a general point of view, they have not been able to assume such a form as to lead to a satisfactory explanation.<sup>1)</sup>

*Anorg. Chem. Laboratory of the University.*

*Amsterdam, January 1913.*

**Chemistry.** — "*The nitration of toluols and its derivatives chlorated in the side-chain*". By Prof. A. F. HOLLEMAN.

(This communication will not be published in these Proceedings).

<sup>1)</sup> It may be expected that in the near future it will appear possible also in many other cases to demonstrate by the use of solvents or chemical reagents the complexity also of those substances which have been considered up to now as behaving exclusively as unary substances.

(September 3, 1913).

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

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**Physiology.** — *“On reinforcement of sound and soundselection by means of microtelephone-apparatus”*. By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of May 31, 1913).

Of the innumerable sonorous vibrations with which the air and the soil are pervaded, only those whose period is comprised between 10 and nearly 22000 per second, are lying within the limit of our audition. Exactly midway between them lies the “a d’orchestre”. The pitch of musicians remains middle tone, even when age has deprived us of a half octave at the extremities. This is no longer so in pathological cases, when large pieces of various lengths are generally cut off on the bass- and on the discant-side.

Among the benefits man derives from his audible scale none excels that of hearing speech-sounds. Compared with this the services our hearing renders for our safety, for technical purposes, for enjoying the pleasures of art etc. are relatively slight. Now there is no part of the scale of such moment to the most important of all functions of our sense of hearing as a small portion just beyond the “a d’orchestre”, stretching from  $b_1$  to  $g_2$  (BEZOLD). Extending it a little further, we get the zone to which local telephones are tuned, viz.  $a_1$  to  $e_3$ . This portion of the human scale must be in good condition, in order to secure a proper function of our sense of hearing speech-sounds.

By confining myself to the speechzone  $a_1$  to  $a_3$ , I have been able to simplify considerably the researches that have occupied me for a couple of years and either concerned the sound of speech in buildings or the use of hearing-apparatus. For this narrow field full knowledge is required of every single tone.

Regardless of resonance an objective measurement of sound can be performed alike for all pitches and impulses after Lord RAYLEIGH’S mode of arrangement. Devised in 1882 it had been worked out theoretically by W. KÖNIG in 1891 and put into practice by ZERNOW in 1907.

This method consists in placing a very small mirror (circular, 3 m.m. in diameter) obliquely to the plane of soundwaves. It is hung by a fine quartz fibre and is kept stationary by a small magnet attached to the back of it. As soon as the sound flows past the mirror in progressive waves or in often repeated pulses, the disc takes up a position parallel to the wave-front, just like a straw on the surface of a river. This occurs with a force proportional to the energy of the sound and *ceteris paribus* expressed in the torsion of the fibre and in the magnetic force.

The formulae show, that in order to attain a high degree of sensitiveness the size and the weight of the mirror should be as small as possible. I also found, that we can do without the magnet if we replace the quartz fibre by a flattened Wollaston-wire<sup>1)</sup>. The sensitiveness can moreover be considerably increased by conducting the sound to the mirror through a short tube whose width and length are in the ratio of at least 2 : 5. The mirror is placed just in front of the aperture of the tube. The diameter of the mirror should not be much longer than the width of the aperture, so as to cause the sound-wave to bend completely round the disc. The position of the mirror is effected entirely by the pulses falling upon it on both sides, not by the sound pressure, which is too feeble for it.

The instrument discussed just now, enables us to arrange the mirror so as to prevent resonance. Only the afferent tube may possibly resonate. Its length is 6 c.m. and its width is a finger's breadth. On this account I chose a mirror of 5 mm., slightly to the detriment of the sensitiveness. Considered as an open organ pipe the peculiar tone of the tube lies somewhere near  $e_4$ , and is beyond the speechzone.

Aided by such an instrument it is quite easy to determine the reinforcement of sound and the sound selection of micro-telephone-apparatus.

First of all we intend to examine technical apparatus such as the common telephone or that used by people hard of hearing. Here element, microphone and telephone are in circuit with each other (induction apparatus being inserted only for long-distance telephony). The conducting tube replaces the ear. As close as possible, free from all foreign sound disturbances, the telephone is placed before the tube that transmits the sound to the mirror, which is placed obliquely in the plane of the soundwave. No sooner does the telephone sound than the mirror shows deviation, and a beam of light directed onto it, is caught up on the scale placed at some distance. The amplitude indicates the torsion of the fibre, i. e. the force that was counteracted by the energy of the sound, while the tone continued.

The following illustrations represent the amplitudes generated by a row of almost uniform stopped pipes, half tone for half tone, with the aid of telephone and microphone fed by two volts.

---

<sup>1)</sup> HERAEUS sent us on application such a wire of 8  $\mu$  thickness. The attendant STELLEMA procures still more suitable wires by flattening round Wollaston wires with a hammer.

It will be seen that the discant of the speech zone is more intensified than the bass.

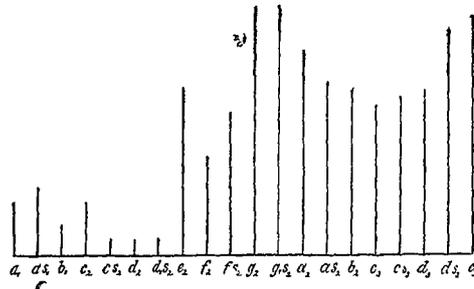


Fig. 1. Relative intensity of sound of a technical micro-telephone apparatus noted tone for tone (max. amplitude called 100).

The sound conveyed to the mirror by the telephone is more intense than that caught up by the microphone. So the circuit appears to intensify the sound. An increment of the available acoustic energy results from a decrement of the energy afforded by the accumulator. By elaborate experimentation this reinforcement

can be determined directly. It may also be promptly done in a rough and ready way, if a second measuring mirror apparatus is put in operation.

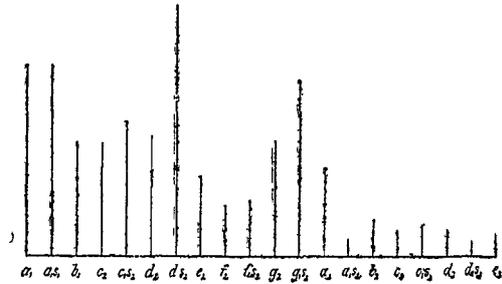
This additional apparatus is provided with the trumpet of a dictating phonograph. It is so sensitive that, even though the scale be placed at  $\frac{1}{3}$  m. only and though a diaphragm of a phonograph has been inserted, a unit of the scale represents one millerg of acoustic energy per second. Such an instrument is competent to register the amplitudes of whispers even, let alone those of spoken words.

In a series of experiments carried out with Dr. REUTER I invariably used 16 monosyllabic words of the sort called isozonal and aequi-intense, because their component speechsounds fulfil certain requirements. We are now in a position to utter these words twice, once with and once without a micro-telephone. The difference in the amplitudes can then be noted. In both cases the intensity of our voice can be registered on the scale, which is furnished with a trumpet and is placed by the side of it. It appears then, that the words spoken with a micro-telephone produce on an average amplitudes exceeding 20 to 30 times those produced without insertion of the electric circuit, which exalts the acoustic energy.

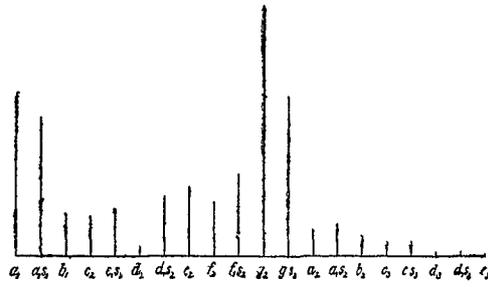
The reinforcement recorded here, occurs with either apparatus of the technique. It is remarkable that, as regards tone-selection, the latter are so constructed as to reinforce the discant of the speechzone more than the bass. It seemed to me, that a greater variety should be aimed at in this respect. I, therefore, combined the microphones and the telephones that were at my hand, in order to obtain this

variety in toneselection. My experience has been represented graphically lower down.

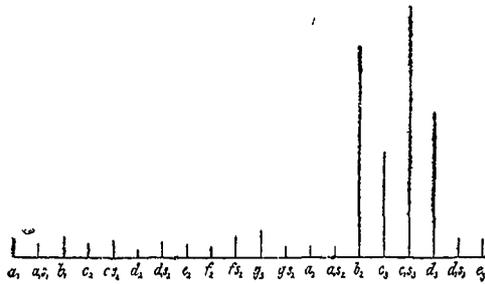
It appeared to me, that for this selection the telephone proved to be of greater use than the microphone. This prevalence is determined



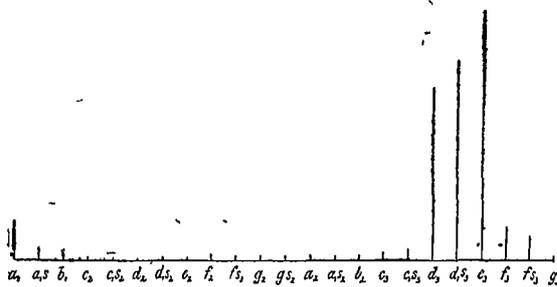
Large telephone-plate.



Middle-sized telephone-plate, thickness 0.11 m.m.



Telephoneplate of 0.16 m.m. thickness



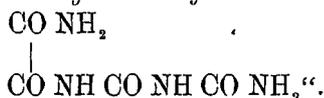
Thickness of plate 0,24 m.m.

Four special combinations of microphone and telephone of different tone-selection. (Max. amplitude for each apparatus called 100).

by the size and the thickness of the membrane, which is quite a natural thing, considering that the membrane vibrates all over ("en masse") with the greatest excursion in the centre. The technique damps it to a certain extent in various degrees of efficiency (damping caused by air and by induction). In circuit with this telephone is the microphone varying considerably as to the number and the size of the carbon granules. Without exception I used for the microphones coal-membranes tuning with the telephone diaphragm selected beforehand, and I regulated the damping by selecting granules of a particular size. This can easily be managed, so that harmony for a broad zone may readily be effected, which is requisite for a proper reinforcement and audibility to be guaranteed by the circuit.

The graphic representations show, that much can be attained in the indicated way even with the present means. If the technique could be improved so as to enable us to apply the principles here brought forward, I doubt not but telephony in private houses, in churches and in assembly-rooms would be made subservient to a much greater number of pathological organs of hearing than the attainable means allow, seeing that hitherto only reinforcement was the object of experimenters and that a reinforcement not always in a zone of sufficient breadth. A new field of research opens up when the zones of reinforcement are extended to different portions of the speechzone  $a_1$  to  $e_3$ . Every ear will then be able to select an apparatus complementary to what it lacks.

**Chemistry.** — "*On the synthesis of amido-oxalybiuret*



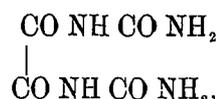
By DR. J. TH. BORNWATER. (Communicated by Prof. A. P. N. FRANCHIMONT).

(Communicated in the meeting of June 28, 1913).

In 1911, I showed that oxalyldiureid is not identical with the compound obtained by GRIMAUX (Bull. 32 (1879) p. 120) on heating parabanic acid with urea and which in the German literature is called wrongly oxalyldiureid, although GRIMAUX rightly calls it "amide d'un acide oxalybiurétique".

The substance of GRIMAUx shows biuret reaction and, after being dissolved in dilute potassium hydroxide solution evolves ammonia in the cold and yields on acidifying with acetic acid a crystalline precipitate.

In the *Berichte der Deutschen chemischen Gesellschaft* 46 p. 1404, H. BILTZ and E. TOPP discuss this oxalyldiureid



obtained by the interaction of oxalylchloride with urea and consider this identical with the "amide d'un acide oxalylbiurétique"



of GRIMAUx. I have now tried to prepare this



compound synthetically in order to be able to show that this substance is different from the true oxalyldiureid.

As has been shown previously, on boiling in dry benzene there are formed in the interaction of oxalylchloride with amides and with similar substances possessing a primary amide function, in most cases the corresponding carbonyl derivatives. On the ground of this experience it was to be expected that, if we allow in the same manner oxaminic acid ethylester and ethylurethane to react in equimolecular quantities a substance might form of the composition



which might be called *a. carbethoxyl*

*b. oxalylethoxyl urea.* This substance indeed formed to the extent of 10% of the theoretical quantity in the presence of other products and after repeated recrystallisations from dry ethyl acetate it crystallised in beautiful glittering needles melting at 152°, the analyses of which were quite in accordance with the theoretical results.

It could not be recrystallised from water as this causes a decomposition to set in with formation of oxaluric acid.

When this substance was dissolved in absolute alcohol and a current of dry gaseous ammonia passed through the solution while cooling in ice, a fine pulverulent substance was deposited which on account of its mode of formation and analysis could be considered to be the amido-oxalylbiuret and in properties agreed entirely with the "amide d'un acide oxalylbiurétique" of GRIMAUx.

This amido-oxalylbiuret also showed the so-called biuret reaction, dissolved in alkali with evolution of ammonia and then gave with acetic acid a crystalline precipitate either as stated by PONOMAREW

(Ber. d. D. ch. G. **18** p. 982) of the acid potassium salt of allantoic acid or, according to BILTZ and TOPP of the potassium salt of oxaluric acid. For want of sufficient material this could not be further elucidated.

From this it may therefore be concluded that the substance obtained by GRIMAUX and the synthetically prepared amido-oxalyl biuret may be considered as identical.

In order to obtain the so-called biuret reaction it seems to me desirable to first add the highly diluted copper sulphate solution and then a solution containing at most 15% of KOH.

BILTZ and TOPP carry out this reaction in the reverse way so that there is a possibility that the substance is already undergoing a partial decomposition before the copper sulphate is added, thus interfering with the biuret reaction. Moreover, they use a KOH solution D. 1.3 which will cause a more rapid decomposition. I have, therefore, mutually compared the reaction obtained with biuret itself, with the amido-oxalylbiuret prepared by my process and with the substance obtained by GRIMAUX and have also compared the colouring with that of the "Code des couleurs" of KLINCKSTECK and VALETTE.

On adding the different reagents rapidly the violet-red colouring 596 was always obtained in all three cases even when the KOH solution was added previous to the copper sulphate. In the latter case, however, the colouring had changed after 5 minutes; with amido-oxalylbiuret and KOH D. 1.1 to 566, with KOH D. 1.3 to 541; with GRIMAUX's substance and KOH D. 1.1 to 561, with KOH D. 1.3 to 528 D, whereas in the first case (CuSO<sub>4</sub> first, KOH afterwards) — with my own preparation as well as with that of GRIMAUX — a change took place, after 5 minutes, to 571 when using KOH D. 1.1 and to 564 with KOH D. 1.3.

In conclusion I wish to call attention to the difference in results obtained by BILTZ and TOPP in the reduction with hydrogen iodide. With oxalyldiureid they obtained hydantoine, with GRIMAUX's substance a compound of the empirical composition C<sub>4</sub>H<sub>6</sub>O<sub>3</sub>N<sub>2</sub> of which they have not been able to give a definite structure. However, it is not impossible that they were dealing here with uramil which has the same empirical composition, begins to decompose above 270° and also forms so-called salts. If we attribute to GRIMAUX's substance the formula of amido-oxalylbiuret the formation of uramil is explained quite as readily as the formation of hydantoine from oxalyldiureid.

**Chemistry.** — “*Economic lixiviation.*” By Dr. P. J. H. v. GINNEKEN.  
(Communicated by Prof. ERNST COHEN.)

(Communicated in the meeting of June 28, 1913).

An economic lixiviation requires the attainment of a sufficient degree of leaching with as little solvent as possible, with the simplest contrivances and in the shortest possible time.

Let us take a mass  $R + Sa\eta$ , consisting of a substance  $R$  insoluble in water<sup>1)</sup> and of a watery solution of the water-soluble substance  $S$ . A definite quantity of this mass has to be lixiviated with water in the most economical manner.

We assume that the solution is combined with the solid substance capillarily, by absorption, by inclusion in permeable walls or by other means, but not chemically; and also that during the lixiviation the volume of the liquid combined with the solid substances in this manner does not change.

We equal this volume of the “combined liquid” in a definite weight of the original mass to  $v$ .

By  $V$  we represent: the volume of the water (or of the solution respectively) which is added to a definite weight of the original mass in each period of the lixiviation. In the following considerations we assume that this volume also does not change during the lixiviation by absorption of the substance  $S$ . The solution obtained after each period has, therefore, also the volume  $V$ . This assumption will (like that about  $v$ ) be only roughly approximate in the case of larger concentrations; in each case, therefore, we shall have to account for the extent of the deviation and of the influence thereof on the results obtained. We put  $\frac{V}{v} = x$ .

By  $b_0$  is represented the concentration<sup>2)</sup> (expressed in grams per 100 cc.) of the substance  $S$  in the combined liquid of the original mass, by  $b_1, b_2, \dots, b_n$  the corresponding concentrations during or after the lixiviation, respectively:

By  $U = \frac{b_0}{b_n}$ : the degree of lixiviation indicating how many times the concentration in the combined liquid has been reduced owing to the lixiviation;

by  $\alpha_0$ : the concentration of the solution resulting from the whole process;

<sup>1)</sup> All this applies mutatis mutandis to an arbitrary solvent.

<sup>2)</sup> Unless stated otherwise, the concentration will in future mean gram per cc

by  $a_1, a_2, \dots, a_{n-1}$ : the concentrations of the solutions obtained in the different periods of lixiviation.

BUNSEN<sup>1)</sup> has shown that on washing a precipitate with water there is obtained, after  $n$  washings with a volume  $V$ , the degree of lixiviation:

$$U = \left(1 + \frac{W}{nv}\right)^n \dots \dots \dots (1)$$

wherein  $W = nV$  indicates the total volume of the added water.

He further shows that the amount of water required to attain a definite degree of lixiviation gets smaller and nears a value limit when the water is added each time in smaller quantities. As value limit for  $U$  we find:

$$U = e^{\frac{W}{v}} \dots \dots \dots (2)$$

If now we wish to go further and try to obtain a larger degree of lixiviation, we shall have to divide the mass itself into smaller portions and apply the counter-current principle. BUNSEN, in his calculation, assumes that on each addition of water, the combined liquid and the water added are mixed homogeneously. In practice, this is mostly not the case. We will, however, provisionally adhere to this assumption in order to deduce a few general *data*.

*Discontinuous lixiviation, according to the counter-current principle, at a very great lixiviation velocity or a very long period of lixiviation.*

Let us suppose that the process is working in the usual manner. In each period of the lixiviation, mixing takes place of definite quantities of the mass (with volumes of liquid  $v$ ) with a definite volume of solution (or water, respectively)  $V$ , after which follows filtration.

Let us place the concentrations of the quantities underneath each other in the following manner:

$$\begin{array}{cccccccc} b_0 & b_1 & b_2 & \dots & b_{n-2} & b_{n-1} & b_n \\ a_0 & a_1 & a_2 & a_3 & \dots & a_{n-1} & a_n = 0 \end{array}$$

After the lixiviation has taken place and filtration has been resorted to, the concentrations of the residual lixiviated quantities and of the appertaining filtrates may then be represented by

<sup>1)</sup> Lieb. Ann 148, 269 (1868). The quantity  $v$  has been defined by BUNSEN slightly differently to that given above.

$$\begin{matrix} b_0 & b_1 & b_2 & b_3 & \dots & b_{n-1} & b_n \\ a_0 & a_1 & a_2 & \dots & a_{n-2} & a_{n-1} & a_n = 0 \end{matrix}$$

A displacement of the symbols  $b$  each a place to the right and of the symbols  $a$  each a place to the left reestablishes the first condition.

For the first element of the series we can now write the equation

$$vb_0 + Va_1 = vb_1 + Va_0$$

or

$$b_0 + xa_1 = b_1 + xa_0 \dots \dots \dots (3)$$

If now we suppose that we are waiting first for a complete setting in of the equilibrium before filtering, it follows that  $a_0 = b_1, a_1 = b_2$  etc. so that the above equation becomes :

$$b_0 + xb_2 = (1+x)b_1$$

and further:

$$b_1 + xb_3 = (1+x)b_2$$

$$\dots \dots \dots$$

$$b_{n-2} + xb_n = (1+x)b_{n-1}$$

$$b_{n-1} = (1+x)b_n$$

From these  $n$  equations we can eliminate  $b_1, b_2 \dots b_{n-1}$  after which there remains a relation between  $b_0, b_n$  and  $x$  which may be written

$$\frac{b_0}{b_n} = U = 1 + x + x^2 + \dots + x^n = \frac{x^{n+1} - 1}{x - 1} \dots \dots (A)$$

From this expression for  $U$  can be deduced:

If  $n$  is constant,  $U$  increases indefinitely with  $x$ .

If  $x$  is constant and  $> 1$ :  $U$  increases indefinitely with  $n$ .

If  $x$  is constant and  $< 1$ :  $U$  increases with  $n$ , but is maximal  $\frac{1}{1-x}$ .

If  $U$  is kept constant,  $x$  decreases with increase of  $n$ , but is minimally equal to  $1 - \frac{1}{U}$ .

Hence, in the most favourable conditions there must be added, in order to lixiviate a mass with a volume of liquid  $v$  to a degree

of lixiviation  $U$ , a volume of water  $\geq \frac{b_0 - b_n}{b_0} v$ .

As a rule the expression found for  $U$  cannot, however, be applied to the methods of leaching used in practice.

If we mix a mass, which in some non-chemical manner holds a liquid in combination, with a more diluted solution, these solutions will not mix immediately, because as a rule the same force that causes the combination of the first liquid will oppose the immediate

mixing. As long as no perfect equilibrium has set in, two layers will continue to exist and the formation of the equilibrium will take place, the solid substance  $S$  diffusing from the more concentrated layer into the other one.

In this sense each lixiviation process is a diffusion process.

We assume that the quantity of weight of the substance  $S$ , which in a short time unit  $dt$ , diffuses from the volume  $v$  into the volume  $V$  can be represented in the following manner:

$$ds = KO(b-a) dt \dots \dots \dots (4)$$

wherein  $K$  represents the quantity of the substance  $S$  which diffuses in the time unit per unit of surface and per unit of (constant) concentration difference;  $O$  represents the surface of the dividing layer between the two volumes of liquid,  $b - a$  represents the (during the time  $dt$ , constant) difference in concentration<sup>1)</sup>.

We now distinguish the following three cases:

I. Discontinuous lixiviation according to the counter-current principle with a limited number of volumes which, in regard to the concentration are homogeneous.

II. Semi-continuous lixiviation according to the counter-current principle with a limited number of volumes which, with regard to the concentration are homogeneous.

III. Continuous lixiviation according to the counter-current principle with a very large number of layers homogeneous with regard to the concentration.

*1. Discontinuous lixiviation according to the counter-current principle.*

We have already detailed above this method of working p. 202). Only, this time the filtration is not postponed until the equilibrium has set in.

Let us consider the changes in concentration in one element during the finite period of lixiviation.

In the first element we have before the diffusion the concentrations  $b_0$  and  $a_1$ , afterwards  $b_1$  and  $a_0$ . This again gives rise to the equation:

$$b_0 + xa_1 = b_1 + xa_0 \dots \dots \dots (3)$$

We can now find another relation between the same quantities if we ascertain how the initial and final condition are converted into each other during the diffusion time  $\Delta t$ .

The amount of the substance  $S$  which in a small unit of time  $dt$  passes from the one layer into the other, may be expressed in three ways:

<sup>1)</sup> Cf. note 2 p. 201.

$$ds = KO(b-a)dt = -vdb = Vda \dots \dots (5)$$

From the two last terms of this equality follows:

$$da = -\frac{1}{v} db.$$

Integration of the two members of this equation over the time  $t=0$  up to  $t=t'$  when  $0 < t' < \Delta t$  and  $b_{t=0} = b_0$  and  $a_{t=0} = a_1$  gives the equation

$$a - a_1 = -\frac{1}{v} (b - b_0),$$

from which follows

$$b - a = \frac{v+1}{v} b - p,$$

wherein

$$p = a_1 + \frac{1}{v} b_0.$$

If in the second term of the equality (5) we substitute this value for  $b-a$ , we obtain from the second and third term, after rearrangement, the equation:

$$\frac{db}{b - \frac{v}{v+1} p} = -\frac{KO}{v} \cdot \frac{v+1}{v} dt$$

in which  $\frac{KO}{v} \cdot \frac{v+1}{v}$  is independent of the time.

Integration yields:

$$b - \frac{v}{v+1} p = e^C \times e^{-\frac{KO}{v} \cdot \frac{v+1}{v} t}.$$

If now we remember that  $b_{t=0} = b_0$ , it follows that

$$b - \frac{v}{v+1} p = \left( b_0 - \frac{v}{v+1} p \right) e^{-\frac{KO}{v} \cdot \frac{v+1}{v} t}.$$

If now we substitute for  $t, \Delta t$  and for  $b$  the corresponding value  $b_1$  and if also we again replace  $p$  by  $a_1 + \frac{1}{v} b_0$ , we obtain after rearrangement having regard to (3)

$$b_0 - a_1 = (b_1 - a_1) e^{\frac{KO}{v} \cdot \frac{v+1}{v} \Delta t} \dots \dots (6)$$

Hence, for each element of the lixiviation battery, we have two equations (3 and 6). If the battery contains  $n$  elements we may put  $\Delta t = \frac{t_n}{n}$  when  $t_n$  represents the total period of lixiviation of a quantity of the mass.

Hence, we find together the following  $2 \times n$  equations:

$$\left. \begin{array}{l} b_0 + xa_1 = b_1 + xa_0 \\ \dots \dots \dots \\ b_{n-2} + xa_{n-1} = b_{n-1} + xa_{n-2} \\ b_{n-1} = b_n + xa_{n-1} \end{array} \right\} \quad (3) \quad \left. \begin{array}{l} b_0 - a_1 = (b_1 - a_0) K' \\ \dots \dots \dots \\ b_{n-2} - a_{n-1} = (b_{n-1} - a_{n-2}) K' \\ b_{n-1} = (b_n - a_{n-1}) K' \end{array} \right\} \quad (6)$$

in which  $K' = e^{\frac{KO}{v} \cdot \frac{x+1}{x} \cdot \frac{t_n}{n}}$ .

If from this we eliminate  $a_0, a_1, a_2, \dots, a_{n-1}$  there remain  $n$  equations, which may be written in this manner

$$\left. \begin{array}{l} pb_0 - (p+q)b_1 + qb_2 = 0 \\ \dots \dots \dots \\ pb_{n-2} - (p+q)b_{n-1} + qb_n = 0 \\ -pb_{n-1} + (q+K'-1)b_n = 0 \end{array} \right\} \dots \dots \dots (7)$$

in which

$$q = K'x + 1 = e^{\frac{KO}{v} \cdot \frac{x+1}{x} \cdot \frac{t_n}{n}} + 1$$

$$p = K' + x = e^{\frac{KO}{v} \cdot \frac{x+1}{x} \cdot \frac{t_n}{n}} + x$$

Elimination of the  $n-1$  values  $b_1, \dots, b_{n-1}$  gives, after rearrangement, the relation

$$\frac{b_0}{b_n} = U = \frac{x \left(\frac{q}{p}\right)^n - 1}{x-1} \dots \dots \dots (I)$$

If we add together the equations (3) then

$$b_0 - b_n = xa_0 \dots \dots \dots (8)$$

Hence, if  $b_0$  is known and  $b_n$  obtained from (I)  $a_0$  may be calculated from (8) also.

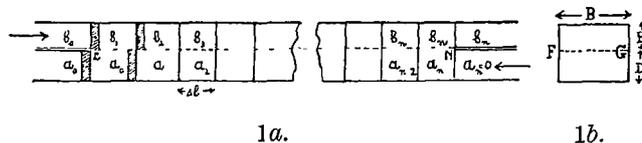
If  $KO$  (or  $t_n$ ) is very large we get  $\frac{q}{p} = x$  so that we find for  $U$  the expression that we have deduced previously for very great diffusion velocity (or a prolonged period of leaching).

The discussion of the expression found will be found below in connexion with the results of the other working processes.

A lixiviation process which is being conducted in a continuous manner may be brought in the following manner in a form, which renders possible a mathematical formulation<sup>1)</sup>.

<sup>1)</sup> See note 1 p. 209.

The space of which fig. 1a represents the longitudinal and fig. 1b the cross section is divided into two parts by a plane  $LN$  (or  $FG$ ,



respectively). In the upper space the mass to be lixiviated moves from the left to the right (we call this direction positive) in the lower space the lixiviating liquid moves in the opposite direction. The wall  $LN$  (or  $FG$ , respectively) which separates the two liquid layers corresponds in reality either with a boundary layer between two layers of liquid or with an actually existing permeable wall. The dimensions of the whole have been chosen in such a manner that the size of the surface  $LNFG$  is equal to the surface of the actual dividing layer between the two volumes of liquid, and also that the volumes of the upper and lower space are in the proportion of  $v:V$ . (Hence, the volume of the insoluble matter  $R$  present in the mass has not been taken into consideration). From this arrangement, it follows that the velocity of motion of the mass to be lixiviated and that of the lixiviating liquid are equal<sup>1)</sup>.

## II. *Semi-continuous lixiviation according to the counter-current principle.*

Let us imagine, as indicated in fig. 1a, the whole space to be divided, by planes perpendicularly to the longitudinal direction, into a finite number ( $n$ ) of equal parts whose length is  $\Delta l$ .

In each of the thus formed divisions the liquid is homogeneous in regard to the concentration. A small quantity of liquid which flows from one division into another will at once mix homogeneously with the liquid contained therein. The condition in the whole system is stationary; hence, the concentration in each division is constant and is indicated by the letters inscribed.

Let us imagine the process to be in operation. The mass is moved along with a velocity  $\frac{dl}{dt}$ , the lixiviating liquid has the velocity

$-\frac{dl}{dt}$ . Let us consider the divisions in which the concentration is  $b_1$  or  $a_0$ , respectively.

The amounts ( $ds$ ) of the substance  $S$  which, in the small period  $dt$

<sup>1)</sup> See note 1 p. 210.

time  $dt$ , passes through the dividing wall from  $[b_1]$ <sup>1)</sup> into  $[a_0]$  can be again expressed in three ways. As  $b_1$  is constant,  $ds$  must also be equal to the difference of the quantities of the substance  $S$ , which enter and leave in the time  $dt$   $[b_1]$ ; the same applies to  $[a_0]$ .

In this way we find:

$$ds = KB \Delta l (b_1 - a_0) dt = BE \frac{dl}{dt} dt (b_0 - b_1) = BD \frac{dl}{dt} dt (a_0 - a_1) \quad (9)$$

If we put  $\frac{dl}{dt} = \frac{n\Delta l}{t_n}$  in which  $t_n$  represents the total period of lixiviation of the mass and if we consider that  $\frac{D}{E} = \frac{V}{x} = x$  and that we can write  $\frac{K \cdot B \cdot \Delta l}{EB\Delta l} = \frac{KO}{v}$  it follows that

$$\frac{KO}{v} (b_1 - a_0) = (b_0 - b_1) \frac{n}{t_n} = x (a_0 - a_1) \frac{n}{t_n} \quad \dots \quad (10)$$

In the same manner may be deduced  $2(n-1)$  other equations (10), which relate to the other divisions.

In an analogous manner as in the discontinuous lixiviation we find from these equations:

$$\frac{b_0}{b_n} = U = \frac{x \left( \frac{q}{p} \right)^n - 1}{x - 1} \quad \dots \quad (II)$$

in which

$$q = \frac{KO}{v} + \frac{n}{t_n}$$

$$p = \frac{1}{x} \frac{KO}{v} + \frac{n}{t_n}$$

This expression shows, therefore, a similarity to that of the discontinuous lixiviation.  $q$  and  $p$ , however, have a quite different value.

From the equations (10) may be again deduced by addition

$$b_0 - b_n = x a_0, \quad \dots \quad (8)$$

by which  $a_0$  is expressed in  $b_0$  and  $b_n$  (or  $U$ , respectively.)

From the equations (10) may be deduced also a universal expression for the concentrations  $b$ .

This expression has the form:

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<sup>1)</sup> By  $[b_1]$  is meant the division containing the concentration  $b_1$ .

$$\frac{b_y}{b_n} = \frac{x \left(\frac{q}{p}\right)^{n-y} - 1}{x-1}$$

in which  $y$  indicates the figure that is written as index at the concentrations  $b$ . With the aid of this equation it is possible to draw a figure which indicates the progressive change of the concentrations  $b$  at the semi-continuous lixiviation.

### III. Continuous lixiviation according to the counter-current principle.

We pass from the semi continuous lixiviation to the continuous one by taking  $n$  very large and  $\Delta l$  very small.

In the same manner as in the continuous lixiviation we find here: <sup>1)</sup>

$$ds = KB \Delta l_b (b_1 - a_0) dt = BE \frac{dl}{dt_b} dt (b_0 - b_1) = -BD \frac{dl}{dt_a} dt (a_0 - a_1). \quad (12)$$

in which

$$\frac{dl}{dt_b} = -\frac{dl}{dt_a} \quad \text{and} \quad \Delta l_b = -\Delta l_a.$$

If now we replace generally  $b_1 - a_0$  by  $b - a$ , ( $b$  and  $a$  being variable quantities dependent on  $l$ ) and write:

$$b_0 - b_1 = -\frac{db}{dl} \Delta l_b$$

and

$$a_0 - a_1 = \frac{da}{dl} \Delta l_a$$

and if we substitute

$$\frac{K}{E} = \frac{KO}{v} \quad ; \quad \frac{K}{D} = \frac{KO}{V} \quad \text{and} \quad \frac{D}{E} = x$$

we get:

$$\frac{KO}{v} (b-a) = -\frac{dl}{dt_b} \cdot \frac{db}{dl} \cdot \dots \dots \dots (13)$$

$$\frac{KO}{V} (b-a) = \frac{dl}{dt_a} \cdot \frac{da}{dl} \cdot \dots \dots \dots (14)$$

$$\frac{db}{dl} dl = x \frac{da}{dl} dl$$

<sup>1)</sup> A deduction which agrees in principle with the one made here is given by VAN LOON (Tijdschrift der Algemeene Technische Vereeniging v. B. en R. 1911—1912 p. 231). In my opinion, however, the method used is not quite correct. This does not prevent, however, that in the article cited there are mentioned many very correct and original remarks on this subject.

The latter equation yields by integration of the two terms

$$a = \frac{1}{x} b + \text{const.},$$

from which follows, because when  $a = 0, b = b_n$

$$a = \frac{1}{x} (b - b_n) \dots \dots \dots (15)$$

or

$$b - a = \frac{x-1}{x} b + \frac{1}{x} b_n.$$

Substitution of this value for  $b-a$  in (13) and rearrangement gives

$$\frac{db}{b + \frac{1}{x-1} b_n} = -\frac{1}{s_b} \cdot \frac{KO}{v} \cdot \frac{x-1}{x} dl$$

in which

$$s_b = \frac{dl}{dt_b}$$

Integration yields:

$$b + \frac{1}{x-1} b_n = e^{\text{const}} \times e^{-\frac{KO}{v} \cdot \frac{x-1}{x} \cdot \frac{l}{s_b}}$$

from which follows, because when  $l = 0, b = b_0$ :

$$b + \frac{1}{x-1} b_n = \left( b_0 + \frac{1}{x-1} b_n \right) e^{-\frac{KO}{v} \cdot \frac{x-1}{x} \cdot \frac{l}{s_b}} \dots \dots (16)$$

This equation is that of the line which represents the progressive change of the concentration  $b$  as a function of  $l$ . If we want to represent  $b$  as a function of the time, we can substitute  $\frac{l}{s_b} = t$ .

By performance of this last substitution and substitution for  $b$  and  $t$  of the corresponding values  $b_n$  and  $t_n$  and some rearrangement, we now find from (16) the expression <sup>1)</sup> for  $U$ :

<sup>1)</sup> The expression found also applies to the case when the volumes of the two spaces in which move the combined liquid and the lixiviating liquid do not stand in the proportion of  $\frac{v}{V}$ . In that case  $\frac{dl}{dt_b}$  is not equal to  $-\frac{dl}{dt_a}$  and  $t_n$  not equal to

$$t_{n_b}. \text{ The deduction is made in the same manner, when } \frac{D \frac{dl}{dt_a}}{E \frac{dl}{dt_b}} = \frac{V}{v} = x.$$

We obtain for  $U$  the expression (III) but must therein replace  $t_n$  by  $t_{n_b}$ .

Hence (with equal  $x$ ) it is a matter of indifference for the leaching whether the

$$\frac{b_0}{b_n} = U = \frac{K O \frac{x-1}{v} \cdot \frac{x-1}{x} t_n - 1}{x-1} \dots \dots \dots (III)$$

in which for  $t_n$  may also be written  $\frac{l_n}{s_b}$  ( $l_n =$  total length).

It is possible to deduce this expression for  $U$  (continuous) straight-way from the expression for  $U$  (semi-continuous) and also from that for  $U$  (discontinuous) by rearranging these expressions in a suitable manner and putting  $n = \infty$ .

From (15) and (16) we find the equation <sup>1)</sup> which indicates the relation between the concentrations  $\alpha$  and the length  $l$  (or the duration  $t$ ):

$$\alpha + \frac{1}{x-1} b_n = \frac{1}{x} \left( b_0 + \frac{1}{x-1} b_n \right) e^{-\frac{K O}{v} \cdot \frac{x-1}{x} \cdot \frac{l}{s_b}} \dots \dots (17)$$

From (15) again follows:

$$\alpha_0 = \frac{1}{x} (b_0 - b_n) \dots \dots \dots (8)$$

from which  $\alpha_0$  can again be calculated if  $b_0$ ,  $U$ , and  $x$  are known.

The relations deduced above furnish a means for calculating for each method of working the results obtainable ( $U$  or  $b_n$ ; and  $\alpha_0$  if the quantities  $K$ ,  $O$ ,  $v$ ,  $V$ ,  $t_n$  ( $l_n$  and  $\frac{dl}{dt}$ , respectively) and  $n$  are known or can be determined.

$K$  and  $O$ . As the quantity  $K$  (the choice of the units being determined) accounts for all the specific properties of the mass to be leached, it will as a rule have to be determined experimentally. Up to now we have assumed silently that  $K$  has no connexion with  $O$ , but this supposition will, in many cases, not be correct. In the lixiviation of masses where the bound liquid is not found at the surface of the solid substance, but must proceed a certain distance dependent on the thickness of the solid particles,  $K$  will, as a rule, change with  $O$ <sup>2)</sup>. As, however, as a rule  $O$  will also not be capable of direct measurement, the product of the two quantities will, in such cases, have to be introduced as a single constant. Of course, the nature of the substance must be such that this quantity remains really constant during the whole process.

space at disposal for the lixiviating liquid is taken larger or smaller. In practice the opinion is often met with that such an influence is really present.

<sup>1)</sup> We may, of course, deduce this equation also from (14) and (15) in the same manner as (16) was deduced from (13) and (15).

<sup>2)</sup> Cf. VAN LOON l.c.

$v$ , for instance can be found from the amount of solid substance  $R$  contained in the mass and the sp. gr. of the bound liquid.

In most cases  $v$  will occur in the formula as a *quantity* specific and constant for the material. If, however, the lixiviation is assisted by pressing so that during, or after each filtration the "natural" volume  $v$  is reduced to  $v'$ ,  $v$  will be variable and the result of the lixiviation be dependent on the value of  $v'$ . Hence the formulae found show also the influence of the degree of pressing on the lixiviation.

I. Because, as we have assumed, this *quantity* remains constant during the process,  $V$  can be measured as the volume of water added, or as the volume of solution obtained. In how far the said assumption is correct or not and its eventual influence on the results, must be ascertained for each case.

$t_n$ ,  $l_n$  and  $\frac{dl}{dt}$  (*continuous and semi-continuous*). By varying these quantities (in which  $t_n \frac{dl}{dt}$  always  $= l_n$ ) we can ascertain the influence of changes in these quantities on the results of the lixiviation. It should be observed here that for a definite apparatus  $\frac{dl}{dt}$  is proportional to the yield.

$t_n$ ,  $n$  and  $\Delta t$  (*discontinuous*). Here  $t \frac{1}{\Delta t} = n$  and  $\frac{1}{\Delta t}$  is proportional to the yield.

$n$ . When in the discontinuous and semicontinuous lixiviation  $n$  is taken very large these two methods of working change into the continuous method, which fact can, moreover, be readily demonstrated mathematically from the formulae found.

If for a definite case we calculate  $U_D$  (discontinuous) and  $U_S$  (semicontinuous) for different values of  $n$  we can ascertain, for both methods of working, what is the influence of the value of  $n$  on  $U$ .  $U_D$  and  $U_S$  then near the value limit  $U_{n=\infty}$  or  $U_C$  (continuous). We have applied this calculation to the following values for  $KO$ ,  $t$ ,  $V$  and  $v$  and  $U_C$ , which values agree with a case met with in practice.

$$\begin{aligned} KO &= 15,6 \\ t &= 75 \quad (\text{minutes}) \\ V &= 105 \quad (\text{cc. } \% \text{ gr.}) \\ v &= 88 \quad (\text{cc. } \% \text{ gr.}) \\ U_C &= 48 \end{aligned}$$

The subjoined table gives the values found:

$n$	$U_D$	$U_S$
10	22.0	11.1
20	37.0	18.3
30	42.4	23.3
100	47.5	36.9
200	47.6	41.8
$\infty$	48	48

In fig. 2 are drawn the lines which have been constructed with these values. They run asymptotical in regard to the line  $U = 48$ .

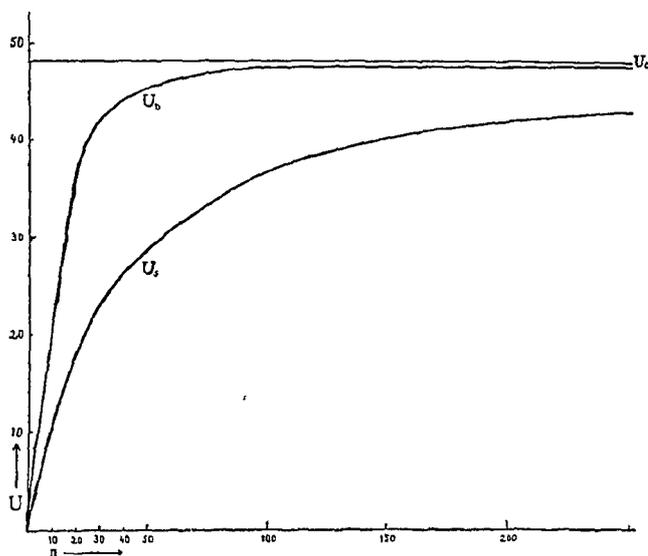


Fig. 2.

It is evident that, for a case as the one cited here,  $n$  being equal, the semi-continuous method gives much less favourable results than the discontinuous one.

Now, in some cases, however strange it may sound, it is not always easy to make out which method we are dealing with. For instance, "battery work" is by no means always discontinuous or even semi-continuous, but is often very much like the continuous method of working. When the succession of the concentration layers is not disturbed by mechanical motion or an unfavourable form of the

space (dead space)<sup>1</sup>), battery work is in many cases to be preferred to other methods of working. The fact that the apparatus which move along the mass to be leached and therefore cause apparently a perfect continuous process, often give results less favourable, is to a great extent due to the mechanical motion disturbing the succession of the concentration layers in the mass; owing to this the process becomes no longer continuous but changes into the most unfavourable semi-continuous form.

Finally, attention may be called to the following application of the matter considered. We have assumed that the liquid used for the lixiviation of the mass  $R + Sag$  consisted of pure water. If now we suppose that the lixiviating liquid was contaminated, before the leaching, with another dissolved substance  $Z$ , the question arises what influence this will exert on the products obtained.

We now readily perceive that in the lixiviation process the action of the two liquids on each other is quite mutual and that we can just as well "lixivate" the lixiviating liquid with the combined liquid as doing the reverse. If the process is conducted in a rational manner this will benefit the one (real) as well as the other (secondary) lixiviation. The bulk of the impurity  $Z$  does not then arrive in the final liquid, but in the exhausted mass. To the secondary lixiviation we can apply *mutatis mutandis* the same formula which applies to the lixiviation proper.

When carrying this out it appears that when a larger  $V$  is taken, the result of the lixiviation proper improves whilst that of the secondary lixiviation gets worse. (Of course, the values of  $K$  are not the same).

This application also has significance in practice. For it has occurred that for the leaching water was used with considerable contamination, and yet the contamination of the liquid obtained proved rather small. Such a method of working will, however, always be attended with the difficulty that a slight disturbance in the continuity of the lixiviation (which disturbance would otherwise cause merely a dilution of the final liquid) will now cause a strong contamination of the resulting liquid.

The above study was carried out with a technical object. On the practical application of the results obtained a communication will be made in a trade journal.

May 1913.

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<sup>1</sup>) VAN LOON l. c.

**Physics.** — “*Vapour pressures of substances of low critical temperature at low reduced temperatures. I. Vapour pressures of carbon dioxide between  $-160^{\circ}$  C. and  $-183^{\circ}$  C.* By H. KAMERLINGH ONNES and SOPHUS WEBER. Communication N<sup>o</sup>. 137b from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES.)

(Communicated in the meeting of June 28, 1913).

§ 1. *Introduction.* The knowledge of the vapour pressures of substances of low critical temperature at low reduced temperatures has recently obtained special importance<sup>1)</sup>. The gradual transformation shown by the reduced equations of state for various substances, when ordered according to their critical temperature, manifests itself in particular in the gradual transformation of the reduced vapour pressure curves, and the deviations from the law of corresponding states, which show themselves clearly in this transformation and are connected with NERNST's heat-theorem, have acquired increased importance by the connection with PLANCK's theory of energy-quanta.

We have therefore undertaken a series of determinations of vapour pressures for substances of low critical temperature at lower temperatures than in previous determinations. The measurement of the very low vapour pressures with which we are concerned in this case forms a separate branch of research. In measuring the pressure in a space at ordinary temperature, connected by a tube with the space, where the vapour and liquid or solid are in equilibrium at a known low temperature, correct results can only be arrived at, if due regard is paid to the theory of the thermal molecular pressure.

KNUDSEN<sup>2)</sup>, who has developed this theory, has shown that, when a temperature gradient exists along a closed tube containing a gas in equilibrium, there will in general be a pressure difference between the ends of the tube, such that the higher pressure is observed where the temperature is higher. The magnitude of the difference depends on various circumstances, specially on the ratio of the radius of the tube  $R$  to the free path of the gas molecules  $\lambda$ . In the limiting

<sup>1)</sup> For the literature and a discussion of the questions referred to here, see: H. KAMERLINGH ONNES and W. H. KEESOM: Die Zustandsgleichung. Enc. d. math. Wissensch. V. 10, Leiden Comm. Suppl N<sup>o</sup>. 23.

<sup>2)</sup> MARTIN KNUDSEN: Ann. d. Phys Bd. 31 p. 205 1910.

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cases, calling  $p_1$  and  $p_2$  the pressures,  $T_1$  and  $T_2$  the absolute temperatures at the ends, we have

$$1. \quad \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}} \quad \text{for} \quad \frac{R}{\lambda} = \frac{1}{\infty}$$

$$2. \quad p_1 = p_2 \quad \text{for} \quad \frac{R}{\lambda} = \infty$$

For intermediate cases KNUDSEN deduces more complicated formulae which may be applied over a wide range. As a rule the matter reduces itself to the application of a correction to one of the limiting cases. The application of the formulae is not allowed over the range defined by

$$1 < \frac{2R}{\lambda} < 10$$

When these limits are exceeded, the accuracy very soon falls below 1%. It is necessary, therefore, to avoid the above range in the measurements by a suitable choice of the tubes connecting the evaporating surface with the measuring apparatus, and by changing them, when occasion arises. When this is found to be impossible, the measuring apparatus will have to be kept at a temperature but little higher than that of the liquid or the thermal molecular pressure will have to be measured experimentally or a different method altogether will have to be resorted to<sup>1)</sup>.

In the range where the measurements can be corrected to the limiting cases by means of the more complicated formulae referred to it may occur, that the corrections cannot be applied for a given tube owing to the free path being unknown and that this quantity cannot be found with sufficient accuracy by extrapolation: in that case the object can be attained by means of measurements with two different tubes suitably chosen, so as to eliminate the pressure and obtain data for the calculation of the free path, which can then be introduced into the formulae.

The pressures which we wished to measure lie between 0.02 baryes and 1 mm. The highest of these might still have been measured with a MAC LEOD gauge, but for the lower ones this method is not applicable owing to the possibility of mercury distilling over at the low pressure to the cold substance. We have therefore used KNUDSEN's heated wire gauge<sup>2)</sup> between 1 mm. and 0.01 mm. and KNUDSEN's absolute manometer<sup>3)</sup> between 0.001 mm. and 0.01 mm.

<sup>1)</sup> E. g. KNUDSEN's method of molecular effusion through a small orifice, in which the amount of vapour passing through is measured instead of the pressure.

<sup>2)</sup> MARTIN KNUDSEN, Ann. d. Phys. Bd. 32, p. 809, 1910.

<sup>3)</sup> MARTIN KNUDSEN, Ann. d. Phys. Bd. 35, p. 389, 1911,

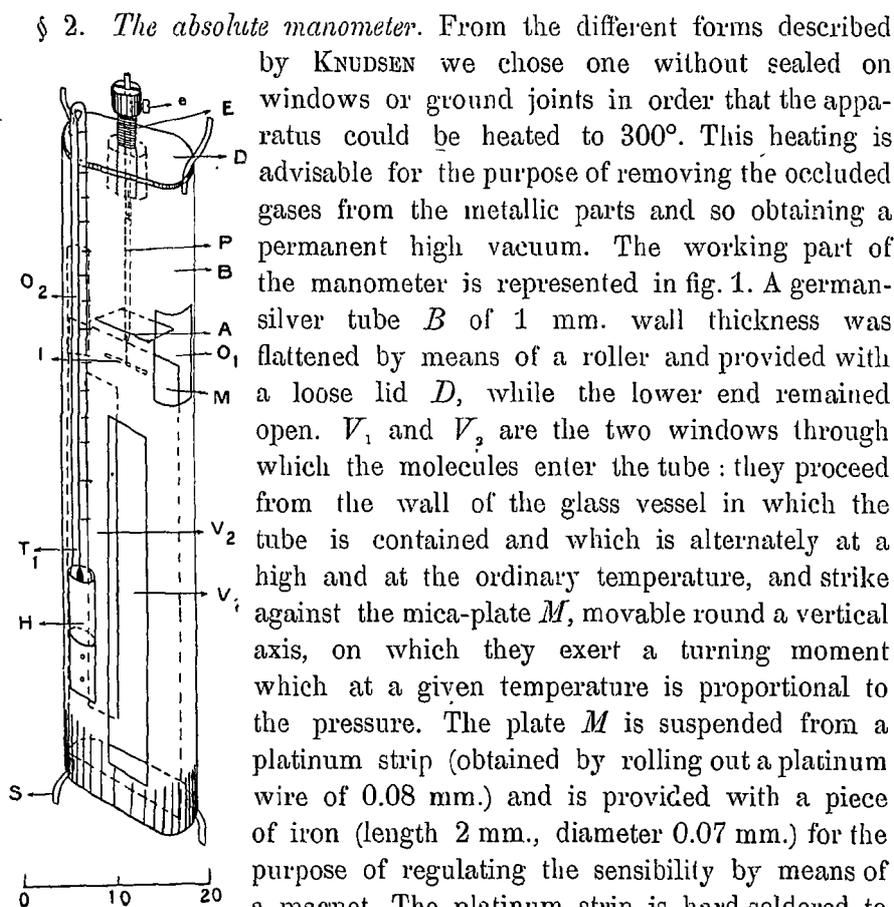


Fig. 1.

*A* is a platinum wire which prevents the mica plate falling down when the apparatus is inverted.

The two windows  $O_1$  and  $O_2$  serve for the reading of the rotation of *M*: for this purpose the outer edge of the mica plate is observed in a LEITZ reading microscope with eye-micrometer. The temperature of the german-silver tube is read on a thermometer which is in metallic connection with it and protected from radiation by means of the tube *H*.

The tube *B* is held in the glass vessel (fig. 2) by the springs *S*.

The dimensions of the various parts of the apparatus were as follows:

area of $V_1$	9.030 . 1.18 cm <sup>2</sup> .
„ „ $V_2$	9.005 . 1.20 cm <sup>2</sup> .

distance between the centres of $V_1$ and $V_2$	
(arm of couple)	1.190 cm.
length of mica plate	12.70 cm.
width " " "	3.117 cm.
moment of inertia	1.415 gr. cm <sup>2</sup> .
time of oscillation (full period)	3.53 sec.
magnification of microscope 4 um. = 87.5 scale divisions on micrometer.	

In fig. 2 is shown the manner in which the manometer was mounted.

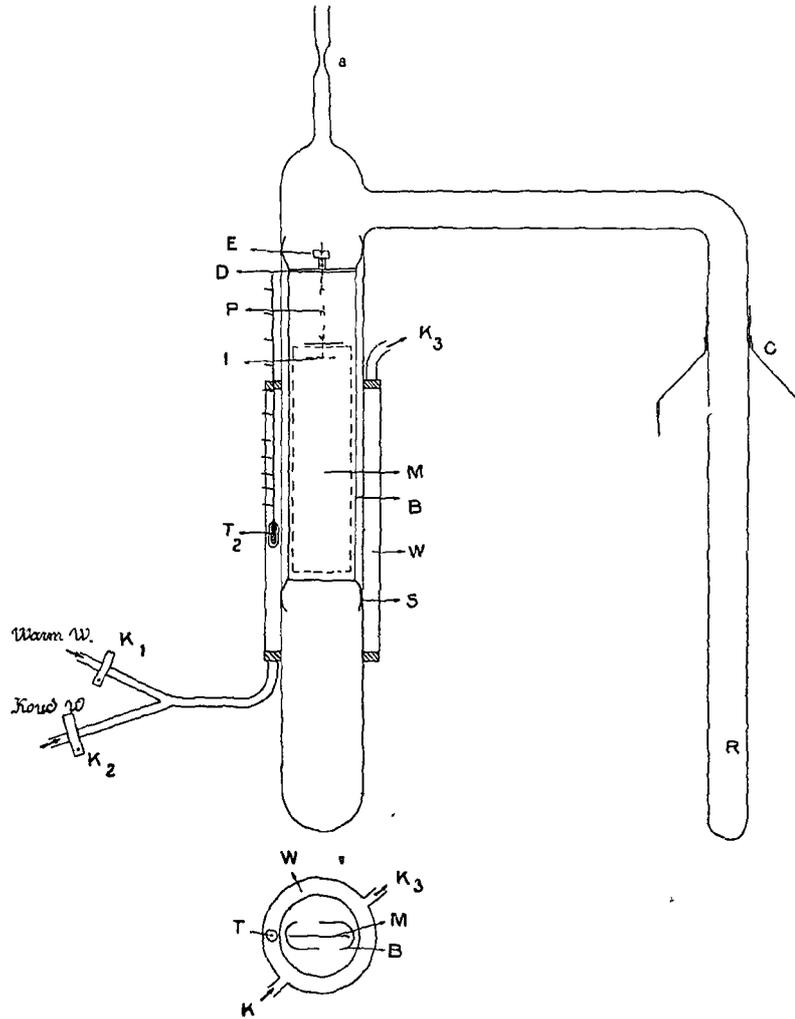


Fig. 2.

The tube  $B$  is placed inside a glass tube which is provided with a water-jacket  $W$ ; through  $W$  hot or cold water can be passed,

as required, by means of the pinching screws  $K_1$  and  $K_2$ . The temperature of the jacket is read on the thermometer  $T_2$ .

The vapour pressure tube  $R$  which is sealed to the manometer tube, bent over and closed at the bottom, is placed in a cryostat with a calibrated resistance thermometer which gives the temperature of the evaporating surface. The diameter of the tube  $R$  was 1.71 cm.

The best method of securing an even temperature in the cryostat is stirring with a "pump-stirrer", in this case however, as the smallest vibrations disturb the readings of the manometer, preference was given to the use of a stream of vapour-bubbles evolved by local heating with an electrically heated wire.

§ 3. *Calibration of the absolute manometer.* In the first place it was necessary to consider for what range of pressures the manometer may be used as an absolute instrument. In the second place seeing that the distance of the mica-plate to the windows  $V$  cannot be treated as infinitely small and the sensibility can thus only be calculated approximately, the value of a scale reading at given difference of temperature between outer wall and mica plate must be expressed in baryes.

According to KNUDSEN the force per  $\text{cm}^2$   $K$  on the plate in the limiting case, when the mutual collisions of the molecules may be disregarded, is given by

$$K = \frac{1}{2}p \left( \sqrt{\frac{T_1}{T_2}} - 1 \right),$$

where  $p$  stands for the pressure,  $T_1$  and  $T_2$  for the temperatures of plate and wall respectively.

As regards the condition under which this formula may be used, it is found that in order to reach an accuracy of  $\frac{1}{2}\%$  in the final result, the free path must be at least ten times the diameter of the tube. The range of the manometer is thus different according to the gas used. For carbon dioxide according to BREITENBACH's measurements of the viscosity at  $20^\circ$   $p\lambda = 7.4$ , if  $p$  is expressed in baryes and  $\lambda$  is the mean free path in cms. From this it follows that the range of our gauge reaches up to about 0.3 barye.

The range can also be determined by connecting the manometer with spaces, where known pressures are established, and ascertaining for what pressures the elongation remains proportional to the pressure. In any case it is necessary, with a manometer such as ours which, as we have seen, does not allow the calculation of the reduction factor from the dimensions of the apparatus, to make measurements for the determination of this factor. By extending the

calibration to pressures at which the elongation is no longer proportional to the pressure (supposing the rotation in any case to be infinitely small) the apparatus can be made into a pressure-indicator for that range, instead of an absolute manometer.

For the purpose of the calibration the manometer was connected with a system of pipettes according to KNUDSEN<sup>1)</sup>, for the description of which we refer to a subsequent paper<sup>2)</sup>. The results are contained in the following table:

T A B L E I.			
Calibration of the absolute manometer.			
Approximate pressure in baryes.	$\Delta$ abs. man.	$\Delta$ according to pipettes in baryes	$\frac{\Delta \text{ pip.}}{\Delta \text{ abs.M.}}$
0.147			
0.574	0.427	0.390	
0.931	0.357	0.385	
1.234	0.303	0.381	
1.497	0.263	0.376	
1.711	0.214	0.372	
0.056			
0.170	0.114	0.1005	0.881
0.283	0.113	0.0996	0.881
0.393	0.110	0.0984	0.895
0.500	0.107	0.0972	0.908
0.605	0.105	0.0960	0.914

The first column gives the pressures calculated according to the indications of the absolute manometer by the formula

$$\frac{1}{2} p \left( \sqrt{\frac{T_2''}{T_1''}} - \sqrt{\frac{T_2'}{T_1'}} \right) = c (\alpha_1 - \alpha_2)$$

<sup>1)</sup> MARTIN KNUDSEN, l. c.

<sup>2)</sup> S. WEBER. Vapour-pressures etc, II. The vapour-pressures of carbon dioxide between  $-140^\circ \text{C.}$  and  $-160^\circ \text{C.}$  Comm. N<sup>o</sup>. 137c. The same pipettes have also been used for the calibration of a hot-wire manometer for the purpose of thermometric measurements, which will be discussed in future communications about experiments with liquid helium.

where,  $T_2''$  and  $T_1''$  represent the temperatures of outer wall and mica plate (properly speaking tube  $B$ ) respectively in the experiment at the ordinary temperature,  $T_2'$  and  $T_1'$  the corresponding temperatures in the experiment at higher temperature,  $c$  the value of the reduction factor calculated from the dimensions of the apparatus (as we have seen this calculation can only give an approximate value),  $\alpha_1$  and  $\alpha_2$  the two elongations. The second column gives the differences of the successive pressures, the third the same differences according to the observations with the pipettes.

In the first series the limits of proportionality are evidently far exceeded: it can therefore serve as a calibration of the manometer as a pressure-indicator. The second series shows clearly that at first the absolute manometer gives greater values for the pressures than the pipettes, which are however in a constant ratio to the latter, while later on its readings are lower than those of the pipettes, as might be expected<sup>1)</sup>. It is also intelligible that our manometer gives higher readings in the beginning than the pipettes considering that the distance between the windows and the mica plate cannot be taken as small as compared with the width of the windows, so that parts of the movable mica plate outside the perpendicular projection of the windows will also be struck by molecules which proceed from the heated wall. This action along the edges owing to which  $c$  can only be approximately calculated was considerable in our case; its influence on the pressure follows immediately from the above calibration numbers: obviously  $c$  has to be replaced by  $\frac{1}{0.881}c = 1.135c$ .

#### § 4. *The measurements.*

*a.* The manometer mounted as in fig. 2 was then exhausted for a long time under strong heating to 300° C.: for this purpose it was joined to a GAEDÉ molecular airpump, for the loan of which we are indebted to the kindness of LEYBOLD'S Nachf. of Cologne, which we here gratefully acknowledge. As appears from the measurements communicated below it is possible to use this excellent, reliable and easily worked instrument continuously at pressures of 0,007 barye without the least trouble. After having been connected to the pump at the temperature mentioned for about a day the manometer ceased to give off gas. The vacuum had become constant. The small remaining pressure was thereupon measured, while the vapour

<sup>1)</sup> DEBIJE (Physik. Zs. 1911, p. 1115) has tried to represent this behaviour by a formula of approximation.

pressure tube  $R$  was first placed in liquid oxygen and afterwards in methane of different temperatures. It appeared that the vacuum remained constant within the limits of accuracy and was independent of the temperature of the vapour pressure tube<sup>1)</sup>. Carbon dioxide carefully dried and repeatedly distilled in vacuo was now introduced through a side tube into the tube  $R$ , which was cooled with liquid air. When a sufficient quantity had passed over, the apparatus was again connected to the molecular pump and evacuated during a considerable time. The manometer was then sealed off from the pump at  $a$  and the pressure measured, while  $R$  was surrounded with oxygen boiling under reduced pressure. It was found that the vacuum was the same as before the introduction of carbon dioxide, from which it follows that at  $-205^{\circ}\text{C}$ . the vapour pressure of carbon dioxide must be smaller than 0,005 barye. A difference of 0,002 barye could be clearly detected and the influence of vibration was also just below this value; 0,005 barye could thus not escape observation.

$\beta$ . As a rule the further observations were made in the following manner: first the manometer is brought approximately to temperature-equilibrium, and the thermometers  $T_2$  and  $T_1$  are read; warm water is then made to pass through  $K_1$  until a suitable temperature is reached;  $T_2$  and  $T_1$  are again read and the reading on the eye-micrometer is taken. Finally cold water is let into  $K_2$  until  $T_1$  has about assumed the original temperature, after which a second observation is made at the same temperature.

The calculation is made in the manner explained in section 2.

As described the vacuum was measured before carbon dioxide was admitted,  $R$  being at temperatures between  $-160^{\circ}\text{C}$ . and  $-200^{\circ}\text{C}$ ., when 0,007 baryes was found for the pressure. After sealing off the same value 0,007 baryes was found. A complete series of observations was then taken, first with methane and then with oxygen in the cryostat. The apparatus was then left standing for a few days, after which a new series of observation was taken. In the mean time the vacuum appeared to have risen to 0,016 barye. If this change is taken into consideration the two series agree well with each other.

In table II the two sets of measurements are combined.

The figures in the 3<sup>rd</sup> column are derived from those in the 2<sup>nd</sup>

<sup>1)</sup> The radiation-pressure did not amount in our case to more than  $0,05 \cdot 10^{-3}$  barye, when the wall was at  $100^{\circ}\text{C}$ .

T A B L E II.			
Vapour pressures of carbon dioxide at temperatures between — 183°.0 and — 167°.04.			
Temp. $T-273^{\circ}.09$	Pressure observed in baryes diminish- ed by residual pressure	Vapour pressure in baryes.	Calculated according to NERNST.
— 183°.0	0.015	0.008	0.0067
179.60	0.047	0.026	0.0241
175.37	0.179	0.106	0.1012
171.01	0.620	0.404	0.4083
168.83	1.143	0.791	0.7782
167.04	1.780	1.310	1.297

by correcting for the thermal molecular pressure. This was done by means of the formula given by KNUDSEN:

$$\frac{p_1}{p_2} = \left(\frac{T_1}{T_2}\right)^{\frac{1}{2}} \cdot \frac{1}{1 + \frac{2R}{\lambda}}$$

where  $p_1$  and  $p_2$  are the measured pressure and the real pressure respectively,  $T_1$  and  $T_2$  the corresponding temperatures,  $2R$  the diameter of the vapour pressure tube and  $\lambda$  the mean free path calculated from  $p\lambda = \frac{1}{2}$ . This relation was thus also applied in conditions, where the mean free path is not well represented by SUTHERLAND's formula<sup>1)</sup>: this may, however, be considered allowable in view of the small influence of the term  $\frac{2R}{\lambda}$ .

It will be seen that the main term of the correction is large: but its value is accurately known and is in no way connected with the additional correction for  $\lambda$ . The latter is only of importance in the last measurements.

It is possible by a suitable choice of the radius of the vapour pressure tube  $R$  to make the additional correction so small, that it may be entirely neglected. It is our intention to do this in future experiments in order to become entirely independent of the small

<sup>1)</sup> The circumstance that in the exponential form the same factor is here used for the residual pressure, although the substance to which this pressure is due, is unknown, is of no importance within the limits of accuracy of the experiments.

uncertainty arising out of this cause at present. In those experiments a little more time will have to be allowed for the setting in of the equilibrium pressure.

§ 5. *Determinations with the hot-wire manometer.*

With regard to the choice of the shape and dimensions of the vapour-pressure tube  $R$ , used in the measurements with the absolute manometer, the question arises whether sufficient account has been taken of two causes of disturbance which may influence the results obtained. The tube being long cannot in itself be considered a sufficient precaution to exclude radiation from above, by which the temperature-equilibrium of the evaporating surface is rendered uncertain, furthermore it has to be ascertained, whether the surface of the liquid bath may possibly be at a lower temperature than the bath at the spot, where the temperature is measured<sup>1)</sup>.

In view of the degree of accuracy of the measurements with our absolute manometer the errors arising out of these causes of disturbance may be neglected.

With our hot-wire manometer the accuracy which could be attained in the region of less low pressures, at which measurements were also intended, was considerably higher. In designing the vapour pressure apparatus intended for the measurements with this manometer the possible influence of the aforesaid causes of error was therefore carefully avoided.

The hot-wire manometer which we used is represented in fig. 3. It consists of a WOLLASTON-wire (0.005 mm. in diameter and about 10 cm. long), stretched in a frame of platinum wire  $abc$  which forms at the same time the one electrode of the current. The second electrode  $e$  is insulated from  $abc$  by means of glass. The WOLLASTON-wire is fastened between  $b$  and  $d$ .

The dimensions are so chosen, that a pressure of 1 barye can be measured with great accuracy. This is the case when the diameter of the wire is small compared with the mean distance described by the molecules since their last collision: for as long as this condition is satisfied, the loss of heat by the wire may be taken approximately proportional to the density (or the pressure) of the gas. Owing to a deviation from proportionality, which is due to the heat flowing

<sup>1)</sup> Comp. KAMERLINGH ONNES and BRAAK, Comm. N<sup>o</sup>. 107a. Even after 6 hours there was no sign whatsoever of a distillation of carbon dioxide at the bottom of  $R$  to the neighbourhood of the level of the liquid in the bath.

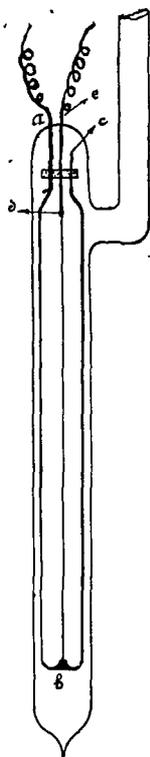


Fig. 3.

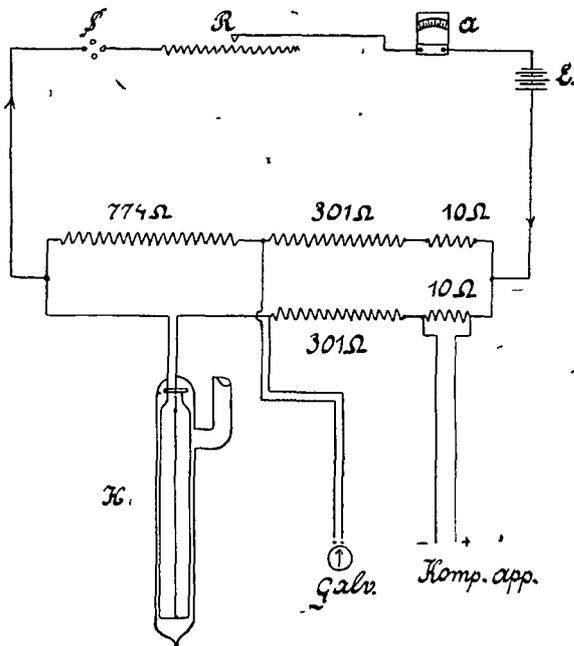


Fig. 4.

off at the ends of the wire, a calibration is required. For this purpose the pressure was determined by means of the set of pipettes referred to before. The loss of heat is measured as follows. The wire forms one of the arms of a WHEATSTONE bridge (fig. 4); the corresponding arm has a resistance approximately equal to that of the wire, when it is heated to the definite temperature, which has been chosen with a view to the sensibility (in our case 86 degrees above  $20^{\circ}$  C.): it is kept at this temperature by regulating the main current. The two other arms have equal resistance (chosen in connection with the galvanometer resistance). The P. D. at the ends of a portion of one of these resistances is measured with a potentiometer free of thermo-effects: this gives the necessary data for the computation of the loss of heat.

The calibration was carried out with the set of pipettes mentioned above. Fig. 5 gives the two

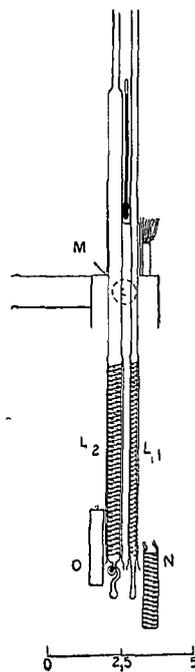


Fig. 5.

15

vapour pressure tubes. They were partly doublewalled; the walls are sealed together at the top and free at the bottom.

Where the external tube ends, the inner tube becomes narrower and is bent round in a spiral finishing up in a small bulb; this bulb is placed at the level of the middle of the thermometer. In the space between the two walls of the tube a wire is inserted which can be electrically heated, so as to secure, that the bulb is the coolest place of the vapour pressure tube. The object of the spiral is to compel the molecules which come in from above to collide a number of times with the wall before reaching the bulb. That part of the tube cannot contribute to the thermal molecular pressure, as it is practically at the same temperature over its entire length.

We have made a series of observations for carbon dioxide with this apparatus<sup>1</sup>).

We confine ourselves here to those measurements which give at the same time a check on the last measurements with the absolute manometer, contained in Table 2. The results were as follows:

TABLE III.		
Vapour pressure of carbon dioxide at about $-168^{\circ}$ .		
Temp. $T - 273^{\circ}.09$ K.	Pressure in baryes.	Vapour pressure in baryes.
$-168.82$	Vapour pressure tube I $2R = 1.57$ cM.	0.806
	1.222	
$-168.82$	Vapour pressure tube II $2R = 0.563$ cM.	0.797
	1.288	
$-167.04$	2.098	1.313

The last value will be seen to agree well with those obtained with the absolute manometer, while the first appears a little too

<sup>1</sup>) The measurements at higher temperatures are dealt with in the next communication: S WEBER The vapour pressures of carbon dioxide between  $-140^{\circ}$  C. and  $-160^{\circ}$  C.

high. We are uncertain as to the cause of this difference: most probably it is due to an uncertainty in the temperature with the absolute manometer.

It is of special interest to compare these observations with NERNST's formula. The fourth column of Table II contains the pressures according to this formula, calculated with the constants which FALCK<sup>1)</sup> has determined with the data at his disposal. FALCK found the following expression

$$\log p = -\frac{6000}{4,571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0,009983}{4,571} T + 3,1700$$

where  $p$  is the pressure in atmospheres.

The correspondence will be seen to be satisfactory considering the degree of accuracy of the observations. It does not look as if the constants could be materially improved.

**Physics.** — “*On the equation of state of an ideal monatomic gas according to the quantum-theory.*” By Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 30a to the Communications from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

(Communicated in the meeting of May 31, 1913).

§ 1. *Introduction.* Summary. DEBIJE<sup>2)</sup> has shown that agreement with the observations concerning the specific heat of solid substances can be obtained by modifying the theory of EINSTEIN<sup>3)</sup> in this sense, that the formula<sup>4)</sup> which PLANCK has given for the mean energy at the temperature  $T$  of a linear electrical oscillator is applied to the different principal modes of vibration of a solid.

It seems natural to apply the same principle to other material systems which can behave as an oscillator and hence to investigate the correctness of the consequences which follow from the hypothesis

<sup>1)</sup> FALCK: Physik. Zeits. 1908, p. 433.

<sup>2)</sup> P. DEBIJE. Ann. d. Phys. (4) 39 (1912), p. 789.

<sup>3)</sup> For the literature see: H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N<sup>o</sup>. 23, § 74c.

<sup>4)</sup> DEBIJE makes use of the original formula of PLANCK, Wärmestrahlung, 1<sup>ste</sup> Aufl., p. 157. The more recent formula, Wärmestrahlung, 2<sup>te</sup> Aufl., p. 140, which differs from the first by the introduction of a zero point energy, leads to the same results as regards the specific heat as long as the frequencies do not depend upon the temperature. For processes in which the frequencies change, cf. P. DEBIJE, Programme for the WOLFSKEHL lecture, Physik. ZS. 14 (1913), p. 259, it can give diverging results for solids too.

that PLANCK's principle of finite elements of energy holds for each principal mode of vibration of an oscillator whose motions can be described by linear differential equations, whatever its constitution may otherwise be.

In this paper those consequences will be deduced for an ideal monatomic gas. Similar applications of the quantum-theory to an ideal monatomic gas were already made by TETRODE<sup>1)</sup> and by LENZ<sup>2)</sup>. SACKUR<sup>3)</sup> also makes use of the quantum-theory for the deduction of the equation of state, but in a different way.

The deductions of TETRODE and of LENZ are based on the supposition that each principal mode of vibration of a gas enclosed in a given vessel exchanges its energy by whole energy elements at once. If this supposition is accepted it can be made probable by contemplating the exchange of energy between the gas and the radiation which is in equilibrium with it, that these energy elements have a magnitude  $\frac{1}{2} h\nu$ ,  $\nu$  being the frequency of the (longitudinal) waves in the gas,  $h$  the well known PLANCK's constant. The mean "temperature energy" per mode of vibration is then found to be

$$\frac{1}{2} \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1},$$

$k$  being the well known constant of BOLTZMANN's entropy

principle.

As Prof. KAMERLINGH ONNES and I communicated to the WOLFSKEHL congress last month, this treatment gives results which do not conflict with observations on the equation of state of helium only<sup>4)</sup> on the condition that, in writing down the mean energy per mode of vibration for an ideal gas, a *zero point energy* to an amount of  $\frac{1}{4} h\nu$  is added to the above-mentioned expression for the temperature energy<sup>5)</sup>. The same zero point energy was recently assumed for

<sup>1)</sup> H. TETRODE. Physik. ZS. 14 (1913), p. 212.

<sup>2)</sup> Cf. A. SOMMERFELD, Programme for the WOLFSKEHL lecture, Physik. ZS. 14 (1913), p. 262.

<sup>3)</sup> O. SACKUR. Jahresber. der Schles. Gesellschaft für vaterl. Cultur, Febr. 1913.

<sup>4)</sup> Viz. on the supposition that the determination of the frequencies of a gas in a way corresponding to that which DEBIJE follows for a solid may be considered as approximately correct.

<sup>5)</sup> Hence the fundamental assumptions of this paper diverge from those of TETRODE and of LENZ by the introduction of the zero point energy, from those of LENZ moreover by the fact (§ 2), that for the magnitude of the energy elements  $\frac{1}{2} h\nu$  is accepted.

the molecular rotations by EINSTEIN and STERN<sup>1)</sup> for the explanation of the behaviour of the specific heat of hydrogen.

The supposition of a zero point energy corresponds to the newest ideas of PLANCK, according to which an electrical oscillator absorbs energy from radiation continuously, but emits energy by whole quanta at once. According to the fundamental hypothesis underlying this paper, a similar behaviour should therefore be made also for the ideal gas.

In order to be able to write down an expression for the total energy of the whole system we need the knowledge of the "spectrum" of the gas. We will suppose, that this spectrum can be determined in a way corresponding to that in which the spectrum of a solid is determined by DEBYE.

With these data the equation of state of an ideal monatomic gas can be deduced, and then all thermodynamic quantities for such a gas can be derived. The pressure is found<sup>2)</sup> to be greater than the "equipartition value"  $p = RT/v$ ; at high temperatures it deviates little from this value, the ratio of this deviation to the value itself approaching ultimately indefinitely to 0; at low temperatures, if the gas may then still be treated as an ideal one, the pressure approaches to a value which depends upon the molecular weight and upon the density, but does not depend upon the temperature. That value we call the *zero point pressure*.

For a gas like helium at normal density and say 0° C. the deviation from the equipartition value appears to be still small. It has, however, already such a value that for instance in determining the VAN DER WAALS quantities  $a_w$  and  $b_w$ , or in the discussion of the virial coefficients, as was done for the second one in Suppl. N<sup>o</sup>. 25 (Sept. '12) and N<sup>o</sup>. 26 (Oct. '12), that deviation has to be taken into account. The zero point pressure for helium at normal density is found to be  $\frac{1}{4}$  mm. At greater densities deviations from the equipartition laws become more important.

For the specific heat at constant volume of a gas like helium (supposed to be ideal) at normal density an appreciable deviation from the constant equipartition value is found only at extremely low temperatures<sup>3)</sup>. Ultimately the specific heat also decreases and

<sup>1)</sup> A. EINSTEIN and O. STERN. Ann. d. Phys. (4) 40 (1913), p. 551. SACKUR, l.c., assumes the zero point energy also, as is done in this paper, for the molecular translations.

<sup>2)</sup> Cf. O. SACKUR, l.c.

<sup>3)</sup> That the specific heat of monatomic gases deviates from the equipartition value in an appreciable measure only at extremely low temperatures was already predicted by NERNST and LINDEMANN, ZS. f. Electrochem. 17 (1911), p. 826, note 1; NERNST, Physik. ZS. 13 (1912), p. 1066. [Note added in the translation.]

approaches to 0. The suppositions underlying the deductions of this paper imply that also for ideal gases NERNST's heat theorem is valid.

The results derived in this paper for an ideal gas may also be of value for the theory of free electrons in metals. For this we refer to the next paper.

§ 2. *The energy elements.* We may imagine the equilibrium between radiation and molecular translatory motion in an ideal<sup>1)</sup> monatomic gas enclosed in a given vessel to be brought about in the following way: let the vessel which contains the gas be surrounded totally or partially by a vessel which contains radiation. The walls of the latter vessel are thought to be perfectly reflecting on the inner side. In the wall which is common to the two vessels a cylindrical hole is made, in which moves a piston (reflecting on the side of the radiation). This piston is held, e.g. by a suitable constructed spring, in such a way that under the action of the pressure of those rays which have a frequency  $\nu'$  it is forced to vibrate. We may interpret the newest theory of PLANCK so that exchange of energy (absorption as well as emission) takes place only by whole quanta at once, if we take care to add the zero point energy to the value of the energy at equilibrium of an oscillator derived on that supposition. So we may suppose that those rays can give their energy to the piston only by quanta of magnitude  $h\nu'$ . The pressure of radiation, being proportional to the product of electric and magnetic force, has the frequency  $\nu = 2\nu'$ . The piston is forced to vibrate with the same frequency under the action of the pressure.

We suppose  $\nu'$  to be chosen in such a way that  $\nu$  is a principal frequency of the gas. The motion of the piston will then excite vibrations in the gas of the same frequency  $\nu$ . We will suppose that the piston can transfer the quanta  $h\nu'$  immediately to the gas in the form of energy of rays with its frequency  $\nu$  (whether the piston transfers all the quanta, which it receives, in this form, or only part of them, and perhaps remits another part to the radiation, is immaterial). A mode of vibration  $\nu$  of the gas then receives energy by quanta  $h\nu' = \frac{1}{2} h\nu$ .

The reverse, *viz.* transfer of energy of a mode of vibration  $\nu$  in the gas by the aid of the above-mentioned piston to the mode of vibration  $\nu'$  in the radiation must also be assumed, in fact in the case of equilibrium to the same amount per unit of time. We could

<sup>1)</sup> By this I understand in this paper a gas such, that the volume of the molecules themselves and their mutual attraction need not be considered.

imagine that the energy transferred to the gas in the first process is remitted to the radiation by another way, *e.g.* with another frequency. In this case energy would, however, move continuously in a cycle. This one will not feel inclined to accept.

In the way indicated above, say by the application of a sufficient number of similar pistons, the equilibrium with the radiation can be brought about for all principal frequencies of the gas. If there are still other ways in which energy can be transferred from radiation to the gas molecules or vice versa, the nature of the equilibrium will presumably not be changed thereby.

The result of these considerations is that we shall admit — in so far as the above argument is not considered sufficiently cogent we will put as a hypothesis which may be justified or not in its consequences — that in the equilibrium between the molecular translatory motion in a gas and radiation energy elements of a magnitude  $\frac{1}{2} h\nu$  play a part, if  $\nu$  is a principal frequency of the gas.

§ 3. *The energy and the entropy of an ideal monatomic gas.* In calculating the mean<sup>1)</sup> energy and entropy to be ascribed to a definite mode of vibration with frequency  $\nu$  of the gas, we follow the reasoning which PLANCK, *Wärmestrahlung* 2<sup>te</sup> Aufl. § 135—143 follows for ideal linear electrical oscillators. Considering that for the gas according to § 2 we have to do with energy elements  $\frac{1}{2} h\nu$  we obtain (cf. PLANCK *l.c.* equation (22)):

$$s_\nu = k \left\{ \left( \frac{2u_\nu}{h\nu} + \frac{1}{2} \right) \ln \left( \frac{2u_\nu}{h\nu} + \frac{1}{2} \right) - \left( \frac{2u_\nu}{h\nu} - \frac{1}{2} \right) \ln \left( \frac{2u_\nu}{h\nu} - \frac{1}{2} \right) \right\}. \quad (1)$$

where  $s_\nu$  and  $u_\nu$  represent the mean entropy and energy for the mode of vibration considered.

The temperature  $T$  is determined by  $\left( \frac{\partial s_\nu}{\partial u_\nu} \right) = \frac{1}{T}$ . In this differentiation at constant volume the wave-length  $\lambda$  remains constant;  $\nu$  is connected with  $\lambda$  by the relation  $\nu = c/\lambda$ ,  $c$  representing the velocity of propagation. In § 4 it will appear that in the gas, when in thermodynamic equilibrium, on the suppositions for which the simple laws of propagation of sound hold,  $c$  is proportional to  $U^{1/2}$ , also when equipartition does not hold, where  $U$  is the total energy of molecular translatory motion of the gas. We will now assume that for each mode of vibration we may put  $c = u^{1/2}$ . This hypothesis is inconsistent with observations for vibrations which we can observe as sound, *e.g.* for vibrations with small amplitude, if they are

<sup>1)</sup> Numerical mean if we think the gas to be repeated many times.

considered isolated. For vibrations with very small wave-lengths, which are here the most important, it may, however, be assumed to hold, in connection with their relation to heat motion, at least as an approximate hypothesis for states which differ only little from the state of equilibrium. It then follows<sup>1)</sup> that

$$u_\nu = \frac{1}{2} \left\{ \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} h\nu \right\} \dots \dots \dots (2)$$

As the different modes of vibration, which are possible in a gas enclosed in a given vessel, must be supposed to have the same  $T$  in the state of equilibrium, equation (2) at the same time represents the part which each mode of vibration in the gas in the state of equilibrium at the temperature  $T$  contributes to the whole energy.

We now assume that we obtain an approximately correct value for the whole energy if, in a way corresponding to that which DEBJÆ follows for a solid, we suppose the number of different principal modes of vibration which are contained in the region determined by the frequencies  $\nu$  and  $\nu + d\nu$  to be equal to<sup>2)</sup>

$$\frac{4\pi V}{c^3} \nu^2 d\nu \dots \dots \dots (3)$$

and cut off the so determined "spectrum" at  $\nu_m$ , given by putting the total number of modes of vibration equal to the number of degrees of freedom  $3N$ .  $V$  represents the volume of the gramme-molecule of the gas,  $N$  is the number of AVOGADRO. We then obtain:

$$U = \frac{9N}{2\nu_m^3} \int_0^{\nu_m} \left\{ \frac{h\nu}{e^{\frac{h\nu}{kT}} - 1} + \frac{1}{2} h\nu \right\} \nu^2 d\nu, \dots \dots \dots (4)$$

where  $\nu_m$  is determined by

$$\nu_m^3 = \frac{9}{4\pi} \frac{N}{V} c^3 \dots \dots \dots (5)$$

For the total entropy an expression can now also be easily given.

<sup>1)</sup> As SOMMERFELD *loc. cit.* observes, the hypothesis mentioned above causes as it were automatically that at high temperatures the mean energy per degree of freedom becomes  $= \frac{1}{2} kT$ , as it must be for the molecular translatory motion. For the difference of equation (2) from the corresponding one of LENZ cf. p. 228 note 5.

<sup>2)</sup> In accordance with a remark by TETRODE, *l.c.* this expression can be easily deduced for a cubical vessel from the formula for the wave-lengths occurring in it: RAYLEIGH, *Theory of Sound II*, 2nd ed. London 1896 p. 71.

§ 4. *The pressure. a.* We will assume that the relation

$$p = \frac{2}{3} \frac{U}{V}, \dots \dots \dots (6)$$

as depending on the isotropy of molecular motion and on the elementary fundamental law of dynamics regarding the connection between force and momentum, remains generally valid. As TETRODE l. c. shows, we have then also in general

$$c^2 = \frac{10}{9} \frac{U}{M}, \dots \dots \dots (7)$$

$M$  being the molecular weight. By (4), (5), (6) and (7) the equation of state of the ideal monatomic gas is given.

It is easily demonstrated, that the expression for the entropy deduced from (1) is consistent with this equation<sup>1)</sup>.

If we introduce

$$\frac{h\nu}{kT} = \xi, \quad \frac{h\nu_m}{kT} = x, \dots \dots \dots (8)$$

we obtain

$$U = \frac{9}{2} Nk T \left\{ \frac{1}{8} x + \frac{1}{x^3} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \right\} \dots \dots \dots (9)$$

By introducing the "characteristic temperature"  $\theta$ , determined by

$$\theta = \frac{h\nu_m}{k} = \frac{h}{k} \cdot \left( \frac{9}{4\pi} \frac{N}{V} \right)^{1/3} \cdot \left( \frac{10}{9} \frac{U}{M} \right)^{1/2}, \dots \dots \dots (10)$$

we can write

$$x = \frac{\theta}{T} \dots \dots \dots (11)$$

*b. High temperatures.* Developing for high temperatures<sup>2)</sup>, we obtain

$$U = \frac{3}{2} Nk T \left\{ 1 + \frac{3}{5} \frac{B_1}{2!} x^2 - \frac{3}{7} \frac{B_2}{4!} x^4 + \frac{3}{9} \frac{B_3}{6!} x^6 \dots \right\} \dots \dots \dots (12)$$

where  $B_1 = \frac{1}{6}$ ,  $B_2 = \frac{1}{30}$ ,  $B_3 = \frac{1}{42}$  are the BERNOULLIAN coefficients, or

$$U = \frac{3}{2} Nk T \left\{ 1 + \frac{1}{20} x^2 - \frac{1}{1680} x^4 + \frac{1}{90720} x^6 \dots \right\} \dots \dots \dots (13)$$

Limiting ourselves to the two first terms the pressure becomes

$$p = \frac{Nk T}{V} \left\{ 1 + \frac{1}{20} \frac{\theta^2}{T^2} \right\} \dots \dots \dots (14)$$

and according to (10), substituting for  $U$  only the first term of (13):

<sup>1)</sup> Cf. H. TETRODE, l. c.

<sup>2)</sup> According to DEBIJE l. c. this development is suitable from  $x=0$  to  $x=2$ .

$$\theta_{(T \gg \theta)} = \frac{h}{k} \cdot \left( \frac{9 N}{4\pi V} \right)^{1/3} \cdot \left( \frac{5 N k T}{3 M} \right)^{1/2} \dots \dots (15a)$$

Taking  $N = 6,85 \cdot 10^{23}$ ,  $\frac{h}{k} = 4,86 \cdot 10^{-11}$ ,  $k = 1,21 \cdot 10^{-16}$ , we obtain

$$\theta_{(T \gg \theta)} = 45,1 \cdot M^{-1/2} V^{-1/3} T^{1/2} \dots \dots (15b)$$

$\theta_{(T \gg \theta)}$  is connected with  $\theta_0$  to be introduced in  $c$  by the relation

$$\theta_{(T \gg \theta)} = \left( \frac{8}{3} \theta_0 T \right)^{1/2} \dots \dots (15c)$$

For helium at  $0^\circ \text{C}$ . and 1 atm. we find  $\theta = 13.2$ . From (14) follows a deviation from BOYLE'S law to an amount of  $0.12\%$ . This deviation is in the direction found by experiment and has such an amount that with reasonable suppositions about the VAN DER WAALS constants it is not in conflict with the value experimentally observed<sup>1)</sup>:  $0.512\%$ . On the other hand there would have been contradiction if in the expression (2) for the energy the zero point energy had not been taken up. This, and a similar result concerning the pressure coefficient of helium between  $0^\circ$  and  $100^\circ \text{C}$ . were the reasons which led Prof. KAMERLINGH ONNES and me in our communication to the WOLFSKEHL-congress to the hypothesis of the zero point energy for an ideal gas.

Although the deviation from BOYLE'S law, which follows from the application of the quantum-theory in the way explained in this paper, is still small in the special case discussed above, it nevertheless appears (and for greater densities this is even more the case), that in discussing the equation of state this deviation has to be taken into account. Further discussion in this direction has to be postponed, however, to a later communication.

*c. Low temperatures.* For low temperatures the following development<sup>2)</sup> is more appropriate:

$$U = \frac{9}{2} NkT \left\{ \frac{1}{8} x + \frac{\pi^4}{15 x^3} - x \sum_{n=1}^{\infty} e^{-nx} \left( \frac{1}{nx} + \frac{3}{n^2 x^2} + \frac{6}{n^3 x^3} + \frac{6}{n^4 x^4} \right) \right\}, (16)$$

with  $x$  according to (11) and (10). The first two terms give ( $T \ll \theta$ ):

$$U = \frac{9}{16} Nk\theta_0 \left\{ 1 + \frac{16\pi^4 T^4}{15 \theta_0^4} \right\}, \dots \dots (17)$$

where

$$\theta_0 = \frac{h^2}{k^2} \cdot \left( \frac{9 N}{4\pi V} \right)^{2/3} \frac{5 N k}{8 M} \dots \dots (18a)$$

or (cf. *b*)

$$\theta_0 = 761 \cdot M^{-1} V^{-2/3} \dots \dots (18b)$$

<sup>1)</sup> H. KAMERLINGH ONNES, Comm. N<sup>o</sup>. 102a, Dec. 1907.

<sup>2)</sup> According to DEBYE, l.c., suitable from  $x = \infty$  to  $x = 2$ .

For the pressure  $p$  is found:

$$p = \frac{3}{8} \frac{Nk\theta_0}{V} \left\{ 1 + \frac{16\pi^4 T^4}{15 \theta_0^4} \right\} \dots \dots \dots (19)$$

For helium at normal density  $\theta_0 = 0.239$ . Hence formula (17) could be valid for helium at normal density at extremely low temperatures only. At these low temperatures helium at that density can no longer exist as an ideal gas. If we call *zero point pressure*, the value which  $p$  according to (19) assumes for  $T=0$ ,  $p_0$  is a quantity which immediately enables us to get an estimate of the deviations from the CHARLES'S law which are to be expected at low temperatures. For helium at normal density the zero point pressure is found to be <sup>1)</sup> 332 baryes = 0.25 mm. If from this we deduced the temperature according to  $p = RT/v$ , a temperature  $\frac{3}{8} \theta_0 = 0^\circ.09$  would correspond to it. The error in the reading of such a thermometer, which would occur according to the above application of the quantum-theory, will remain below this amount.

For the purpose of the theory of free electrons in metals we write (19) in the form <sup>2)</sup>

$$p = a V^{-1/3} + b T^4 V \dots \dots \dots (20)$$

where  $a$  and  $b$  are constants whose values can be easily derived. It is easily verified that the first term of (20) does not cause any decrease of temperature at adiabatic expansion: external work done at  $T=0$  at the expense of the zero point energy.

§ 5. *The specific heat. a.* From (4) the specific heat at constant volume can be derived: for this purpose it is to be taken into consideration that  $v_m$  depends according to (5) and (7) on the temperature <sup>3)</sup>. We will write down only a few terms of the two corresponding developments.

<sup>1)</sup> The result obtained here differs from that obtained by SACKUR l.c., although the above deductions in many respects run parallel to his.

<sup>2)</sup> The occurrence of the positive power of  $V$  gives a warning that the range of validity of this formula at larger  $V$  extends to correspondingly lower  $T$  only.

<sup>3)</sup> An expression is found, which can be brought to the following form:

$$\frac{C_v}{C_{v\infty}} = \frac{2}{5} \left( \frac{C}{C_\infty} \right)_{sol} \cdot \frac{\left( \frac{C}{C_\infty} \right)_{sol} + \frac{3}{2} x \frac{e^x + 1}{e^x - 1}}{\left( \frac{C}{C_\infty} \right)_{sol} + \frac{3}{10} x \frac{e^x + 1}{e^x - 1}}$$

For the values of  $\left( \frac{C}{C_\infty} \right)_{sol}$ , i.e. the ratio of the specific heat for a solid belonging to its limiting value at high temperatures see DEBYE l.c. p. 803, or NERNST, in Sitz.-Ber. 5 Dec. 1912.

*b. High temperatures.* For high temperatures ( $T \gg \theta$ ) we find:

$$C_v = \frac{3Nk}{2} \left( 1 - \frac{1}{525} \frac{\theta^4}{T^4} \right) \dots \dots \dots (21)$$

Hence the deviation in the specific heat is of a smaller order of magnitude than that in the pressure. The temperature at which  $C_v$  deviates 1% from the constant equipartition value, is determined by  $x = 0,85$ . For helium at normal density this temperature is found to be  $T = 0,9$ ; hence except at a considerably larger density a deviation of the specific heat from the equipartition value could not be observed experimentally.

*c. Low temperatures.* For the theory of free electrons in metals it is of interest to develop the formula for the specific heat at low temperatures. From (17) we find immediately ( $T \ll \theta_0$ ):

$$C_v = \frac{12\pi^4}{5} Nk \left( \frac{T}{\theta_0} \right)^3 = \frac{8\pi^4}{5} C_{v\infty} \left( \frac{T}{\theta_0} \right)^3 \dots \dots \dots (22)$$

$C_{v\infty}$ , the value to which  $C_v$  approaches at high  $T$ , being one half of the corresponding value for a solid the multiplicand of  $\left( \frac{T}{\theta_0} \right)^3$  is equal to that for a solid: cf. DEBJE, *l.c.* p. 800.

From (20) in connection with (22) it follows on account of the well known thermodynamic relation between  $C_p$  and  $C_v$  that their ratio  $\alpha$  approaches to the value 1 as  $T$  approaches to 0.

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(Communicated in the meeting of May 31, 1913).

§ 1. *Introduction. Summary.* It seems natural to transfer to the theory of free electrons<sup>1)</sup> in metals the considerations of the former paper regarding the application of the quantum-theory to the equation of state of an ideal monatomic gas. The frequencies in an electron

<sup>1)</sup> PLANCK, Berlin Sitz.-Ber. April 3, 1913, has recently treated the equilibrium between oscillators, free electrons and radiation on very special suppositions, which for the free electrons lead to the equipartition laws. The mode of treatment followed in this paper may in some measure be considered as the reverse of that by LORENTZ, These Proceedings April 1903, where from the motions of the free electrons (in the case of equipartition) he deduced the law of radiation (which holds in that case).

gas with the same order of magnitude of the number of particles per unit of volume, become very much higher than in the ordinary material gases. Hence the limiting laws deduced for low temperatures may be valid for a system of free electrons up to much higher temperatures, possibly even in the region of temperature which can be reached experimentally. The consideration of the dynamic equilibrium between the free electrons and the electrons within the molecules of the metal leads (§ 2) to the supposition, that at low temperatures the number of free electrons per unit of volume approaches to a constant finite value. The same is then the case for the mean velocity of the free electrons.

In this manner the application of the quantum-theory to the free electrons in a metal leads for low temperatures to the suppositions regarding velocity<sup>1)</sup> and density of electrons, on which WIEN<sup>2)</sup> recently based his theory of electric conduction, in which theory further, as was done previously by KAMERLINGH ONNES<sup>3)</sup> and by LINDEMANN<sup>4)</sup>, the quantum-theory is applied to the molecular oscillations which impede the motion of the free electrons. On the other hand the application of the quantum-theory to the free electrons leads for high temperatures, e.g. for the region of temperatures, which is characterised by phenomena as those investigated by RICHARDSON (perhaps even for still higher temperatures only), to the theory of free electrons in metals in the form in which it has been developed by RIECKE<sup>5)</sup>, DRUDE<sup>6)</sup>, LORENTZ<sup>7)</sup>, and which we can call the equipartition-theory. Hence the quantum-theory appears to be able to unite both the theories mentioned into one simple and coherent whole.

By it at the same time two great difficulties, which were inherent to the equipartition-theory, are solved.

In the first place it does not follow, any more, as was to be assume on the equipartition-theory, that on approaching to  $T=0$  the electrons all "freeze down"<sup>8)</sup>, a phenomenon which is contradicted

1) At least as regards the mean velocity.

2) W. WIEN. Berlin. Sitz.-Ber. 16 Jan. 1913, p. 184.

3) H. KAMERLINGH ONNES. Comm. No. 119 (Febr. 1911).

4) F. A. LINDEMANN. Berlin Sitz.-Ber. 1911, p. 316.

5) E. RIECKE. Wied. Ann. 66 (1898), p. 353, 545.

6) P. DRUDE. Ann. d. Phys. (4) 1 (1900), p. 566.

7) H. A. LORENTZ. These Proceedings Dec. 1904, Jan. 1905.

8) A number of the images used here, borrowed from the comparison of electrons with a substance, such as the idea of the equation of state of the electrons, saturated electron-vapour, equilibrium with precipitated electrons, and frozen down electrons were developed by KAMERLINGH ONNES (On the importance

by the observations of KAMERLINGH ONNES down to the lowest temperatures at which electric conductivity has been investigated. The application of the quantum-theory given here again allows us to consider the equilibrium between the free electrons and the electrons within the molecules as a dissociation equilibrium in the way as lately brought to the front particularly by KOENIGSBERGER for the purpose of the theory of electric conductivity.

In the second place the difficulty disappears which in the equipartition-theory followed from the small contribution made by the free electrons to the specific heat of the metal<sup>1)</sup>, a difficulty which — Dr. OOSTERHUIS drew my attention to this fact — even more sharply appears in the theory of the THOMSON-heat (§ 2). The solution of these difficulties can at present be adduced in favour of the application of the quantum-theory as considered here. For a further confirmation it will be particularly required, that on the theory it will be found possible to ascribe to the free electrons in the metal at different temperatures definite densities, which on the one side bring into proper mutual connection the different phenomena which depend on those densities, and which on the other side also change with temperature in a way which seems reasonable.

This paper, which bears only an introductory and surveying character, cannot go so far. We will, after having given some general considerations, limit ourselves to the treatment of the thermoelectric power, with which the PELTIER-effect and the THOMSON-effect are connected.

As limiting laws for the thermoelectric power between two metals and for the THOMSON-effect in a metal a decrease to 0 at  $T=0$  proportional to  $T^3$ , for the PELTIER-effect a decrease to 0 proportional to  $T^4$  are found. These results *e.g.* as regards the decrease of the thermoelectric power are confirmed by the present observations, and may perhaps give a method for a direct experimental test of the theory<sup>2)</sup>.

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of accurate measurements at very low temperatures, Leiden 1904, Comm. Leiden Suppl. N<sup>o</sup>. 9 p. 25 sqq, cf. also J. BECQUEREL and H. KAMERLINGH ONNES, Comm. N<sup>o</sup>. 103, Febr. 1908, § 7).

<sup>1)</sup> These and the preceding considerations were for the greater part given by me before in the discussion at the WOLFSKEHL congress April 25 and 26 last.

<sup>2)</sup> Since these considerations were developed by me, the article of K. F. HERZFELD. Wien Sitz. Ber 121, Oct. 1912, p. 1449 on contributions to the statistical theory of radiation came into my hands, in which the suggestion occurs that the supposition, according to which for the energy of the free electrons in a metal a formula would hold corresponding to that which is valid for the PLANCK's

§ 2. In order to make an estimate of the characteristic temperatures of a definite system of free electrons it is necessary to have an estimation of the density of the electrons in the system, or, which comes to the same, about the volume  $V$  of a gramme-molecule of the electron gas. It is well known that the opinions about the density of free electrons in metals diverge largely. To obtain such an estimation we will start in this paper from the following fact. The THOMSON constant, which (cf. § 5) may be considered as the specific heat of the "saturated electron vapour", can be written as the difference of two terms, of which the first represents the specific heat at constant volume, whereas the second depends on the change of the density of electrons with temperature. If the first term is calculated according to the equipartition-theory and compared with the value experimentally found, the latter appears to be always (in absolute value) many times smaller than the first term, on the average about  $1/5$ , of it. The equipartition-theory was therefore obliged to suppose the second term mentioned above to be constantly and for all the metals nearly equal to the first. According to J. J. THOMSON<sup>1)</sup> this would be the case if the number of free electrons is always nearly proportional to  $T^{1/2}$ . The theory of LORENTZ, to which the mode of calculation followed in §§ 3—5 leads in the case of equipartition, would require  $n$  (the number of electrons per  $\text{cm}^3$ ) to be nearly proportional to  $T^{3/2}$ , DRUDE's theory  $n$  to be nearly proportional to  $T^{3/4}$ . As far as I know for no one of these modes of dependence on the temperature a reasonable explanation has been given. Considered from the point of view of the dissociation-theory they hardly can be accepted as generally valid.

It seems to me to be more reasonable to suppose, that for the metals the specific heat at constant volume itself has a small value compared with the equipartition value. If for a definite metal at  $0^\circ \text{C}$ . we put  $C_v = 1/5 C_\infty$ , it follows from equation (22) with (18b) of the former paper (with  $M = N \times 0,8 \cdot 10^{-27}$  for the electrons) that for the free electrons in that metal at the temperature oscillator, would cause different difficulties of the equipartition-theory, which are also mentioned in this section, to disappear. Cf. further the article of HERZFELD, Ann. d. Phys. (4) 41 (1913), p. 27, which has just appeared; a similar remark was made by J. KOENIGSBERGER, Verh. d. D. physik. Ges. 1911, p. 934. A. L. BERNOULLI, ZS. f. Elektrochem. 17 (1911), p. 689, used also the PLANCK-EINSTEIN's formula for the energy in treating the thermo-electric phenomena, but in quite a different manner from the one in this paper (cf. in particular also the remarks by KRUGER, on p. 693 of the same volume).

<sup>1)</sup> J. J. THOMSON. Die Korpuskulartheorie der Materie, Braunschweig 1908, p. 77.

mentioned  $V = 4.10^3$ . This corresponds to a number of electrons per  $\text{cm}^3$   $n = 1.7.10^{20}$ .  $\theta_0$  then has the value 5500.

Hence it appears that in this region of temperature the formulae given in §§ 4c and 5c of the former communication for the low temperatures, will be applicable.

At decreasing temperature the density of the electrons, for a metal like platinum, decreases, as follows from the THOMSON-constant of this metal being negative. Later on in this section it will be shown that for low temperatures a finite limiting value has to be assumed for  $n$ . We will for a moment suppose that for the temperatures, which can be obtained with liquid helium, for the metal considered above  $V = 10^3$ . For this density of electrons  $\theta_0 = 139$ , so that for these low temperatures also the same formulae are valid. A fortiori this will be the case if the density of electrons is greater than has been supposed.

For such metals as the one considered above there will therefore be a region of temperature larger or smaller according to the density of electrons, in which the supposition of WIEN: the velocity of electrons = const., is nearly fulfilled as regards the mean velocity, if in that region the density of the electrons does not change appreciably with temperature.

It can easily be seen that this second supposition of WIEN: the number of electrons per  $\text{cm}^3$ . = const., will also be nearly fulfilled at sufficiently low temperatures. The number of free electrons is determined by the dynamic equilibrium between the free electrons in the intermolecular space and the electrons within the molecules. Concerning the latter different suppositions may be made, *e.g.* that they, or a number of them, are moving freely within the molecules. In this case, as in general, at least at low temperatures, the density of electrons will be greater within the molecule than outside it, the velocity of the electrons within the molecule will in the region of temperature considered be a fortiori constant if the density does not change. It can also be supposed that the electrons inside (or on the surface of) the molecule are more or less strongly bound to the molecule; the frequencies of those electrons will then depend on the nature of this binding and perhaps also on the frequencies of the molecules. Be that as it may, in following up the hypothesis regarding the zero point energy (cf. the former paper) consistently we shall have to admit that, when taking the temperature sufficiently low, we shall come to a region in which the motions within the molecule will be nearly independent of the temperature. In this region, in so far as it lies in the corresponding region for the electrons

inside the molecules, the density of the latter may be supposed to be nearly constant.

It was already remarked in § 1 that in this manner two great difficulties of the equipartition-theory are solved. In the first place regards the contribution by the free electrons to the specific heat of the metal, the heat necessary for the free electrons dissociating away from the molecules being included, with the values of the density of the electrons and of its change with temperature accepted above, this is found, at ordinary temperatures, to be only a small fraction of the whole specific heat (order of magnitude  $1/1000$ ).

At the same time, as was also indicated, the considerations given above show how the "WIEN-region", and the "RICHARDSON-region" may be connected together. For this a closer consideration of the association equilibrium: free electrons  $\rightleftharpoons$  electrons within the molecules is necessary. In any case it may be conjectured that the curve which will represent the density of the free electrons as a function of  $T$  will have, besides the part parallel to the  $T$ -axis mentioned above for low temperatures, a similar part for high temperatures<sup>1)</sup> (when all the available electrons have been dissociated off), and that between these two parts a region lies in which the density of the electrons changes with temperature. When this "boundary curve" or the corresponding "vapour pressure curve" is all known, the mean velocity of the electrons will follow by the relations of the former paper. Inversely the fact that the velocity of the electrons is connected in that way directly with the density, may be of advantage in deducing both from observations.

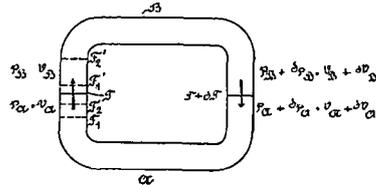
We will suppose for a moment that for a metal such as the one considered above<sup>2)</sup> at  $1800^\circ$  K.  $V = 4.10^8$ . For the energy of the free electrons a value is then found which is more than ten times as large as the equipartition value. It will afterwards have to be investigated whether this result, that the mean velocity of the free electrons at these high temperatures, for densities of electrons such as follow from the estimations indicated above from the RICHARDSON-heat, appears to be considerably larger than would be the case according to the equipartition-theory, is excluded by the obser-

<sup>1)</sup> Probably this region (in so far as it should be realisable) lies for most of the metals considerably higher than that over which the observations of RICHARDSON and those on thermoelectric powers extend.

<sup>2)</sup> The number of electrons per  $\text{cm}^3$ :  $n = 1.7 \cdot 10^{21}$ , is then still below the number admitted for platinum by BAEDERER, Die elektrischen Erscheinungen in metallischen Leitern, Braunschweig 1911, p. 12, in his discussion of the RICHARDSON-effect

vations of RICHARDSON, or on the contrary whether it will be able to clear up the difficulties which still present themselves in the discussion of the RICHARDSON-effect.

§ 3. *The thermoelectric power.* To calculate the thermoelectric power (for 1 degree temperature difference between the two joints)



in a circuit of two metals *A* and *B*, we assume<sup>1)</sup> 1 coulomb of free electrons to be driven round in the direction of the arrows in the figure, calculate the external work which in that process has to be performed on

the electrons as on an ideal gas, divide by  $dT$  and multiply by  $-1$ . We then obtain :

$$F = 10^{-8} \cdot \int_{v_A}^{v_B} \left( \frac{\partial p}{\partial T} \right)_v dv \dots \dots \dots (1)$$

Here  $F$  is the thermoelectric power in Volts and  $v$  represents the volume of 1 coulomb of electrons.

With the aid of equation (1), which can also be written in the form  $F = 10^{-8} \cdot \frac{\partial (\psi_A - \psi_B)}{\partial T}$  ( $\psi$  being the free energy), from the values of  $U$  and  $S$  of § 3 of the former paper a general formula for  $F$  can be derived. We shall only give the limiting laws for the high and for the low temperatures.

For the high temperatures, *viz.* such at which equipartition prevails, from equation (14) of the former paper the well known formula

$$F = 10^{-8} \frac{k}{e} \ln \frac{V_B}{V_A} \dots \dots \dots (2)$$

follows, if  $e =$  the charge in coulombs of 1 electron.

For low temperatures equation (20) of the former paper leads to<sup>2)</sup>:

<sup>1)</sup> Cf. K. BAEDER, l. c. Cf. also F. KRÜGER, Physik. Zeitsch. 11 (1910), p. 800, 12 (1911), p. 360.

<sup>2)</sup> We remark that for these low temperatures the following simple relation exists between the thermoelectric power and the specific heat of the electrons

$$F = 10^{-8} \cdot \frac{1}{Ne} \cdot \frac{1}{3} (C_{vB} - C_{vA}).$$

$$F = 10^{-8} \cdot \frac{1}{N_e} \cdot 2b T^3 (V_B^2 - V_A^2) \dots (3)$$

Substituting the value of  $b$ , with  $e = 1.4 \cdot 10^{-19}$ , we find

$$F = 2.52 \cdot 10^{-22} \cdot T^3 (V_B^2 - V_A^2) \dots (4)$$

From this result we see in the first place that the thermoelectric power in approaching to  $T = 0$  approaches to 0. As a matter of fact the observations<sup>1)</sup> for combinations of pure metals actually point in this direction.

For a combination of the metal considered in § 2 ( $V_B = 10^6$  for low temperatures) with a metal in which the density of free electrons is twice as large ( $V_A = 1.5 \cdot 10^6$ ), for  $T = 4$  from (4)  $F = 1.2 \cdot 10^{-8}$  Volt is derived. For high temperatures, on the supposition that the ratio of the densities of electrons is the same there as at the low temperatures, from (2)  $F = 6 \cdot 10^{-6}$  is found. Hence at the temperatures of liquid helium the thermoelectric power of that combination would on the supposition mentioned decrease to  $1/500$  (and at the lowest helium temperatures to still less) of its amount at high temperatures.

A decrease of the thermoelectric power has been deduced by NERNST<sup>2)</sup> from the recent formulation of his heat theorem. Here according to (4) this *decrease of the thermoelectric power* is found to take place finally *proportionally to  $T^3$* . This law, if it should be confirmed, and if the difficulties inherent to the measurement of the small thermoelectric powers at the extremely low temperatures can be sufficiently overcome, may be of importance for thermometry in the region concerned.

§ 4. *The PELTIER-effect.* To calculate the PELTIER-effect we consider

<sup>1)</sup> L. HOLBORN and A. DAY. Berlin Sitz. Ber. 36 (1899), p. 691. According to KAMERLINGH ONNES and CLAY, Comm. No. 107b, May 1908, the thermoelement gold-silver does not yet show that decrease at hydrogen temperatures.

Prof. KAMERLINGH ONNES further tells me that observations by KAMERLINGH ONNES and HOLST, which will soon be published, show that this is still the case at helium temperatures. Down to the boiling point of helium and a little lower the gold-silver thermometer even indicates the temperatures fairly accurately. Hence the importance of the further result that, when proceeding to the lowest helium temperatures the thermoelectric power decreases rapidly to small values. Other combinations of metals and alloys were also investigated by KAMERLINGH ONNES and HOLST with a view to thermometric determinations at the lower helium temperatures. With all of them the same phenomenon was observed of a rapid decrease of the thermoelectric power. The thermoelectric power was in general still considerable between hydrogen and helium temperatures. In these cases the decrease mentioned took place at liquid helium temperatures.

<sup>2)</sup> W. NERNST. Theoretische Chemie, 7<sup>te</sup> Aufl. Stuttgart 1913, p. 753.

the work which must be done on 1 coulomb of free electrons, when these are transferred at a temperature  $T$  from the metal  $A$  (where they may be contained between the planes  $F_1$  and  $F_2$ ) to the metal  $B$  (where they may then be contained between the planes  $F'_1$  and  $F'_2$ ). It is clear that peculiarities in the boundary layer between the two metals can be left out of consideration. This work is equal

to  $u_B - u_A + \int_{v_A}^{v_B} p \, dv$ , where the quantities  $u$  and  $v$  relate to 1 coulomb.

The expression represents the heat absorbed at the transfer from  $A$  to  $B$ , or the heat developed at the transfer from  $B$  to  $A$ . Passing to the quantities  $U$  and  $V$ , which refer to the molecular quantity, the PELTIER-effect, expressed in Joules, becomes

$$H = 10^{-7} \cdot \frac{1}{N_e} \left\{ U_B - U_A + \int_{V_A}^{V_B} p \, dV \right\} . . . . . (5)$$

We shall only consider what this expression leads to for the low temperatures. In the first place we remark that the first term in the second member of equation (20) of the former paper, the zero point pressure  $a V^{-5/3}$ , does not give a contribution for the PELTIER-effect. This corresponds to the remark made in § 4 of that paper, that at the adiabatic expansion of an ideal gas at  $T=0$  external work is done at the expense of the zero point energy. The second term in the development of  $U$  and  $p$  for low temperatures gives:

$$H = 10^{-7} \cdot \frac{1}{N_e} \cdot 2bT^4 (V_B^2 - V_A^2) . . . . . (6)$$

If attention is paid to the units in which  $F$  and  $H$  are here expressed, it is immediately seen that the KELVIN's relation between  $H$  and  $F$  is satisfied.

It appears that the PELTIER-effect in approaching to  $T=0$  will decrease to 0 and that the decrease will finally take place according to  $T^4$ .

§ 5. *The THOMSON-effect.* Applying a reasoning similar to that of the former section to the THOMSON-effect we find, that, as is well known, the THOMSON-coefficient  $\sigma$  represents the specific heat for the free electrons if in heating the volume of the electrons considered is changed so that the electron gas as a "saturated vapour" remains continually in equilibrium with the electrons within the metal atoms (which also change in temperature). Hence it is the specific

heat of the "saturated electron vapour". As according to our theory the density of the saturated electron vapour becomes constant at low temperature,  $\sigma$  there reduces to the specific heat at constant volume. Paying attention to the units used we therefore obtain for  $\sigma$ , expressed in Joules, at those low temperatures

$$\sigma = 10^{-7} \cdot \frac{1}{N_e} \cdot C_v, \dots \dots \dots (7)$$

or

$$\sigma = 10^{-7} \cdot \frac{1}{N_e} \cdot 6b \cdot T^3 V^2 \dots \dots \dots (8)$$

Again it is easily verified that the KELVIN's relation is satisfied.

Hence the THOMSON-effect also approaches to 0 at  $T=0$ , and this according to  $T^3$ .

**Physics.** — *"Isothermals of di-atomic substances and their binary mixtures XIII. Liquid-densities of hydrogen between the boiling point and the triple point; contraction of hydrogen on freezing."*  
By Prof. H. KAMERLINGH ONNES and Dr. C. A. CROMMELIN.  
Comm. N<sup>o</sup>. 137a from the Physical Laboratory at Leiden.

(Communicated in the meeting of June 28, 1913).

Densities of liquid hydrogen have so far only been determined by DEWAR<sup>1)</sup>. As a more accurate knowledge of this quantity is of importance for the equation of state the following measurements were undertaken. They were made with the same apparatus as served for argon.<sup>2)</sup>

The temperature was determined by measuring the vapour pressure of the hydrogen in the cryostat. The sensibility of this method is very great, as 1 mm. difference in vapour pressure corresponds to 0°.004 at the boiling point and to 0°.02 at the triple point. The measurement does not therefore require great care being taken. As shown by measurements by KAMERLINGH ONNES and KEESOM, the vapour pressure may be determined by reading the pressure in the cryostat itself, instead of in a special vapour pressure tube filled with pure hydrogen and placed in the cryostat, if an accuracy of 0°.02 or 0°.03 is considered sufficient.

<sup>1)</sup> J. DEWAR, Proc. R. S. (A) 73 (1904) p. 251.

<sup>2)</sup> E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proc. Oct. and Dec. 1912 and Jan 1913 Comm. N<sup>o</sup>. 131a.

The temperature on the KELVIN-scale<sup>1)</sup> corresponding to these vapour pressures are taken from measurements by KAMERLINGH ONNES and KEESOM, not yet published. Their results have not been definitely calculated, but the small corrections which may be as yet required are of no importance for the object of this paper.

For the method of calculating the volumes we may refer to the paper on the diameter of argon quoted above.

The results are contained in the table. It also gives the densities calculated by the quadratic formula

$$\rho_{\text{liq}} = a + bT + cT^2$$

with the following values of the constants:

$$a = + 0.084404$$

$$b = - 0.0002230$$

$$c = - 0.00002183$$

made to fit the readings at  $-258^{\circ}.27$ ,  $-255^{\circ}.99$  and the boiling point.

The deviations from this formula will be seen to be very small; they are within the limits of accuracy of the observations, except possibly at the highest temperature. It may be added, that the density at the boiling point was not directly observed, but was calculated from the neighbouring observations.

The first column contains the number of the observation, the second the temperature below  $0^{\circ}$  C., on the KELVIN-scale, the third the density observed referred to the density of water at  $4^{\circ}$  C., the

N <sup>o</sup> .	$\theta$	$\rho_{\text{liq}}^{\text{obs.}}$	$\rho_{\text{liq}}^{\text{calc.}}$	obs.—calc.
VIII	$-252.68$	0.07081	0.07076	+ 0.00005
—	$-252.77$ boiling point	7086	7086	—
XIV	$-253.24$	7137	7138	— 1
XIII	$-253.76$	7192	7194	— 2
XII	$-255.19$	7344	7342	+ 2
XI	$-255.99$	7421	7421	—
X	$-256.75$	7494	7493	+ 1
III	$-257.23$	7538	7538	0
IX	$-258.27$	7631	7631	—

<sup>1)</sup> The corrections for the reduction of the hydrogen-scale to the KELVIN-scale are given by H. KAMERLINGH ONNES and W. J. DE HAAS, Proc. Sept. 1912. Comm. N<sup>o</sup>. 127c.

fourth the density according to the formula and the fifth the difference of the latter two.

In addition to the liquid-densities the density of solid hydrogen was also determined. It was first of all ascertained that *solid hydrogen is heavier than liquid hydrogen* and, therefore, that *on freezing contraction takes place*. For this purpose the hydrogen in the cryostat was frozen; a solid crust is then formed on the liquid. If the pressure is now made to rise slowly, this crust divides into fragments which sink down in the liquid and collect at the bottom of the vacuum-glass. It was not till this observation was made, that we ventured to freeze the hydrogen in the dilatometer without fear of bursting the very carefully calibrated instrument.

In order to be sure, that the freezing would proceed from the bottom, the tube of the dilatometer was movable in a stuffing box, which was fitted in the lid of the cryostat. After the hydrogen in the cryostat had been frozen to an opaque solid mass, the dilatometer was pushed down slowly. The hydrogen in the dilatometer was then frozen to a homogeneous transparent mass. At the moment of reading the volume of the solid hydrogen, the pressure in the cryostat was 0.66 cm.

In order to obtain an estimate of the temperature, the vapour pressures of solid hydrogen being practically unknown, the vapour pressures according to KAMERLINGH ONNES and KEESOM were extrapolated by means of the  $\log p, \frac{1}{T}$  diagram, in which the vapour pressure curves are known often to be very nearly straight lines, neglecting the break in the curve at the triple point. In that manner the temperature  $\theta$  corresponding to a pressure of 0.66 cm. was found to be

$$- 262^{\circ}.0.$$

The density of solid hydrogen at this temperature was found to be

$$\rho_{\Gamma \text{sol}} = \underline{0.08077}.$$

Putting the triple point temperature, according to the same measurements at

$$\theta_{\text{coex. liq. vap. sol.}} = - 259^{\circ}.2$$

extrapolation by means of the above formula gives for the liquid density at that point

$$\rho_{\Gamma \text{coex. liq. vap. sol.}} = \underline{0.07709}.$$

Assuming that the density of solid hydrogen at the triple point does not differ appreciably from that at  $- 262^{\circ}$ , the contraction on freezing is found to be about 4.8 % of the liquid volume.

**Physiology.** — *Further experimental investigations of the internal secretion of the pancreas.* (By N. WATERMAN M. D.). (Communicated by Prof. Dr. C. A. PEKELHARING).

(Communicated in the meeting of June 28, 1913).

In a previous publication <sup>1)</sup> we discussed some properties of the blood from the pancreatic vein (containing what may presumably be considered as the internal secretum), and concluded from our experimentation that the secretum of the pancreas subserves the glycogenesis of the liver. No effort was made to detect whether this influence is due to a diminished splitting of the glycogen in the liver or perhaps to an increased formation of glycogen. As known, J. DE MEIJER <sup>2)</sup> has pointed out that various pancreatic extracts, which are made to pass artificially through the liver, cause a relative increase of glycogen. On the basis of these investigations DE MEIJER accepted the second alternative. I have also endeavoured to make up my mind about this question, in a different way from DE MEIJER'S though, partly because circumstances compelled me to adopt a different method, in default of the expensive apparatus for artificial circulation, partly because the results of DE MEIJER'S experiments did not appear to me altogether conclusive on the following grounds:

1. frequent errors are incidental to artificial circulation, so that out of 17 of DE MEIJER'S experiments 6 (= 1/3) were discarded outright;

2. after all, we are disposed to think that critics must find fault with the values DE MEIJER obtains in his glycogen-determinations and especially with his way of calculating large percentages from insignificant absolute differences. Some examples to illustrate this;

i.e. page 48 we are told that a double circulation evolves an increase of 0.00158 % of glycogen. In the 4<sup>th</sup> experiment on page 49 the examination of about 70 grs of liver yielded an absolute difference of 0.00428 grs. of glycogen. Still the percentage differences for these experiments were given even as high as 15 and 20 perc.

I, therefore, followed out another plan, which of course will also be at fault in one way or other, but which, in my opinion, resulted in very serviceable evidence. I proceeded as follows:

A number of dogs were put under a profound narcosis and during one hour and a half they were given in most cases per jugular vein, rarely per pancreatic duodenal vein, a certain dose of LOCKE'S

<sup>1)</sup> These Proc. Vol. XVI, p. 2.

<sup>2)</sup> J. DE MEIJER, Archives Internat. de Physiologie, Vol. IX, 1910.

olution or of venous blood from a normal dog or of blood from the pancreatic duodenal vein. The amount of glycogen was estimated before and after the irrigation.

To this conduct of the experiment the following objections may be raised:

1. One dog is more susceptible to the narcotic than another, and moreover reacts in a different way (to mention an essential point, there is a difference in the duration and in the intensity of the stage of excitation).

2. A laparotomy is performed and part of the liver is extirpated *durante vita*, to which stimulant acts various dogs are apt to respond in different ways.

3. Some loss of blood is inevitable.

We should bear in mind, however, that every experiment upon a living organism must involve errors, but also that if the experiment is performed upon a large number of animals these errors may probably neutralise each other in part or altogether.

*Method:* Dogs of from 4 to 22 KGs. were narcotized with chloroform; the abdomen was opened and a portion of the liver was removed. The following precautions were taken; the operation was always performed in a very warm room (21°—26° C.) to minimize the fall of temperature. The narcosis was as profound and as restful as possible. The portions of liver removed varied between 20 and 50 grs.; they were cut off by means of scissors that were rather blunt and had been warmed beforehand; there was no fear of parenchymatous bleeding and only some large veins had to be ligated. The abdomen was left open only for a very short space except of course in the two cases of injection per pancreatic vein) and even then the laparotomy-wound was covered throughout the whole experiment with a warm tampon, soaked with physiological salt solution. Subsequently fluids were injected per jugular vein for one hour and a half in most of the experiments. Irrigation was performed from a burette on stand, so that the velocity of the flowing liquid could be regulated by means of a tap.

After one hour and a half another piece of liver of approximately equal weight was cut off as fast as possible.

Finally a determination was made of the amount of glycogen of both pieces of liver. In order to ensure a proper amount of glycogen the animals had been given about eight hours before the operation a diet consisting of 100 grs. of cake. Owing to outward circum-

stances this was not done in one case, and in another the meal was given only 5 hours prior to the operation.

The amount of glycogen was estimated after PFLÜGER's method; immediately after the extirpation the portions of liver were put in a 60% solution of KOH and were weighed.

The detailed reports of the experiments contain particulars relative to the fluids injected intravenously.

#### FOURTH SERIES (D).

1. On the 24th of December 1912 I extirpated 38 grs. of the liver of a dog, weighing  $5\frac{1}{2}$  KG, which had been fed with amylacea eight hours before. The piece of liver was forthwith subjected to the process described. Hereafter I injected per pancreatic duodenal vein 50 cc. of a mixture of 100 cc. of serum + 50 cc. of defibrinated blood + 50 cc. of LOCKE's solution.

The remaining 150 cc. of this mixture was injected slowly per jugular vein. After an hour's irrigation another portion of liver of 24 grs. was removed and subjected to the same process.

The blood and the serum had been obtained the evening before from the pancreatic vein of a dog under the influence of a subcutaneous injection of 50 cc. of secretin. The blood had been kept cool, not in the refrigerator.

The glycogen of the 1st portion of liver amounted to 3.825 %.

" " " " 2d " " " " 3.905 %.

So there was a slight increase of glycogen of 3 %.

2. On the 28th of December 1912 26 grs. of liver were taken from a dog of 12 KG. Directly after this 180 cc. of LOCKE's solution was given per jugular vein from a burette in the space of two hours. The laparotomy-wound was covered with warm tampons. At the end of the experiment the rectal temperature was 36.7°. The solution had been heated to 30° C., the room-temperature was 20—22° C. After the irrigation a second portion of the liver (29 grs.) was excised.

The amount of glycogen of the 1st portion was 1.71 %.

" " " " " " 2d " " " " 0.895 %.

This reveals a considerable loss of glycogen of 50 %.

3. On the 30th of December 1912 a dog weighing 15 KG. was irrigated in a similar manner with 180 cc. of LOCKE's solution during one hour and a half. Beforehand 41 grs. of liver had been extirpated and again 37 grs. after one hour and a half.

The amount of glycogen of the 1st portion was 3.995 %.

" " " " " " 2d " " " " 1.712 %.

Consequently a loss of 56 %.

4. A dog of 8 KG., which had not had the ordinary diet, was irrigated intravenously with the following mixture: 60 cc. of defibrinated blood + 40 cc. of serum, obtained from jugular blood collected the day before from a healthy dog. To this mixture was added 50 cc. of LOCKE's solution. The irrigation lasted one hour and a half. Beforehand a portion of the liver (31 grs.) had been removed. After the irrigation a piece of 34 grs.

The amount of glycogen of the 1st piece was 0.171 %.

" " " " " " 2d " " 0.11 %.

So the loss was 36 %.

5 On the 6th of January 1913 the following mixture was thrown into a dog of 9 KG. per jugular vein during one hour and a half: 88 cc. of blood + serum (obtained from the pancreatic duodenal vein under the influence of secretin) + 70 cc. of Locke's solution. Room-temperature somewhat lower than usual (20° C.). The abdomen was covered with warm cloths soaked with a physiological salt-solution.

39 grs. of liver had been removed before the process, 30.8 grs. after it.

The amount of glycogen of the first portion was 4.23 %.

" " " " " " second " " 4.17 %.

In neutralizing portion 1 after the inversion a slight excess of KOH was added somewhat too quickly, which originated a light brown decoloration.

6. On the 19th of January 1913 a dog of 11 KG was given per jugular vein during one hour and a half a mixture of 100 cc. of serum + blood + 40 cc. of Locke's solution. The blood had been obtained the previous evening from the pancreatic vein under the influence of secretin. The dog from which it had been drawn was very old. The pancreas had greyish white spots, rather smaller than a threepence; there was besides suppuration of the cysts in the postate; the urine, however, contained no trace of sugar whatever.

After the first extirpation of liver venous hemorrhage ensued, which could be staunched only by ligation. The room-temperature was 19° C.

Previously 26.6 grs of liver had been excised. After one hour and a half 29 grs.

The amount of glycogen before the irrigation was 3.61 %.

" " " " " " after " " " 2.87 %.

This points to a loss of 21 %.

7. On the 25th of January 1913 the following mixture was used per jugular vein upon a dog of 5.5 KG.: 60 cc. of defibrinated blood + 30 cc. of serum from the jugular vein of a normal dog + 50 cc. of Locke's solution. Room-temperature 26°—22° C. Duration of the test one hour and a half.

32 grs. of liver had been removed previous to the irrigation, 29.7 grs. after it.

Amount of glycogen before the irrigation 2.638 %.

" " " " " " after " " " 1.677 %.

Loss 33 %.

8. On the 28th of January 1913 24.8 grs. of the liver of a dog (6 KG.) was excised. Injection per jugular vein of: 25 cc. of defibrinated blood + 40 cc. of serum from the pancreatic vein (obtained the evening before) taken up with 20 cc. of Locke's solution are freed from protein by three times their quantity of 96 % alcohol. After filtration the mixture is evaporated down to 80 cc. at 70° C. and again Locke's solution is added to 150 cc. A filtration error causes a loss of 50 cc. so that an equivalent volume of Locke's solution has to be added again.

24.8 grs. of liver had previously been removed and 23.8 grs. after one hour and a half.

Amount of glycogen before irrigation 2.024 %.

" " " " " " after " " " 1.03 %.

Loss 50 %.

During the irrigation the dog had two syncopes so that the respiration had to be maintained artificially.

9. On the 31<sup>st</sup> of January 1913 a dog of 7 KG. was given 200 cc. of a mixture of 50 cc. of blood + 100 cc. of serum obtained the previous evening under the influence of secretin from the pancreatic vein of a dog. Lockæ's solution was added to 200 cc. Besides a secretin injection this dog had also had a light meal of carbohydrates.

The irrigation lasted one hour and a half; only once breathing came to a standstill.

Beforehand 25.1 grs. of the liver had been excised, afterwards 28.4 grs.

Amount of glycogen of the 1<sup>st</sup> portion was 2.36 %.

" " " " " 2<sup>nd</sup> " " 1.77 %.

Loss 20 %.

10. The same large dog from which pancreatic blood had been drawn for injection of the dog in N<sup>o</sup>. 9, had the pancreas removed. Part of this ( $\frac{2}{3}$ ) was rubbed up with about 40 cc. of Lockæ's solution and mixed with three times this quantity of 96 % alcohol. After filtration this liquid was evaporated down to  $\frac{1}{3}$  of its volume in a porcelain dish at 70° C. and subsequently Lockæ's solution was added to 180 cc.

Three days after the preparation (on the 3<sup>rd</sup> of February) the liquid was thrown into a dog of 4 KG.

Previously 13.2 grs. of liver had been extirpated. 12.4 grs. one and a half hour later.

The amount of glycogen of the first portion was 2.41 %.

" " " " " second " " 1.48 %.

The loss, therefore, appeared to be 37 %.

11. On the 11<sup>th</sup> of February 1913 a dog of 12 KG. was given during one hour and a half per jugular vein normal blood (100 cc. made up to 140 cc. with Lockæ). First I tried to inject part of it per pancreatic vein. However, when 10 cc. had been injected a venous hemorrhage had to be staunched. We therefore performed further injections per jugularis.

Four hours before the dog had taken a copious meal of amylacea so that the digestive process was at its height. The narcosis proceeded regularly.

Of the liver 14.6 grs had been removed before the injection and 40 grs an hour and a half after it.

Amount of glycogen of the first portion 7.823 %.

" " " " " second " " 6.433 %.

Here the loss was 18 %.

12. An extract of the pancreas of the dog whose normal blood had been used in N<sup>o</sup>. 11 was used upon a dog of 5 KG. The extract had been prepared as follows: The pancreas, weighing 23 grs, was rubbed up with Lockæ, then heated for one hour and a half to 60° C. to destroy the ferments; after this it was subjected to a low temperature (about 5° C.) and used next day after filtration through cotton wool and addition to 190 cc. After precisely an hour's irrigation a shock occurred; in less than no time a portion of the liver was cut off.

Extirpation of 14.6 grs of liver before injection; after an hour 13.3 grs.

Amount of glycogen of the 1<sup>st</sup> portion 10.88 %.

" " " " " 2<sup>nd</sup> " " 6.76 %.

\* Loss after an hour 38 %.

13. On the 25<sup>th</sup> of February a mixture of secretin and Locke's solution was thrown into the jugular vein of a dog weighing 7 KG. The secretin had been prepared as follows: In the space of 2 × 3 hours an extract was made of the mucous membrane of the duodenum with absolute alcohol in Soxhlet's apparatus; only then it was macerated with HCl and after boiling up neutralized with sodium. There was a secretin solution of 50 cc. to which 130 cc. of Locke's solution had been added. Irrigation for one hour and a half.

Of the liver 24 grs had been excised before the injection and 33 grs one hour and a half after it.

Amount of glycogen of the 1<sup>st</sup> portion 4.356 %.

" " " " " 2<sup>nd</sup> " 2.697 %.

Loss of glycogen 37 %.

14. On the 3<sup>rd</sup> of March a dog of 6 KG. was given per jugular vein 50 cc. of pancreas blood + 60 cc. of serum + 50 cc. of Locke's solution, obtained the preceding evening from a dog under the influence of secretin.

The dog was very restless under the narcosis; vomiting occurred twice.

Before the injection 37 grs of liver had been removed; 21.9 grs one and a half hour after it.

Amount of glycogen of the 1<sup>st</sup> portion 9.035 %.

" " " " " 2<sup>nd</sup> " 6.683 %.

Loss 26 %.

T A B L E I.

Liquid injected	Gain or Loss of glycogen	Time of irrigation	Particulars
Secretin-Pancreas venous blood	+ 3 %	1 hour	
" " " "	- 20 %	1 1/2 "	Bloodserum from old dog
" " " "	- 1 %	1 1/2 "	
" " " "	- 25 %	1 1/2 "	
" " " "	- 26 %	1 1/2 "	Excitation under narcosis
Normal blood	- 36 %	1 1/2 "	No diet
" "	- 33 %	1 1/2 "	Copious diet
" "	- 18 %	1 1/2 "	
Aqueous extract of the pancreas	- 50 %	1 1/2 "	Restful narcosis
Alcoholic extract	- 37 %	1 1/2 "	
" "	+ 5 %	1	
Secretin	- 37 %	1 1/2 "	
LOCKE's solution	- 47 %	2 "	
" "	- 56 %	1 1/2 "	
Aqueous extract of the pancreas	- 38 %	1	

15. An alcoholic extract of the pancreas, the blood of which had been used in the foregoing test was given to a large dog of 30 KG. The extract had been prepared in the following manner: 20 grs of pancreas had been rubbed up and macerated with 100 cc. of 65% alcohol. During  $\frac{3}{4}$  hour this macerated substance was evaporated down to  $\frac{1}{3}$  of its volume at 65°C., made up to 180 cc with LOCKE's solution and filtered through wadding.

The dog received this fluid during one hour through the jugular.

The first portion removed from the liver was 33 grs.

The second (an hour later) 35 $\frac{1}{2}$  grs.

Amount of glycogen of the 1<sup>st</sup> portion 4.124 %.

" " " " " 2<sup>d</sup> " 4.356 %.

The narcosis was remarkably restful, without any disturbance

In this experiment there was a gain of 5%.

For an easy survey we summarize the results of this series of experiments in the preceding table.

### CONCLUSIONS.

Above all we observe that narcosis, laparotomy and liver-extirpation, in spite of continual irrigation by injection of a fluid deemed favourable, result in a loss of glycogen. This is after all not surprising, if we bear in mind that a number of glycolytic factors act upon the liver. Among others: the narcosis per se, often associated with considerable agitation; the animal's emotions; sometimes spasmodic contractions caused by vomiting; loss of blood; fall of body-temperature. Nevertheless the fact deserves consideration in view of the surgical process. The loss of glycogen averaged about 50%. Furthermore it follows from our experiments, that if defibrinated blood and serum is given instead of LOCKE's solution, the decrease of glycogen is considerably less. An injection of venous blood from a normal dog lowers the amount of glycogen to about 29% i.e. about half of the average. The average fall is still greater if irrigation is accomplished with blood collected from an active pancreas. Then the average decrease is only about 15%, i.e.  $\frac{1}{3}$  of the splitting caused by irrigation with LOCKE's solution.

Irrigation with normal blood, more particularly with pancreatic blood, therefore, inhibits the loss of glycogen in the liver, nay in one very successful experiment even a slight increment of glycogen was noticeable.

We have now to consider the problem as to how this result was effected. Three hypotheses offer themselves for discussion.

a. The blood favours glycogenesis.

b. The blood impedes glycogenolysis.

c. The blood neutralizes the inimical influence of the narcosis.

As for the third theory it seems to me that the volume of the injected blood and serum (about  $\frac{1}{10}$  of the blood of the body) is too small to act vigorously. With regard to the other two, I do not think it quite possible as yet to decide in favour of either of them. Still, I incline towards the former, because occasionally an augmentation of glycogen was to be noted, which on no account can be originated by prevention of splitting alone. It is obvious that most often the splitting prevailed over the formation of glycogen.

Additional conclusions from this series of experiments are the following:

In two cases an aqueous extract of the pancreas yielded negative results; positive results, however, were obtained twice from an *alcoholic* extract. Aqueous extracts and LOCKE'S solution resulted in an equivalent fall of the glycogen, alcoholic extracts in one instance in  $\frac{2}{3}$  of the average, in another a rise of 5% was observed. It seems then that *the exciting agent of the pancreas is soluble in alcohol*, not in *water*. It is probable therefore, that this agent is present in the blood rather in physical adsorption than in chemical solution.

Again the thermostability was proved in both experiments. Lastly we notify that a secretin deprived by alcohol of its vaso-dilating substances acted favourably upon the amount of glycogen in the liver.

#### *Results compared with those of DE MEYER.*

Broadly speaking also this series of experiments lends support to J. DE MEYER'S evidence. Our methods of investigation differ essentially, which renders the ultimate accordance in our results all the more satisfactory. My plan differs from DE MEYER'S 1. in experimenting *in vivo* with all its drawbacks and advantages; 2. in the lack of double circulations in the liver.

The accordance in our results consists in:

1. aiding the glycogenesis even through normal blood more than through a physiological salt solution.
2. a greater activity in this respect of blood that has passed through the pancreas.

It may also be remarked that the volume of the injected fluid is considerably smaller than DE MEYER uses in his experiments. It should be borne in mind, however, that I worked *in vivo*, an advantage of which is that glycogenetic factors are allowed to exert an action beforehand, since a normal fluid containing sugar passes through the liver.

## Recapitulation :

1. Normal blood, in a higher degree still blood from the pancreatic vein, aids the glycogenesis of the liver.
2. Alcoholic extracts of the pancreas seem to have the same effect.
3. The material which incites this action is thermostable.

## FIFTH SERIES (E).

We considered the following problem. If it is a fact that the pancreas furnishes the venous blood with a substance, that promotes the glycogenesis, it follows that in the case of experimental pancreatic diabetes, when especially also the liver-glycogenesis is disturbed, a favourable influence of this blood upon the progress of the disease must be noticeable. We have set ourselves the task to ascertain this.

*Method.* Of some dogs the pancreas was extirpated in the following way: With the utmost attention to asepsis the abdomen was opened by an incision parallel to the right arcus costalis. While the bleeding was being stopped with due care, the pancreas was searched for and extirpated after HEDON's method. An essential characteristic of this process is that no ligatures are applied along the duodenum, but that the pancreas is separated from the duodenum by scratching with a sharp nail and the bleeding is staunched only by plugging vigorously with a tampon, another characteristic is that particular caution is given to ligation of a small vein, which joins the tail of the pancreas to the spleen. Now in reality HEDON's method applies to extirpation of the entire pancreas in two stages (part of the proximal extremity of the pancreas, which is provided with a separate vascular bundle, is transplanted under the skin of the abdomen). However, extirpation of the entire pancreas did not answer our purpose, because it quickens and aggravates the pathological progress to such an extent that it becomes difficult to watch the effect of some therapeutic procedures. We did not see the necessity for transplanting part of the pancreas, and only left a piece of it intact (at a rough estimate 2 to 3 grs) in the neighbourhood of the place where the ductus choledochus enters into the duodenum. An additional advantage of this method is that icterus, which often ensues from an extirpation of the pancreas, can be avoided. The abdomen was irrigated with a warm physiological solution, after which the different layers were closed successively. Most times the animals recovered pretty soon. We subjoin the experiments which resulted in diabetes after a partial excision of the pancreas. Parenthetically I wish to recall to mind an extirpation,

TABLE II

Date	Weight	Diet	Urine	D percentage	D total	N total	D/N	Acetone	GERHARD	Particulars
ne 14	4.4 KG.	none	80 cc	0.4 ‰	0.32	—	—	—	—	
" 15	4.4 "	vomiting	175 "	0.2 "	0.35	—	—	—	—	
" 16	"	100 grs of horse flesh + 350 grs of milk	230 "	6.48 "	15.55	2.92	5.36	—	—	
" 17	"	"	320 "	4.6 "	15.04	3.83	3.82	—	—	{ very hungry and thirsty as on all following days
" 18	"	"	120 " } 145 " }	4.1 "	10.86	2.445	4.44	—	—	
" 19	"	"	121 " } 70 " }	6.7 " } 10.8 " }	8.107 } 7.56 }	1.50 } 1.00 }	5.30 } 5.8 }	—	—	At 8 p. m. i. e. after the first 12 hours subcuta- neous injection of 35 c.c of blood from the panc- vein collected the previ- ous evening under the influence of secretin.
					15.66	2.80				
" 20	4.35 "	"	162 " } 142 " }	5.8 " } 4.2 " }	9.39 } 5.96 }	1.92 } 1.68 }	4.88 } 3.58 }	—	—	
					15.35	3.60				
" 21	"	"	144 " } 142 " }	4.1 " } 3.8 " }	5.96 } 5.39 }	1.90 } 1.60 }	3.20 } 3.36 }	—	—	
					11.35	3.50				
" 22	"	"	112 " } 140 " }	2.43 " } 6.35 " }	12	1.80 } 3. — }	2.6	—	—	
" 23	4.2 "	"	180 " } 110 " }	7.03 " } 3.15 " }	16	5	3.2	—	—	
" 24	"	"	160 " } 160 " }	6.2 "	19.8	4.33	4.6	—	—	
" 25	4.1 "	"	205 " } 113 " }	5.2 " } 10.4 " }	10.60 } 11.3 }	1.91 } 2.17 }	5.56 } 5.40 }	—	—	After these 12 hours another subc. inj. of 20 c.c of blood from the pancr. vein. One hour after the inj. the values of bloodsugar are compa- red. Before the injection 0.227‰; after it 0.237‰. Blood was drawn under a light narcosis by chlo- roform.
					21.9					
" 26	4.1 "	"	232 " } 160 " }	6.9 " } 6.7 " }	26.7	6.2	3.66	—	—	
" 27	"	"	324 " } 120 " }	7.2 "	31.5	7.75	4	—	—	

which did not lead to diabetes even after 6 weeks, although the venous blood of this dog (see Exp. 34. Table V of the previous publication) was competent to occasion a fall of the N-metabolism in another dog in N-equilibrium.

*Experiment 55.* A little dog ( $4\frac{1}{2}$  KG.) had on the 13<sup>th</sup> of June 1912 its pancreas (14 grs.) removed in the manner just described. The animal passed well through the operation. The table on page 257 gives the history of the disease together with the particulars worth mentioning.

For want of further particulars I leave off tabulating. Suffice it to say here, that glucosuria was increasing all along to as much as 40 grs. and more, that the N-metabolism was maintained constant, that, however, on the 1<sup>st</sup> of July acetone appeared for the first time and the animal was killed on July 4. The section brought to light a small portion of the pancreas of the size of a die, which looked unimpaired.

All organs had exchanged their natural colour for a yellowish white. This was due to strong lipemia, which made the bloodserum creamlike.

The effect of our injections is of course a matter of the highest interest to us. From the values recorded above we may be justified in deducing the following:

The first injection of 35 cc. of pancreatic blood lessens the diuresis and raises the glucose percentage to such an extent (from 6 to 10%) that it cannot be a matter of mere chance. However, the N-percentage does not rise so much, so that D/N increases. For all this there is no augmentation of the quantity of sugar secreted on the day itself nor on the two subsequent days. On the contrary it is slightly lowered (15—11 grs.), which can neither be a casual fluctuation, as for instance on the 18<sup>th</sup> of June, since the decrease continued for more than twice 24 hours. This decrease coincides with a process in the composition of the urine which is the reverse of the one just mentioned, viz. an increase of the N-amount and of the diuresis and a fall of the glyco-se-percentage. The effect of the second injection, on the 25<sup>th</sup> of June, is far less obvious, it is almost negative. It is true, only 20 cc. is injected and the dog is subjected to a slight narcosis with chloroform prior to the puncture of the vein, but here a temporary rise of the glycogen-percentage is followed by a fall; the quantity of urine, however, first remains constant and increases later on. Absolute decrease of the sugar secreted is out of the question, rather the reverse takes place. Neither do we note any favourable influence of the injection on the hyperglykemia.

*Experiment 57.* On the 19th of September 1912 a rather large dog (11 KG.) has  $21\frac{1}{2}$  grs. of the pancreas extirpated after the ordinary method: a small duodenal portion is left in the abdomen. The operation was attended with some troubles: frequent escape of blood and repeated vomiting occurred. Recovery ensued without complication and on the 22d of September the dog was restored so far, that he took meat and drank milk. The urine contained bile-pigments but no sugar.

TABLE III.

Date	Diet	Weight	D per-centage	D total	N total	D/N	Acetone	Urine	Particulars
ct. 2	300 grs of horse flesh, 150 grs of cake. 200 grs of water. Afterwards unlimit.	10.7 KG.	3.5 %	7 Gr.	—	—	—	200	Greedy for food and drink.
, 3	"	—	4.25 "	8.5	4.96	1.7	—	200	
, 4	"	—	3.6 "	8.2	8.05	1	—	230	
, 5	"	—	—	—	—	—	—	465	Severe diarrhea interrupting the experiment for some days.
, 10	"	—	9.6 "	46	—	—	—	480	Towards the close of these 24 hours the animal is given subcutaneously serum of the blood from the pancreas vein, obtained the previous evening under the infl. of secretin (100 c.c.)
, 11	"	—	9 "	57.6	10.7	5.4	—	640	
, 12	"	10.3	8.2 "	77.9	10.45	7.6	—	950	
, 13	"	—	11.33 "	56.6	not determined	—	—	500	
, 14	"	—	10.2 "	66.3	7.8	8.5	—	650.	
, 15	"	—	8.7 "	73.9	9.35	7.9	—	850	
, 16	"	—	10.5 "	89.2	8.4	8.8	—	850	
, 17	"	—	10.4 "	100.8	10.3	10.1	—	1050	Great thirst. Appetite lessens.
, 18	"	—	10.3 "	103	11.6	9.1	—	1000	
, 19	"	—	10.8 "	92	7.9	11.6	—	850	The animal stops eating and declines rapidly.
, 20	"	?						800	The animal is killed.

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On the 2d of October i.e. only a fortnight after the operation the first traces of sugar appear. The substances just mentioned have disappeared.

The following table gives particulars about the experiment with this animal.

*Retrospect.* Here we have a case of a typical incomplete pancreatic diabetes (SANDMEYER). Not until a fortnight after the extirpation diabetes is gradually evolved and reaches its acme only after three weeks.

With regard to the injection of blood from the pancreatic vein, obtained the previous evening under the influence of secretin, we notice an effect similar to that of the foregoing experiment. In the first place a smaller quantity of urine associated with a rise of the D-percentage. As for the N-percentage the values are not very demonstrative, because the urine had been standing for more than 24 hours. We could not make a reliable Kjeldahl-determination on the most important day (Oct. 13). Still also in this case a relative decrease seems to have occurred, succeeded by an insignificant increase.

Lastly it appeared again that after injection the total D-secretion was for some days considerably lower than before.

On the 19<sup>th</sup> of October the animal was sinking so fast, that sub finem vitae D-secretion as well as N-elimination was retroceding. On this account the animal was despatched.

At the section no considerable modifications (lipemia) were detected; owing to several adhesions nothing was to be seen of residues of the pancreas.

*Experiment 59.* In my judgment the following test yields weighty evidence. The time of observation was longer. Four injections of pancreas secretum were given.

In the ordinary way 20½ grs. of the pancreas of a dog is extirpated on the 22d of September 1912. At a rough guess 2 grs. is left in the abdomen. Operation comes off quickly and without a hitch. As early as the 23d of Sept. the dog takes water and milk. A trace of protein and a small quantity of sugar is present in the urine. On the 24th of September the dog is tolerably well, only somewhat languid, vomits once more, but eats some horseflesh and cake. A considerable amount of sugar is present in the urine. The following table illustrates our subsequent experience.

*Retrospect.* This is a serious case of diabetes, clearly demonstrating the influence of different acts. The first two injections were attended by an irregular secretion of urine on the preceding days, as evidenced respectively by 8 and 17 grs. of sugar on the 27<sup>th</sup> and 28<sup>th</sup> of September, which, when expressed graphically, yields

T A B L E I V.

	Diet	Urine	D %	D total	N total	D/N	Acetone	Particulars
25	150 grs flesh 10 » cake	292	3.6%	10.6	3.89	2.7	—	Dog languid, not greedy, not very thirsty.
26	»	214	5.1 "	10.9	3.616	3.3	—	
27	200 grs flesh 10 » cake	150	5.3 "	8	2.41	3.—	—	
28	»	234	7.3 "	17	6.22	2.7	—	
29	»	38	2.9 "	1.1	1.9	3.3	—	50 c.c of pancreas serum obtained the previous evening and maintained at 0-6° C. is injected intravenously after first 12 hours.
		144	7.4 "	10.6	3.14			
30	»	186	6.1 "	11.3	4.27	2.6	—	
1	»	100	8.6 "	8.6	1.99	4.3	—	Again 50 c.c. of the same serum 72 hours old is injected at the beginning of the following 24 hours.
2	»	228	10.2 "	23.2	7.43	3.1	—	
3	»	150	7.5 "	11.25	3.—	3.75	—	
4	»	240	8.1 "	19.4	6.9	3.2	—	
5	»	180	10.6 "	19	5.99	3.1	—	
6	»	100	8.7 "	8.7	3.5	2.5	—	After the first 12 hours subcut. inj of 120 c.c of defibrinated blood collected the evening before under the influence of secretin from the pancr. vein and kept cool. Greater appetite.
		78	9.1 "	7.1	3.25			
7	»	183	9.1 "	16.67	5.83	2.9	—	
8	»	182	9.2 "	16.6	4.51	3.3	—	
9	»	170	9 "	15.3	4.42	3.5	—	
10	»	278	6.9 "	18.9	6.83	2.7	±	
11	»	255	8 "	20.4	6.63	3.1	—	
12	»	170	9.38	27.2	6.11	4.4	+	After the first half of the 24 hours 95 c.c. of pancreas blood-serum of the previous evening and kept cool, is injected subcutaneously.
		120						
13	»	200	11.1 "	22.2	5.84	3.8	++	Even now the dog refuses any food. No appetite at all.
14	»	66	7 "	4.6	3.—	1.5	+++	
15	»	68	10 "	6.8	2.56	3.6	++	
16	»	224	10.6 "	23.7	5.42	4.—	+++	
17	»	118	8.3 "	9.79	4.41	2.2	+	After the 17 <sup>th</sup> the dog declines rapidly, does not eat and cannot be made to move.
		205	7.5 "	15.3	3.15	4.9	±	
18	»							
19	»	58	5 "	2.9	1.62	1.7	±	
		78						
		136						
21	»							Dog despatched forthwith after complete paralysis had set in also of the muscles of the maxilla.

false apices. To all appearance the average value approximates the truth. It was moreover a mistake to make the second injection after too short an interval from the first; this was done lest the activity of the substance should get lost, it would have been better to inject both portions simultaneously. Yet also after these injections a relatively slight fall of the *D*-secretion appears to take place, which is still perceptible after a few days. Furthermore a short increase of the *D*-percentage is to be noted especially after the second injection by virtue of which the *D/N* coefficient rises considerably.

The results of the third and the fourth injections are still more demonstrative. At the third the *D*-secretion during three days falls short of what could be expected from the rise of the previous days. Later on the excretion of sugar, likewise that of urine increases rapidly. The changes in *D*- and *N*-concentration are not conspicuous. The fourth injection results in still more striking alterations. The total *D*-secretion is lowered from 27 grs to 22 grs and 6 grs. The quantity of urine diminishes from about 300 to 200 and 60 cc. The *D*-percentage is suddenly exalted to rather more than 11 % and the *D/N*-coefficient to 4,4, and 3,8 to fall again later on to 1,5. Here then we have an accumulation of all the alterations announced beforehand. Some particulars however must not be forgotten, viz. after the 13<sup>th</sup> of October the dog declines nearly all food. However, this fact does not in itself elucidate matters satisfactorily, since on the 16<sup>th</sup> of October the sugar-secretion is normal again.

Secondly the table shows that on the 12<sup>th</sup> of October acetone is found in the urine for the first time, which no doubt will be attended with other changes in the metabolism. Even this, however, does not lessen the value of our results, seeing that acetonuria was on the decrease and ultimately disappeared entirely, when the animal was sinking rapidly and was *sub finem vitae* on the 17<sup>th</sup> of October. This proves that spontaneous lowering of the *D*-secretion *sub finem vitae* (a well-known phenomenon) must be carefully distinguished from the *D*-secretion after injection which contrariwise evolves a separation of large quantities of acetone.

We have to add in this connection, that we suspect the 4<sup>th</sup> injection to have been noxious to the animal's condition, which was not surprising after all. At the section a considerable loss of flesh was demonstrated; there was no lipemia; no trace of pancreatic residue was found.

We record one noteworthy experience. In examining the mouth cavity of the animal bulbous tumours at the mucous membrane of

the lips drew our attention; at the section it appeared that as well at the lips as at the sublingual and buccal membrane these greyish white protuberances were visible and arranged symmetrically. Especially in the sublingual membrane, symmetry was most pronounced at the excretory ducts of the salivary glands. Thinking of the relation between the pancreas and the salivary glands we supposed this to be a vicarious hypertrophy of the salivary glands. A microscopic examination however did not lead to detection of any glandular tissue but only to a rankling growth of the epithelium.

### CONCLUSIONS.

*A* The blood obtained under the influence of secretin from the pancreatic vein is capable of lowering the total secretion of sugar for some days, but also of raising the sugar-percentage temporarily.

*B.* The blood commonly evolves a relative fall of *N*-elimination close upon the injection, later on a relative rise

These experiences fall in with those recorded in our earlier publications. For instance the rise of the *D*-percentage after injection of blood from the pancreatic vein is in perfect concordance with the fact that the same blood, thrown into normal dogs, also incites glucosuria. On the other hand the influence on *N*-elimination in dogs suffering from pancreatic diabetes, is just the reverse of the influence in normal dogs.

*Critical summary.* A comparison of our results with those of other researchers shows some notable differences. It is self-evident that soon after the theory of the internal secretion of the pancreas had been propounded, efforts should be made to render pancreatic diabetes less virulent by throwing blood of healthy dogs into dogs suffering from the disease. MINKOWSKI and HÉDON were the first to make the effort. Their failure strengthened PELUGER's contrary views. Afterwards, indeed, some positive evidence was brought forward by FORSCHBACH<sup>1)</sup>, who, by application of the parabiosis between healthy and diabetic dogs elaborated a decrease of sugar secretion. EHRMANN, who also applied transfusion, failed again. Latterly similar experiments have been made by DRENMAN<sup>2)</sup> and HÉDON<sup>3)</sup>. DRENMAN obtained a very marked decrease of sugar secretion, after intravenous injection of large quantities of normal blood. This blood, however, had lost

<sup>1)</sup> FORSCHBACH, Arch. f. exp. Path. u. Pharmat. Bd. IX, 1908.

<sup>2)</sup> DRENMAN, American Journal of Physiol. Vol. XXVIII, 1111.

<sup>3)</sup> HÉDON, Refer. Dr. v. HERWERDEN. Nederl. Tydsch. v. Geneesk. 1913.

its activity about 12 hrs after having been collected, which proved, according to DRENMAN that the exciting factor is highly labile and that the dilution of the diabetic blood cannot be responsible for the result. HÉDON, on the contrary, inquiring into the effect of transfusion of blood by vascular connection, from normal into diabetic dogs, ascribes the decrease of sugar secretion in the diabetic animal only to the dilution of the hyperglycemic blood, while he attributes a strong inhibitory influence on the renal secretion to transfusion.

My experience differs from DRENMAN's in that I did not detect anything at all of a marked lability of the active factor in the pancreatic blood; anyhow, after more than 20 hours subsequent to the removal of the blood, activity was still noted. This may be only a quantitative difference, because in theory there are more active materials in the pancreatic blood than in the general circulation. It also seems to me a sheer impossibility, to attribute the results, reported here, to dilution of blood; first and foremost because the quantity injected was too small in most cases; secondly the injection was subcutaneous, so that resorption was slow; thirdly the action was continued too long (on an average 2 days). In concordance with HÉDON's experiments I detected an influence upon the renal secretion, not in such a marked degree, however, that it could bear up my results. Lastly a permanent influence on the N-elimination was demonstrated.

**Physics.** "*On the interpretation of photospheric phenomena*". By Prof. W. H. JULIUS.

(Communicated in the meeting of May 31, 1913).

§ 1. It is a common belief that a body always presenting the appearance of a circular disk, from whichever side it is looked at, must be bounded by a spherical surface. The general conviction that the bulk of the sun is an incandescent sphere rests on that belief, and was a natural starting-point for solar theories.

After the effective solar temperature had been found so high as to exceed the critical temperatures of perhaps all known substances, the earlier idea that the main body of the sun was in the liquid or the solid state had to be replaced by the hypothesis that it is substantially gaseous. This new idea involved the necessity of explaining the phenomenon of the apparent "solar surface". One had to choose between YOUNG's view, that the photosphere was a

layer of incandescent clouds produced by condensation of certain substances having exceptionally high critical temperatures, and SECCHI's hypothesis (afterwards developed by SCHWARZSCHILD and EMDEN), which dispenses with assuming cloud-formation by supposing the density of the solar gases to increase so rapidly with depth near the level called "solar surface", that within a layer no more than a thousand kilometers thick, their united radiating power increases from a very low value (in the chromosphere) up to that of the black body (in the photosphere).

In 1891, AUGUST SCHMIDT took a new departure by showing that an entirely gaseous body of the dimensions of the sun, in which the density and the radiating power gradually decrease from the center outward — be it even at a slow rate — must appear like a circular luminous disk with a sharp edge, as a mere consequence of ray-curving caused by the radial density gradient. So the circular aspect of the sun is *not* a sufficient ground for admitting the existence of a real "photosphere", that is, of a layer characterized by some abrupt, or even only rapid change of physical properties.

SCHMIDT's well-known solar theory, however, met with the severe objection that it did not duly consider the effect of absorption and scattering of the light<sup>1)</sup>. Rays having accomplished such long distances on their spiral paths inside the critical sphere would be almost wholly extinguished before emerging; they could not possibly bring along so much energy from the incandescent core, as would be required in order to account for the brilliancy observed in the marginal parts of the disk. In its original form the optical interpretation of the sun's edge cannot be maintained.

It is also impossible to accept the cloud-theory of the photosphere, because the results of the radiation-measurements made at Maastricht during the annular eclipse of 1912<sup>2)</sup> forbid making an absorbing or scattering solar atmosphere responsible for the fall of the sun's brightness from the center toward the limb. Indeed, the absorbing and scattering power of the gases lying outside the photosphere proved to be relatively insignificant. The photosphere, therefore, cannot be of such a nature that it would appear like a *uniformly* luminous disk if the surrounding gases were absent. On the contrary, it must have in itself the property of appearing much brighter when looked at in the direction of a radius than at an angle with the

<sup>1)</sup> R. EMDEN, Gaskugeln, S. 388—394.

E. PRINGSHEIM, Physik der Sonne, S. 266—270.

<sup>2)</sup> Proc. Roy. Acad. Amsterdam. XV, 1451, 1913; Astrophysical Journal 37, p. 225, 1913.

radius; and the law of variation of brightness with the angle is different for different wave-lengths.

Whichever the causes may be, that make the sun radiate more intensely in the direction of the radius than in directions slanting to it, they must be looked for in layers lying *below* the level generally called the surface of the photosphere. Those layers consist of transparent gases, for the slightest haze of condensation products, occupying a stratum some thousand kilometers thick, would provide it with a radiating and scattering power almost independent of direction, which power the photosphere does not possess.

Assuming, on the basis of the Maastricht results, that the extinction effected by the sun's outer layers is comparatively small, we derive from direct observations on the distribution of brightness on the sun's disk (VOGEL, ABBOT), how much light of a given wave-length a point  $M$ , lying somewhere in the photospheric level, transmits on the average along the various directions. The result may conveniently be described, for every wave-length separately, by means of an "irradiation surface"  $q p q_1$  (Fig. 1)<sup>1)</sup>, the radii vectores of which

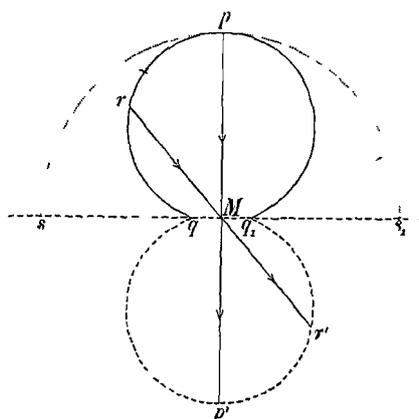


Fig. 1.

represent the average intensities of the light reaching  $M$  from different sides. We obtain the "irradiation or emission surface"  $p p' q_1$  of  $M$  by prolonging the radii  $rM$  and making  $Mr' = rM$ .

If we wish to explain the sun's apparent, fairly sharp, boundary, and the law of varying brightness of the solar disk, we shall have to consider, besides emission and absorption, the effects of dispersion, refraction, and molecular scattering of the light traversing an entirely

<sup>1)</sup> For a method of constructing these surfaces we refer to these Proceedings XIII, 1263; or: Physik. Zeitsch. 12, 677, 1911, or: Handwörterbuch der Naturwissenschaften, VII. 830, (1912).

gaseous medium. This is a great physical problem, toward the complete solution of which only the first steps are as yet being made<sup>1)</sup>; but awaiting the final results of such investigations, we may already attempt to apply our present knowledge of the matter to the interpretation of solar phenomena.

From the astrophysical point of view one of the questions material to the case is what can be presumed about the general radial gradient of the density in the layers we are concerned with?

This subject has been treated very fully and ingeniously, on the basis of thermodynamics, by EMDEN in his book "Gaskugeln." EMDEN arrives at the conclusion already mentioned above, that the fall of the density must be extremely rapid; but the inference is open to doubt, for in his calculations EMDEN presupposes gravitation to be the only radial force acting on solar matter. According to the present state of our physical knowledge, however, we decidedly must admit that on the sun gravitation is counteracted by the pressure of radiation, and by the emission of electrons and perhaps of other charged particles.

Basing on purely theoretical grounds an estimate of the intensity of that counteraction would, for the present, be as rash as denying its existence, but some evidence in favour of its essentiality is given by the fact, that many solar phenomena are much better understood if we assume a radial gradient many times smaller than the one that would correspond to gravitational conditions only. In this connection we would call attention to the puzzling properties of quiescent, hovering prominences. Father FÉNYI, in his interesting discussion of the long series of prominence observations made at Haynald Observatory, Kalocsa<sup>2)</sup>, is very positive in his assertion that several well-established facts concerning quiet prominences can only be accounted for, if in the solar atmosphere gravity is reduced, by certain repulsive forces, to a small fraction (something of the order  $1/_{80}$ ) of its commonly accepted value.

Our hypothesis, that a similar counteraction, opposing the effect

<sup>1)</sup> RAYLEIGH, Phil. Mag. [5] 47, 375, 1899.

A. SCHUSTER, Astrophysical Journal 21, 1, 1905.

H. A. LORENTZ, The theory of Elections, Leipzig 1909.

L. NATANSON, Bulletin de l'académie des sciences de Clacovic, Avril 1907, Décembre 1909.

W. H. JULIUS, Physik. Zeitsch 12, S 329 und 674, 1911.

L. V. KING, Phil Trans. Roy. Soc. London, A 212, 375, 1912.

<sup>2)</sup> Publikationen des Haynald Observatoriums, Heft X, 138, (1911). Cf. also FÉNYI, Ueber die Höhe der Sonnenatmosphäre. Mem. Spett.ital. (2), 1, 21, (1912).

of gravitation, prevails throughout the visible layers of the sun, is certainly not less plausible, therefore, than the exclusive hypothesis, usually admitted, which makes gravitation the only effective agent in determining the radial gradient<sup>1)</sup>.

§ 2. We must now endeavour to conceive the appearance of the sun's edge in a transparent gaseous medium where the pressure varies but slowly along the radius.

As already remarked, SCHMIDT's ingenious optical explanation cannot be adhered to. Nevertheless the principle of ray-curving introduced by that author is extremely suggestive; it leads to the following interpretation of the solar limb, which appears not to encounter similar difficulties.

Let fig. 2 represent an equatorial section of the sun. It can hardly be doubted that besides the gradual, perhaps slow variation of optical density corresponding to the outward decrease of pressure, there are many *irregular optical density gradients* connected not only with the local differences of pressure that accompany the convection currents and solar vortices, but also with the differences of temperature and of composition occurring in the gaseous mixture.

Now, the average magnitude of those irregular gradients of optical density will very probably decrease as we proceed from a level  $P$  toward a level  $Q$ .

Let us imagine the "irradiation surfaces" to be constructed for a point  $P_1$  of the level  $P$  and for a point  $Q_1$  of  $Q$ . At the level  $Q$  the irregular gradients may in general be so small that rays, leaving it along a tangent  $Q_1E$  in the direction of the earth, are hardly ever sufficiently curved to be the continuation of rays coming from within the irradiation surface of  $Q_1$ . This condition will obtain if the average radius of curvature of rays tangent to the level  $Q$  is more than,

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<sup>1)</sup> In the *Astrophysical Journal* 31, p. 166 (1910) Mr. J. A. ANDERSON has criticized the conclusions arrived at in my paper "Regular Consequences of Irregular Refraction in the Sun" (*Proc. Roy. Acad. Amst.* Oct. 28, 1909). His refutation of the idea that refraction might be very momentous in solar physics is entirely founded on the following two assumptions: 1. the photosphere may be represented by a perfectly uniform self-luminous surface, radiating approximately according to the cosine law, and 2. on the sun the weight of a gas is 27.3 times as great as on the earth. I think we may now safely state that the first assumption is contrary to observed facts, and that the second assumption is an unproved dogma, subject to well-founded doubts.

Moreover, a very important point, overlooked by Mr. ANDERSON is, that considerable optical density gradients may result from differences of temperature or of composition, even at uniform pressure.

say, three times as great as the radius of the sphere  $Q$ . Then the observer receives little light from  $Q_1$ ; he will consider the level  $Q$  to lie outside the solar limb.

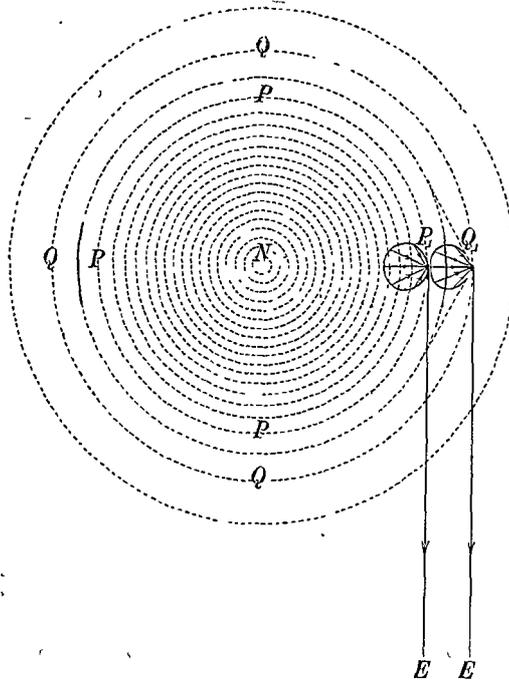


Fig. 2.

If, on the other hand, in a layer  $P$  the gradients are so much steeper, that there the average radius of curvature of tangential rays is smaller than, say, one third of the radius of the sphere  $P$ , we may expect a sensible fraction of the light that  $P_1$  receives from the interior to get sufficiently deviated in the region surrounding  $P_1$ , so as to proceed toward the earth along the tangent  $P_1E$ . The observer will now consider  $P_1$  to belong to the solar disk.

The transition from disk to surroundings will appear abrupt if the minimum distance between levels like  $P$  and levels like  $Q$  be less than 700 kilometers (one second of arc). This condition is compatible with a rather slow radial pressure gradient, because it only requires that the average radius of curvature<sup>1)</sup>  $\left(\rho = n \frac{dn}{ds}\right)$  of rays

<sup>1)</sup> "Average radius of curvature" is here used as an abbreviated expression for: "the radius of curvature corresponding to the average value of that radial component of the irregular density gradients, which is directed toward the centre of the sun."

deviated by irregular gradients of optical density be about 9 times greater in  $Q$  than in  $P$ . (Even a smaller ratio would probably suffice). There will then appear a circular boundary between  $P$  and  $Q$ , lying in a plane through the sun's centre perpendicular to the line of sight, but there is no particular "solar surface" corresponding to it.<sup>1)</sup>

In a level  $P$  just inside the apparent photosphere the average value of  $\varrho$  may still be of the order of magnitude  $10^{10}$  cm. We can easily show that to such curvatures of rays correspond quite reasonable density gradients. For if we suppose hydrogen to be a principal constituent of the visible layers, the average refraction-constant  $R = \frac{n-1}{\Delta}$  of the medium may be estimated at 1.5. Putting this value, and  $\varrho = 10^{10}$ , into the relation<sup>2)</sup>

$$\frac{d\Delta}{ds} = \frac{1}{R\varrho},$$

we obtain the density-gradient  $6 \times 10^{-11}$ , which means that in two points one kilometer ( $10^5$  cm.) distant from each other the density only differs 0,000006, i.e. 0,5 % of the density of our terrestrial atmosphere. It would be very remarkable indeed, if the general circulation in the sun did not bring along local differences of temperature and of composition sufficient to account for density gradients

<sup>1)</sup> At first sight one might be inclined to think that the boundary thus defined has the same radius as SCHMIDT's critical sphere would have. On closer examination, however, the two notions appear to be entirely different. This is clearly brought out with the aid of the following analogous conception. Imagine a spherical mass of liquid (radius  $R$ ) of constant *average* optical density, and, as a source of light in the middle of it, an incandescent lamp provided with a big globe of milky glass. As there is no radial density-gradient, a critical sphere in the sense of SCHMIDT's theory could not appear in that medium. Let the liquid be a mixture of a solution of common salt and a solution of glycerine in water, both solutions having the same specific weight but different refracting power (cf. Physik. Zeitschr. 11, 59, 1910). If we now suppose that only in the outer spherical shell (radii  $R$  and  $\frac{3}{4}R$ ) the solutions are completely mixed, whereas in the inner shell, surrounding the luminous globe, the liquids are only stirred, but still honeycombed with irregular gradients of optical density — the *average* optical density of the shells being the same — then the inner shell will seem to be a self-luminous body. The origin of its boundary is comparable with that of the solar limb according to our theory.

The above interpretation of the photosphere evidently involves an explanation of the reversing layer and the chromosphere as soon as we take account of anomalous dispersion. On this subject, however, we shall not expatiate in the present paper.

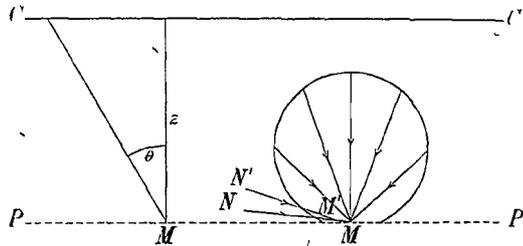
<sup>2)</sup> Cf. these Proceedings IX, p. 352, 1907.

of that order of magnitude. In a layer, for instance, where the average density does not exceed the density of our own atmosphere at sea-level, a temperature gradient of 1°.4 C. per kilometer is all that would be required.

§ 3. The above dioptrical conception of the photosphere implies the following explanation of the variation of brightness across the disk.

This problem, indeed, may also be expressed as follows: what is the cause of the fact, that the *irradiation surface* of a point  $M$ , lying somewhere in or near the "photospheric level", has that particular shape (different according to the selected wave-length), which direct observation assigns to it?

Let  $PP'$  (Fig. 3) represent a part of the photospheric level,  $CC'$



of another level lying so much deeper, that there the solar matter is dense enough to emit light giving a continuous spectrum.

Although the medium surrounding  $M$  be a mixture of selectively absorbing gases, transparent to the greater part of the spectrum, that transparency is not absolute. *Molecular scattering* (RAYLEIGH)<sup>1)</sup> weakens a *direct beam* according to the law

$$I = I_0 e^{-sz}, \text{ in which } s = \frac{32\pi^3(n-1)^2}{3\lambda^4 N};$$

but if the source of light be an incandescent surface  $CC'$ , radiating the energy  $I_0$  per square unit, and if the diffused light itself be taken into consideration, the energy emerging per square unit from  $PP'$  will (as found by SCHUSTER)<sup>2)</sup> be expressed thus:

$$I = I_0 \frac{2}{2 + s z}.$$

<sup>1)</sup> RAYLEIGH, Phil. Mag. [5] 47, 375, (1899).

<sup>2)</sup> SCHUSTER, Astroph. Journ. 21, 1, (1905).

ABBOT, in his valuable book "The sun", (1911), also introduces molecular scattering as a principal agent in producing the appearance of the photosphere.

We are aware that this formula does not hold exactly for non-homogeneous media, nor for oblique directions when simply replacing  $z$  by  $z \sec \theta$ ; but as a first approximation we shall put

$$J = J_0 \frac{2}{2 + sz \sec \theta},$$

where  $J$  and  $J_0$  now bear on units of surface located in the layers  $PP'$  and  $CC'$  respectively, and taken perpendicular to the direction considered. Supposing  $J_0$  to be independent of direction, we find that  $J$  decreases as  $\theta$  increases, in agreement with the characteristic of the irradiation surface<sup>1</sup>).

One of the causes why the latter equation cannot be expected to represent the conditions completely is, that it does not allow for possible incurvation of the direct beams passing through the medium. If  $\theta$  approaches the value  $90^\circ$ , our formula makes  $J$  tend toward zero, whereas in reality the brightness at the limb only falls to values between 0,13  $J_{\theta=0}$  and 0,30  $J_{\theta=0}$  with different colours.

Now, it is evident that refraction by the irregular density gradients at once accounts for the discrepancy; indeed, a beam reaching  $M$  along  $NM$  ( $\theta$  nearly  $= 90^\circ$ ) might have been turned into that direction out of another direction  $F'M'$  for which  $\theta$  has a smaller value, so that  $J$  will have a greater value than the one corresponding to the formula. It is exactly this process on which our explanation of the sun's edge was based.

If, therefore, we consider both scattering and irregular refraction effects, the conclusions to which the theory leads are compatible with the observed shape of the irradiation surface, or with the law according to which the average intensity of a given kind of light decreases from the centre toward the limb of the solar disk.

The agreement also prevails when kinds of light of different wave-lengths are considered. Let us distinguish between, e.g., red and violet, by introducing the subscripts  $r$  and  $v$ .

<sup>1</sup>) A full comparison of the theoretical with the observational irradiation surfaces for different wave-lengths will be published at a later date. If  $2 \cos \Theta$  may be neglected as compared with  $sz$ , the expression becomes

$$J = J_0 \frac{2}{sz} \cos \theta,$$

the equation of a sphere, tangent to the photopheric level in  $M$ . The irradiation-surface, as constructed with the values for violet light taken from H. C. VOGEL's well-known table (Ber. der Berl. Akad. 1877, p. 104), is in its main part strikingly similar to such a sphere.

At the center of the disk ( $\theta = 0$ ) we have between the intensities of red and violet light the proportion

$$p_0 = \frac{J_r}{J_v} = \frac{J_{o,r}}{J_{o,v}} \cdot \frac{2 + s_v z}{2 + s_r z},$$

in which, according to RAYLEIGH'S formula,  $s_v > s_r$  (if cases of anomalous dispersion be excluded, so that the disparity between  $n_v$  and  $n_r$  may be neglected).

At a point, corresponding to the angle  $\theta$ , we have

$$p_\theta = \frac{J_{o,r}}{J_{o,v}} \cdot \frac{2 + s'_v z \sec \theta}{2 + s_r z \sec \theta}.$$

The second<sup>s</sup> factor of  $p_\theta$  is greater than unity, and  $p_\theta$  is greater than  $p_0$ . This means, that the longer waves preponderate as we move from the center of the disk toward the limb. With increasing values of  $\sec \theta$ ,  $p_\theta$  approaches the limit

$$p_{\infty} = \frac{J_{o,r}}{J_{o,v}} \cdot \frac{s_v}{s_r} = \frac{J_{o,r}}{J_{o,v}} \cdot \frac{\lambda_r^4}{\lambda_v^4};$$

this proportion, however, will be more or less modified by irregular refraction.

§ 4. Taking all in all, the above theory of the photosphere thus appears to account for the sun's edge, and for the principal features of the results of VOGEL'S well-known spectrophotometric measurements.

It implies at the same time an interpretation of the *granular structure* of the solar disk as an effect of refraction. If ANDERSON<sup>1)</sup> and other astrophysicists were right in assuming the irradiation surface of a point  $M$  near the photospheric level to be a hemisphere  $sps_1$  (Fig. 1 p. 266), irregular gradients of optical density could not produce any sensible disturbance in the uniform brightness of the disk, except in special cases. But their assumption certainly is erroneous; the average intensity of the light passing through  $M$  varies considerably with the value of the angle  $\theta$ ; so the irregular refraction of the light must necessarily result in variegation of luminosity.

Waves that undergo anomalous refraction will of course be deviated to a higher degree in the same gradients. Following out this line of thought, we arrive at explanations of spectroheliograph results<sup>2)</sup>, on which we shall not now insist.

A few remarks may be added in connection with the sun-spot

<sup>1)</sup> *Astroph. Journal* **31**, 166 (1910).

<sup>2)</sup> Cf. *Astroph. Journal*, **21**, 278, 1905; **28**, 360, 1908; **31**, 419, 1910.

hypothesis suggested in 1909<sup>1)</sup>. A spot was supposed to be a region where, from a central minimum outward, the optical density increases with a gradually decreasing gradient. If sun-spots are solar vortices, such conditions are very likely to obtain. It was then argued that, when a similar structure is traversed by the light from an extensive source radiating, as the photosphere does, with intensities decreasing from the center toward the limb, refraction must exactly produce the characteristic optical features observed in a spot: an umbra surrounded by a penumbra. Taking anomalous dispersion effects into consideration, one is led by the same argument to an explanation of the principal properties of the spot-spectrum. Lately we succeeded in realizing, in the laboratory, the formation of a typical "sun-spot" by refraction of light in a whirling mass of gas, and could witness several phenomena, rather closely resembling the appearances produced by the real solar objects. A description of those experiments, together with a discussion of their possible bearing on several spot-problems (e.g. on the apparent effect of the earth on the formation and growth of sun-spots) must be deferred to a separate paper.

We now only wish to emphasize the fact that the above conception of sun-spots naturally fits in with our dioptrical explanation of the photosphere. The levels where vortex-motion should occur so as to produce the appearance of a spot, will be found somewhere between spheres corresponding to  $PP$  and  $QQ$  of our Fig. 2. The conditions in a spot need not differ very much from those obtaining in the surrounding regions. Their chief characteristics are: 1. the rotary motion, which determines a magnetic field and a systematic arrangement of density gradients (which need not be steeper than the average irregular gradients otherwise present in the same levels), and 2. the differences of temperature and of composition connected with the special form of circulation.

#### *Summary.*

Various views concerning the nature of the photosphere are criticized, and a new dioptrical interpretation of several photospheric phenomena is proposed.

<sup>1)</sup> Proc Roy. Acad. Anst 12, 273, 1909; Physik. Zeitschr. 11, 62, 1910.

**eology.** — “On zonal amphiboles, in which the plane of optic axes of the margin is normal to that of the central part”. By H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of February 22, 1913).

Especially in rocks, which are rich in alcalies various rare amphiboles with peculiar optical properties have been described from different localities. Their chemical and optical properties have not yet been sufficiently determined for their classification.

In dynamometamorphic basic eruptive rocks from the island of Leti, which have been collected during Prof. Dr. G. A. F. MOLENGRAAFF'S *imor-Expedition*, intergrowths of different amphiboles occur; of these intergrowths zonal crystals, which partly consist of actinolite or common hornblende and partly of crossitic amphiboles<sup>1)</sup>, in which the plane of optic axes is normal to the plane of symmetry, are especially interesting. In connection with these intergrowths of amphiboles, which are chiefly formed in metamorphic rocks, other zonal crystals of pyrogenetic amphiboles, which occur in aegurineamphibolefoyaïtes from Zandriverspoort (332), in the southwestern part of the Pilandsberg-complex (Transvaal), will be mentioned. In the central part of the latter amphiboles, the plane of the optic axes lies in the plane of symmetry, in the marginal part it is normal to the plane of symmetry. Where amphiboles with the plane of optic axes perpendicular to the plane of symmetry have been mentioned from other localities, their intergrowth with the normal amphiboles is also a common phenomenon.

#### 1. *Zonal amphiboles from the island of Leti.*

In a diabasic rock from a conglomerate near the well Prigi Tiga, in which the augite has been partly converted into amphiboles, the crossite occurs in numerous crystals, which often show a zonal structure with different extinction angles for the central and marginal parts. Many crystals of crossite are surrounded by a narrow marginal zone of actinolite and zonal amphiboles with a central part of common

<sup>1)</sup> Crossite, according to ROSENBUSCH (Mikrosk. Physiographie, I. 2, p. 246), is not the amphibole with the plane of optical axes in the plane of symmetry which originally has been described by PALACHE (comp. Univ. of California, Bull. ep. of Geology 1894, p. 181).

The crossite in rocks from the island of Leti has already been mentioned by ERBEEK (comp. Molukken Verslag, Jaarb. v. h. Nynwezen, Wetensch. Ged. p. 591) according to the determination of GRUTTERINK.

hornblende and a margin of a crossitic amphibole, are found in small quantities in the rock.

Intergrowths of crossite and actinolite have been described from other localities, those of crossite and common hornblende will be described more in detail.

In a section, the crossitic amphibole of which showed a strong pleochroism from blue to nearly colourless, the central part was pleochroic from light brownish yellow to darker brownish yellow; in the marginal zone the crossite showed an extinction angle of  $14^\circ$ , which towards the centre gradually decreased to  $9^\circ$ , whilst in the common hornblende this angle gradually increased to  $17^\circ$ . In both amphiboles the prism axis is parallel to the slow ray.

In a section, the crossitic amphibole of which was pleochroic from slightly bluish violet to blue, the central part showed the darker brownish yellow colour and was only very little pleochroic.

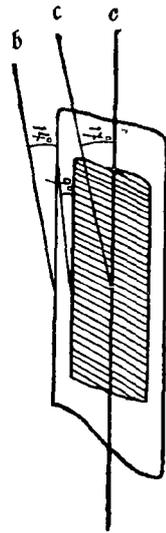


Fig. 1.  
Intergrowth of crossitic and brownish yellow amphibole.  
Section  $\pm$  parallel to (010);  $\times 200$ .

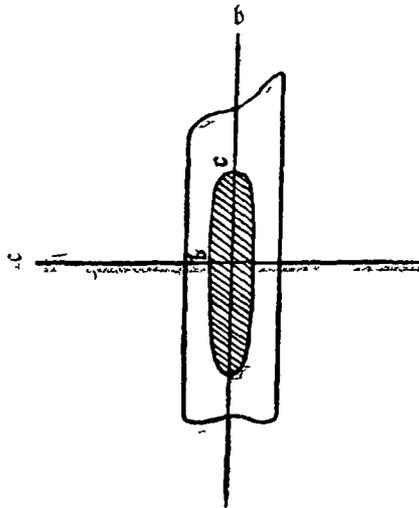


Fig. 2.  
Id. Section  $\pm$  parallel to (100);  
 $\times 200$ .

In this section the prism axis of the marginal zone was parallel to the fast ray, whilst that of the central zone was parallel to the slow ray. In the section small oblique extinctions were seen, so that it was not exactly perpendicular to the plane of symmetry.

The pleochroism for the central and marginal amphiboles is as follows:

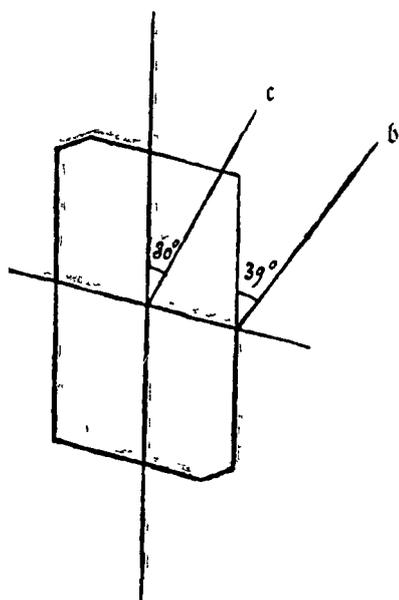
<i>Centre.</i>	<i>Margin.</i>
c brownish yellow	c slightly bluish violet
b brownish yellow	b blue
a light yellow	a nearly colourless.

It is evident that the crystallographic axes of both amphiboles coincide, whilst the plane of optic axes of the central amphibole is in the plane of symmetry and that of the marginal one is perpendicular to the plane of symmetry. The angle  $b:c$  is smaller than that of the typical crossites, whilst only in some of the zonal crystals of crossite, this angle increases to  $30^\circ$ .

The limit between the different amphiboles in the zonal crystals is rather irregular and there is only a narrow zone of transition between them.

## 2. Zonal amphiboles from the Pilandsbergen.

In aegirine-amphibole-foyaite, which have been collected on Zandriverspoort (332) to the South-West of the Pilandsberg complex,



crystals of zonal amphiboles which are tabular on the clinopinacoid, occur. In a section, which was nearly parallel to (010) the central part had a brownish colour, whilst in the marginal zone the colour was more greenish and darker, to darkgreen. The angle between the *c*-axis and the axis of smallest absorption was  $30^\circ$  for the central and  $39^\circ$  for the marginal zone; these angles and the colours of the central and the marginal zone are not the same in different crystals, but the brownish colours are always found in the central and the greenish colours in the marginal zone.

3. Amphibole of Zandriverspoort (332). Section  $\pm$  parallel to (010).

Sections, in which both central and marginal part are nearly perpendicular to the negative bisectrix so that the angle of optic axes is small for the central part and very large for the marginal one. The plane of optic axes is perpen-

dicular to the plane of symmetry in the marginal zone. These amphiboles resemble those in the shonkinite of the Katzenbuckel (Odenwald)<sup>1</sup>).

The relation between these peculiar amphiboles and the normal types can be seen from the study of the zonal crystals in which these peculiar amphiboles are found together with the normal types. With regard to the common hornblendes, the basaltic ones are characterized by smaller extinction angles and smaller angles of optic axes, their alkali- and high iron content.

Similar differences seem to exist between the amphiboles in the zonal crystals with crossite, in which the extinction angles decrease from  $17^\circ$  to  $9^\circ$  in the brown amphibole. After the turning of the plane of optical axes the margin consists of a crossitic amphibole which is rich in iron and alkalis. In the zonal crystals with crossite and actinolite, the content of sesquioxides and alkalis strongly increases from the margin to the centre, the turning of the plane of optic axes takes place in a zone of transitional chemical composition. Other amphiboles, which are connected by transitions with the common hornblendes are especially found in igneous rocks rich in alkalis, they are characterized by a larger angle  $c:c$  and a smaller axial angle, and are chemically characterized by a high content of iron and alkalis. However their optical and chemical properties are not known in detail. From the description of the zonal crystals of the Pilandsbergen and those of the Katzenbuckel, it is evident, that the turning of the plane of optic axes can result from a small change in the chemical composition of such amphiboles, whilst in other cases (Katoforites) the plane of optic axes remains in the plane of symmetry, whilst the angle  $c:c$  can increase from  $30^\circ$  to  $60^\circ$  and so passes into that of the arfvedsonites.

The anoforites from the Katzenbuckel in which the plane of the optic axes is normal to the plane of symmetry (comp. Neues Jahrbuch f. Min. 1910. 1. p. 34), and which in zonal crystals are connected with katoforitic amphiboles, differ chemically from the Katoforites by a lower  $FeO$ - and a higher  $MgO$  content. The extinction angles are  $20-27^\circ$  in the acute angle  $\beta$ . There are amphiboles without the large angle  $c:c$ , in which the turning of the plane of the optic axes may be expected in zonal crystals. This is probable for certain amphiboles from pegmatitic segregations in the aegirine-amphibolefoyaïtes from Buffelspan (585). Their plane of the optic axes was normal to the plane of symmetry, the angle  $b:c = 14^\circ$

<sup>1</sup>) W. FREUDENBERG. Geologie und Petrographie des Katzenbückels im Odenwald. Mitt. der Groszh. Badischen Geol. Landesanstalt. Band V. 1906.

and  $c = b$ . Their angle  $2V$  is small or very small, sometimes these amphiboles are nearly uniaxial and are connected with the distinctly uniaxial ones in zonal crystals.

These amphiboles sometimes are intergrown with biotite or aegirine and also with a bluish green amphibole, in which the plane of optic axes is also normal to the plane of symmetry, if they have the same crystallographic orientation as the brownish green amphiboles. In sections parallel to (100) of the latter ones, the prism axis is parallel to the fast ray in the bluish green amphiboles, whilst in sections parallel to (010) it is nearly parallel to the slow ray.

From the facts, which have been mentioned above, it is evident, that amphiboles, in which the plane of optic axes lies in the plane of symmetry, very probably occur at the same locality.

**Astronomy.** — “*On canonical elements.*” By Prof. W. DE SITTER.

In the developments of the planetary theory each of the three anomalies has been used as independent variable: the mean anomaly by LAGRANGE, the excentric anomaly by HANSEN and the true anomaly by GYLDÉN. All systems of canonical elements, however, which have been in use up to the present time, are only modifications of the system of DELAUNAY, which is based on the use of the *mean* anomaly. Recently<sup>1)</sup> LEVI-CIVITA has proposed a new system of elements, in which the *excentric* anomaly appears instead of the mean anomaly, most simultaneously<sup>2)</sup> HILL has called attention to another system in which the *true* anomaly appears as one of the variables. The method by which HILL arrived at his system is, however, very different from that by which the systems of DELAUNAY and LEVI-CIVITA were developed. The object of the present paper is to show how these three systems, as well as others, can be derived from the same fundamental principle.

Let  $x_i$  be the co-ordinates of a body  $P$ , and  $y_i = m \frac{dx_i}{dt}$  the components of its momentum ( $i = 1, 2, 3$ ). The equations of motion are then

$$\frac{dx_i}{dt} = \frac{\partial H}{\partial y_i}, \quad \frac{dy_i}{dt} = -\frac{\partial H}{\partial x_i}, \quad \dots \dots \dots (1)$$

<sup>1)</sup> T. LEVI-CIVITA, Nuovo sistema canonico di elementi ellittici. Annali di Matematica, Ser. III, Tom. XX, p. 153 (Aprile 1913).

<sup>2)</sup> G. W. HILL. Motion of a system of material points under the action of gravitation. Astronomical Journal, Vol. XXVII, Nr. 646—647, p. 171 (1913 April 28).

where

$$H = T - K,$$

$T$  representing the kinetic energy and  $K$  the force-function. In the problem of planetary motion we have

$$K = \frac{k}{r} + S,$$

where  $S$  is the perturbative function. According to a theorem discovered by JACOBI, any new system of canonical variables  $p_i, q_i$  can be derived from an arbitrary function  $\Phi(x_i, q_i)$  of  $x_i$  and  $q_i$ , by putting

$$\frac{\partial \Phi}{\partial x_i} = y_i, \quad \frac{\partial \Phi}{\partial q_i} = p_i \dots \dots \dots (2)$$

If then, by means of (2), we replace  $x_i$  and  $y_i$  in  $H$  by  $p_i$  and  $q_i$ , the equations for the new variables are

$$\frac{dp_i}{dt} = \frac{\partial H}{\partial q_i}, \quad \frac{dq_i}{dt} = -\frac{\partial H}{\partial p_i} \dots \dots \dots (3)$$

JACOBI'S method of integration, which has led to the system of canonical elements introduced into astronomical practice by DELAUNAY, consists in so choosing  $\Phi$  that the equations (3) are of a much simpler form than (1). For this purpose JACOBI chooses for  $\Phi$  an integral of the partial differential equation, which bears his name, and which is constructed as follows. In the function  $H(x_i, y_i)$  replace  $y_i$  by  $\frac{\partial \Phi}{\partial x_i}$ , then JACOBI'S equation is

$$H\left(x_i, \frac{\partial \Phi}{\partial x_i}\right) = h.$$

The constant  $h$  is the energy of the motion.

If we take  $S=0$ , and, instead of  $x_i, y_i$  introduce polar coordinates  $r, s, w$ , and the corresponding momenta  $r' = m \frac{dr}{dt}, s' = mr^2 \frac{ds}{dt}, w' = mr^2 \cos^2 s \frac{dw}{dt}$ , the energy function becomes

$$H_0 = \frac{1}{2m} \left( r'^2 + \frac{s'^2}{r^2} + \frac{w'^2}{r^2 \cos^2 s} \right) - \frac{k}{r} = h \dots \dots \dots (4)$$

Then JACOBI'S equation admits the integral

$$\Phi_0 = \Theta w + \int_0^s \sqrt{G^2 - \frac{\Theta^2}{\cos^2 s}} ds + \int_{r_0}^r \sqrt{2hm + \frac{2km}{r} - \frac{G^2}{r^2}} dr,$$

where  $\Theta$  and  $G$  are constants of integration. JACOBI now takes

$\Phi = \Phi_0$  and for the variables  $q_i$  he takes  $\Theta$ ,  $G$  and  $h$ . In order to get a more general point of departure I take for the function  $\Phi$  which serves to define the new variables

$$\Phi = \Theta w + \int_0^s Q ds + \int_{r_0}^r R dr, \dots \dots \dots (5)$$

where

$$\left. \begin{aligned} Q^2 &= G^2 - \frac{\Theta^2}{\cos^2 s}, \\ R^2 &= m \left( -\alpha^2 + \frac{2\beta^2}{r} - \frac{\gamma^2}{r^2} \right) \end{aligned} \right\} \dots \dots \dots (6)$$

We have thus

$$r' = \frac{\partial \Phi}{\partial r} = R, \quad s' = \frac{\partial \Phi}{\partial s} = Q, \quad w' = \frac{\partial \Phi}{\partial w} = \Theta,$$

and therefore

$$H = -\frac{\alpha^2}{2} + \frac{\beta^2 - k}{r} + \left( \frac{G^2}{m} - \gamma^2 \right) \frac{1}{2r^2} - S \dots \dots \dots (7)$$

I will now for two of the variables  $q_i$  take  $\Theta$  and  $G$ , for the third I take either  $\alpha$ ,  $\beta$  or  $\gamma$ , or a function of one of these parameters.

We have thus in all cases

$$\vartheta = \frac{\partial \Phi}{\partial \Theta} = w - \int_0^s \frac{\partial Q}{\partial \Theta} ds \dots \dots \dots (8)$$

If now we introduce the auxiliary angle  $\zeta'$  by

$$\zeta' = w - \vartheta = \int_0^s \frac{\partial Q}{\partial \Theta} ds,$$

and then construct the right-angled spherical triangle of which the sides next to the right angle are  $\zeta'$  and  $s$ , it is easily seen that in

this triangle we shall have  $\frac{d\zeta'}{ds} = \frac{\partial Q}{\partial \Theta}$  if we put

$$\Theta = G \cos i,$$

where  $i$  is the angle opposite the side  $s$ . Consequently  $i$  and  $\vartheta$  are the inclination and node of the instantaneous orbital plane, i. e. the plane which contains the origin of co-ordinates and the velocity of the body  $P$ . Introducing now the argument of the latitude  $\zeta$ , i. e. the angle between the line of nodes and the radius-vector, or the side opposite the right angle in the above mentioned triangle, we

find from simple geometrical considerations  $\zeta' \cos i + \int_0^s \frac{Q}{G} ds = \zeta$ ,

and consequently

$$\Phi = \Theta \mathcal{D} + G\zeta + \int_{r_0}^r R dr. \quad (9)$$

Next calling the values of  $r$  for which  $R$  vanishes  $a(1-e)$  and  $a(1+e)$  respectively, we find

$$a = \frac{\beta^2}{\alpha^2}, \quad a^2(1-e^2) = \frac{\gamma^2}{\alpha^2}, \quad (10)$$

$$R^2 = \alpha^2 m \left[ -1 + \frac{2a}{r} - \frac{a^2(1-e^2)}{r^2} \right].$$

I now introduce a new parameter  $\delta$  by

$$\gamma = \frac{G}{\sqrt{m}} + \delta \quad (11)$$

We have then

$$g = \frac{\partial \Phi}{\partial G} = \zeta + \frac{1}{\sqrt{m}} \int_{r_0}^r \frac{\partial R}{\partial \gamma} dr. \quad (12)$$

Putting now

$$f = \zeta - g = - \frac{1}{\sqrt{m}} \int_{r_0}^r \frac{\partial R}{\partial \gamma} dr,$$

we find from (12) and (10)

$$\frac{dr}{df} = \frac{r^2 R}{\gamma \sqrt{m}} = \sqrt{-\frac{r^4}{a^2(1-e^2)} + \frac{r^3}{a(1-e^2)} - r^2}. \quad (13)$$

This is the differential equation of an ellipse of which  $a$  is the semi major axis and  $e$  the excentricity. If the constant of integration is so chosen that  $r_0 = a(1-e)$ , then  $f$  is the true anomaly. We have then

$$r = \frac{a(1-e^2)}{1+e \cos f}, \quad R = \alpha \sqrt{m} \frac{e \sin f}{\sqrt{1-e^2}} \quad (14)$$

We can now in this ellipse introduce by definition the excentric anomaly  $\mathbb{E}$  and the mean anomaly  $\mathbb{M}$ . We find

$$r = a(1-e \cos \mathbb{E}), \quad R = \alpha \sqrt{m} \frac{ae \sin \mathbb{E}}{r},$$

$$d\mathbb{E} = \frac{\alpha}{2\beta\sqrt{m}} \frac{\partial R}{\partial \beta} dr; \dots \dots \dots (15)$$

$$M = \mathbb{E} - e \sin \mathbb{E} \quad , \quad dM = - \frac{\alpha^2}{\beta^2 \sqrt{m}} \frac{\partial R}{\partial \alpha} dr \dots \dots (16)$$

In all these formulas  $\alpha$  and  $e$  are written as abbreviations for certain functions of  $\alpha, \beta, \gamma$  defined by (10).

All this is independent of the choice of the third pair of canonical elements. We must now specialize the values of the parameters  $\alpha, \beta, \delta$ , which were so far left entirely indeterminate. Now we can distinguish three cases. In each case two of these parameters are constant, while the third is variable, and a function of it is taken as the element  $q_3$ .

*Case I.*  $\beta = \beta_0 = \text{const.} \quad , \quad \delta = \delta_0 = \text{const.}$

The third linear element is a function of  $\alpha$  and will be called  $L$ . Therefore the conjugated variable  $l$  is given by

$$l = \frac{\partial \Phi}{\partial L} = \frac{\partial \Phi}{\partial \alpha} \frac{d\alpha}{dL} = \frac{d\alpha}{dL} \int \frac{\partial R}{\partial \alpha} dr = - \frac{\beta_0^2 \sqrt{m}}{\alpha^2} \frac{d\alpha}{dL} \int d\mathbb{M}.$$

Thus, if we wish to get

$$l = \mathbb{M} = \text{mean anomaly},$$

we must take

$$\frac{dL}{d\alpha} = - \frac{\beta_0^2 \sqrt{m}}{\alpha^2},$$

from which

$$L = \frac{\beta_0^2 \sqrt{m}}{\alpha} = \beta_0 \sqrt{m} \cdot \sqrt{a} \dots \dots \dots (17)$$

Since  $\beta_0$  and  $m$  are constants, the semi major axis  $a$  is variable. We find at once from (10)

$$L \sqrt{1-e^2} = G + \delta_0 \sqrt{m} \dots \dots \dots (18)$$

*Case II.*  $\alpha = \alpha_0 = \text{const.}, \quad \delta = \delta_0 = \text{const.}$

The third linear variable  $U$  is a function of  $\beta$ . Therefore the conjugated variable is

$$u = \frac{\partial \Phi}{\partial U} = \frac{d\beta}{dU} \int \frac{\partial R}{\partial \beta} dr = \frac{2\beta\sqrt{m}}{\alpha_0} \frac{d\beta}{dU} \int d\mathbb{E}.$$

Thus in order to get

$$u = \mathbb{E} = \text{excentric anomaly},$$

we must take

$$\frac{dU}{d\beta} = \frac{2\beta\sqrt{m}}{\alpha_0},$$

and consequently

$$U = \frac{\beta^2 \sqrt{m}}{\alpha_0} = \alpha_0 \sqrt{m} \cdot a \dots \dots \dots (19)$$

Here again  $\alpha_0$  and  $m$  being constant,  $a$  is variable. We find further

$$U \sqrt{1-e^2} = G + \sigma_0 \sqrt{m} \dots \dots \dots (20)$$

Case III.  $\alpha = \alpha_0$  const.,  $\beta = \beta_0$  const.

The third linear element  $V$  is now a function of  $\sigma$ . Therefore

$$v = \frac{\partial \Phi}{\partial V} = \frac{d\sigma}{dV} \frac{\partial \Phi}{\partial \sigma} = \frac{d\sigma}{dV} \int \frac{\partial R}{\partial \gamma} dr = - \sqrt{m} \frac{d\sigma}{dV} \int df.$$

Consequently, if we wish to have

$$v = f = \text{true anomaly}$$

we must take

$$\frac{dV}{d\sigma} = - \sqrt{m},$$

and therefore

$$V = V_0 - \sigma \sqrt{m}.$$

Now we can introduce a new variable  $v$  by

$$\sigma \sqrt{m} = \frac{\beta_0^2}{\alpha_0} (\sqrt{m} - v).$$

Putting then

$$V_0 = \frac{\beta_0^2 \sqrt{m}}{\alpha_0} = \beta_0 \sqrt{m} \cdot \sqrt{a} = \alpha_0 \sqrt{m} \cdot a, \dots \dots \dots (21)$$

we find

$$V = \frac{\beta_0^2 v}{\alpha_0} = \beta_0 v \sqrt{a} \equiv \alpha_0 v a \dots \dots \dots (22)$$

In this case,  $\alpha_0$  and  $\beta_0$  being constant  $a$  is also constant, by (10), and  $v$  is variable. We have now

$$V_0 \sqrt{1-e^2} = G + \sigma \sqrt{m} = G + V_0 - V. \dots \dots (23)$$

The energy  $H$  is in the three cases:

$$\left. \begin{aligned} I. \quad H &= -\frac{\beta_0^4 m}{2L^2} + \frac{\beta_0^2 - k}{r} - \sigma_0 \left( \frac{2G}{\sqrt{m}} + \sigma_0 \right) \frac{1}{2r^2} - S. \\ II. \quad H &= -\frac{\alpha_0^2}{2} + \left( \frac{\alpha_0}{\sqrt{m}} U - k \right) \frac{1}{r} - \sigma_0 \left( \frac{2G}{\sqrt{m}} + \sigma_0 \right) \frac{1}{2r^2} - S. \\ III. \quad H &= -\frac{\alpha_0^2}{2} + \frac{\beta_0^2 - k}{r} + \frac{(V - V_0)(2G + V_0 - V)}{m} \cdot \frac{1}{2r^2} - S. \end{aligned} \right\} (24)$$

Here  $r$  must be understood to be written for brevity's sake instead of its expression in function of the elements.

In the cases I and II it is advantageous to take  $\delta_0 = 0$ .

In the cases II and III the value of  $\alpha_0$  is of course immaterial, the first term of  $H$  may as well be omitted. As to the value of  $\beta_0$  in the cases I and III, it is customary in classical celestial mechanics (case I) to take  $\beta_0 = \sqrt{k}$ . This however is not at all necessary, and the term  $\frac{\beta_0^2 - k}{r}$  can be taken advantage of by an appropriate choice of  $\beta_0$  to cancel a term in  $S$ . This is also advocated by HILL in the paper already quoted. Though HILL does not say so (and doubtlessly does not intend to say), a casual reader may easily be led to assume that the possibility of this device is one of the advantages of the system of elements of case III. It is therefore well to point out that it does not depend on the choice of elements, and can as well be applied in case I.

By each of the three sets of elements

$$\left\{ \begin{array}{l} L, G, \Theta \\ l, g, \vartheta \end{array} \right\}, \quad \left\{ \begin{array}{l} U, G, \Theta \\ u, g, \vartheta \end{array} \right\}, \quad \left\{ \begin{array}{l} V, G, \Theta \\ v, g, \vartheta \end{array} \right\}$$

the motion of the body  $P$  is described as a Keplerian motion in an ellipse with varying parameters. In the cases I and II the variable instantaneous ellipse has a point of contact with the true orbit, and can therefore be called an osculating ellipse. But the definition of this osculating ellipse is different in each case. In fact at every point of the orbit there is an infinity of ellipses having that point and the tangent at that point in common with the orbit and all having one and the same given point as a focus. In case I we choose from this family of ellipses that ellipse that would be described by a body of mass  $m$  starting from the given point with the given velocity

under the action of a central force  $\frac{\beta_0^2}{r^2}$  emanating from the common focus. The constant  $\beta_0^2$  here has a prescribed value, the same for all points of the orbit. The elements thus derived are those of DELAUNAY. They are called by LEVI-CIVITA *isodynamic* elements.

In the second case we choose that ellipse in which the energy of a Keplerian motion of a body of mass  $m$  starting with the given velocity from the given point has a prescribed fixed value  $h_0 = -\frac{1}{2}\alpha_0^2$ . The elements which we then get are those of LEVI-CIVITA, and are by him called *isoenergetic* elements.

In the third case the ellipse has a prescribed semi major axis  $a = \frac{\beta_0^2}{\alpha_0^2}$ . There is no osculation, the tangent of the ellipse in the

common point being different from the tangent of the orbit.<sup>1)</sup> If a name analogous to those coined by LEVI-CIVITA for the other two systems were required, we might call these elements *isoprotometric* elements, since the quantity  $a$ , which here remains constant, is called the protometer by GYLDEN, who was the first to use a system of elements belonging to this class.

If at a given point of the true orbit, i.e. for given values of  $r, s, w, \frac{dr}{dt}, \frac{ds}{dt}, \frac{dw}{dt}$ , we wish to determine the instantaneous elements

in the three cases, the method of procedure is as follows. First we determine geometrically the inclination  $i$ , and node  $\vartheta$  of the plane containing the origin of coordinates and the velocity of the body  $P$ .

With the aid of these we find  $\zeta$  and  $\frac{d\zeta}{dt}$ . Then

$$G = mr^2 \frac{d\zeta}{dt} \quad \Theta = G \cos i.$$

For the determination of the third linear element we require the living force, or kinetic energy:

$$2T = m \left( \frac{dr}{dt} \right)^2 + mr^2 \left( \frac{d\zeta}{dt} \right)^2.$$

We have then in the three cases (taking  $\sigma_0 = 0$  for the cases I and II):

$$\left. \begin{aligned} I. \quad 2T &= \frac{2\beta_0^2}{r} - \frac{m\beta_0^4}{L^2} \\ II. \quad 2T &= \frac{2\alpha_0 U}{r\sqrt{m}} - \alpha_0^2 \\ III. \quad 2T &= \beta_0^2 \left( \frac{2}{r} - \frac{1}{a} \right) + \frac{(V - V_0)(2G + V_0 - V)}{mr^2} \end{aligned} \right\} \quad (25)$$

From these formulas we find  $L, U, V$ . Next  $a$  and  $e$  are determined by (17), (18), (19), (20), (21), (23) and then the ordinary elliptic formulae give  $r$  and the true, excentric or mean anomaly. Finally we have

$$g = \zeta - v.$$

The differential equations for the elements are given below for the three cases. In the cases I and II I take  $\sigma_0 = 0$ , or  $\gamma = \frac{G}{\sqrt{m}}$  and in the cases I and III I put

<sup>1)</sup> HILL l.c. p. 176, states that the ellipse has a point of contact with the orbit. This, however, is an oversight.

$$S' = S + \frac{k - \beta_0^2}{r}$$

$$\text{I. } \left. \begin{aligned} \frac{dl}{dt} &= \frac{\beta_0^4 m}{L^3} - \frac{\partial S'}{\partial L} & \frac{dL}{dt} &= \frac{\partial S'}{\partial l} \\ \frac{dg}{dt} &= -\frac{\partial S'}{\partial G} & \frac{dG}{dt} &= \frac{\partial S'}{\partial g} \\ \frac{d\vartheta}{dt} &= -\frac{\partial S'}{\partial \Theta} & \frac{d\Theta}{dt} &= \frac{\partial S'}{\partial \vartheta} \end{aligned} \right\} \dots \dots \dots (26)$$

$$\text{II. Put } U = \frac{k\sqrt{m}}{\alpha_0} + \Delta U$$

$$r = \frac{U}{\alpha_0 \sqrt{m}} (1 - e \cos u) \quad \sqrt{1 - e^2} = \frac{G}{U}$$

$$\left. \begin{aligned} \frac{du}{dt} &= \frac{k}{U^2} + \frac{\Delta U (1 - e^2)}{mr^2} \cos u - \frac{\partial S}{\partial U} & \frac{dU}{dt} &= -\frac{\Delta U}{mr^2} e U \sin u + \frac{\partial S}{\partial u} \\ \frac{dg}{dt} &= -\frac{\Delta U \sqrt{1 - e^2}}{mr^2} \cos u - \frac{\partial S}{\partial G} & \frac{dG}{dt} &= \frac{\partial S}{\partial g} \\ \frac{d\vartheta}{dt} &= -\frac{\partial S}{\partial \Theta} & \frac{d\Theta}{dt} &= \frac{\partial S}{\partial \vartheta} \end{aligned} \right\} (27)$$

If at  $t=0$  we start with  $\Delta U=0$ , and if  $S=0$ , then the motion is Keplerian:  $U, G, \Theta, g, \vartheta$  are constants. In the general case, when  $S$  differs from zero,  $\Delta U$  is of the order of  $S$ , i. e. of the order of the perturbing masses.

$$\text{III. Put } V = V_0 + \Delta V$$

$$r = \frac{a(1 - e^2)}{1 + e \cos v} \quad \sqrt{1 - e^2} = \frac{G - \Delta V}{V_0}$$

$$\left. \begin{aligned} \frac{dv}{dt} &= \frac{G - \Delta V}{mr^3} - \frac{\Delta V(2G - \Delta V)}{mr^3} \cdot \frac{\sqrt{1 - e^2}}{e V_0} \frac{\partial r}{\partial e} - \frac{\partial S'}{\partial V} \\ & \frac{dV}{dt} = -\frac{\Delta V(2G - \Delta V)}{mr} \cdot \frac{e \sin v}{a(1 - e^2)} + \frac{\partial S'}{\partial v} \\ \frac{dg}{dt} &= \frac{\Delta V}{mr^3} + \frac{\Delta V(2G - \Delta V)}{mr^3} \cdot \frac{\sqrt{1 - e^2}}{e V_0} \frac{\partial r}{\partial e} - \frac{\partial S'}{\partial G} & \frac{dG}{dt} &= \frac{\partial S'}{\partial g} \\ \frac{d\vartheta}{dt} &= -\frac{\partial S'}{\partial \Theta} & \frac{d\Theta}{dt} &= \frac{\partial S'}{\partial \vartheta} \end{aligned} \right\} (28)$$

$\Delta V$  again is of the order of the perturbing masses. For  $S'=0$  the motion is Keplerian and  $V, G, \Theta, g, \vartheta$  are constants.

In all cases the choice of the original variables  $x, y, z$  is of course

entirely free. It only affects the form of the perturbative function  $S$ , which plays no part in the definition of the elements. We can either use ordinary relative co-ordinates ( $S$  being in that case different for each planet), or we can introduce canonical relative co-ordinates, either by the method of JACOBI-RADAU ("élimination des noeuds") or by POINCARÉ'S "transformation  $\alpha$ " (Acta Mathematica, Vol. XXI, page 86). [In these last two cases the body  $P$  of course is not the true planet, but a fictitious planet, different according to the choice of co-ordinates]. LEVI-CIVITA uses POINCARÉ'S co-ordinates, but this is not material: the isoenergetic elements may as well be used with any other system of relative co-ordinates.

Also it is hardly necessary to point out that in all three cases we can introduce new elements by canonical transformations and thus derive from the isoenergetic or the isoprotometric elements the same modifications which have been derived from DELAUNAY'S elements. Thus e.g. we have the three corresponding transformations:

$$I. \quad \begin{array}{lll} A = L & \Pi = L - G & \Psi = G - \Theta \\ \lambda = l + g + \vartheta & \pi = -g - \vartheta & \Psi = -\vartheta \end{array}$$

$$(\text{where we have } \Pi = L(1 - \sqrt{1 - e^2}) \quad , \quad \Psi = 2G \sin^2 \frac{1}{2} i)$$

$$II \quad \begin{array}{lll} H = U & \Pi = U - G & \Psi = G - \Theta \\ \eta = u + g + \vartheta & \pi = -g - \vartheta & \psi = -\vartheta \\ (\Pi = U(1 - \sqrt{1 - e^2}) \quad , \quad \Psi = 2G \sin^2 \frac{1}{2} i) \end{array}$$

$$III. \quad \begin{array}{lll} W = V & \Pi = V - G & \Psi = G - \Theta \\ w = v + g + \vartheta & \pi = -g - \vartheta & \psi = -\vartheta \\ (\Pi = V_0(1 - \sqrt{1 - e^2}) \quad , \quad \Psi = 2G \sin^2 \frac{1}{2} i), \end{array}$$

from which again we can derive the elements of POINCARÉ-HARZER:

$$\begin{array}{ll} h = \sqrt{2\Pi} \cos \pi & p = \sqrt{2\Psi} \cos \psi \\ k = \sqrt{2\Pi} \sin \pi & q = \sqrt{2\Psi} \sin \psi. \end{array}$$

If in case III we make the transformation

$$\left. \begin{array}{ll} F = V - G & Z = G \\ f = v & \zeta = v + g \end{array} \right\}$$

we find the elements used by HILL. We have indeed  $F = m \cdot \eta$ ,  $Z = m \cdot u$ ,  $\zeta = u$  (where  $\eta$ ,  $u$  and  $u$  are the symbols used by HILL), and the letter  $f$  is used by HILL with the same meaning as in the present paper.

These elements can also be derived directly from the function  $\Phi$ . The condition (11) must then be omitted:  $R$  must be assumed not to contain  $G$ .

If then we write  $Z$  for  $G$ , we find at once

$$\frac{\partial \Phi}{\partial Z} = \xi.$$

The element  $F$  now is a function of  $\gamma$ , and consequently

$$f = \frac{\partial \Phi}{\partial F} = \frac{d\gamma}{dF} \int \frac{\partial R}{\partial \gamma} dr = -\sqrt{m} \frac{d\gamma}{dF} \int df.$$

Therefore

$$\frac{dF}{d\gamma} = -\sqrt{m},$$

from which

$$F = \text{const.} - \gamma\sqrt{m} = V_0 - \gamma\sqrt{m}.$$

Now, by (10) we have  $\gamma = \frac{\beta_0^2}{\alpha_0} \sqrt{1-e^2}$ , therefore, with the value (21) of  $V_0$ , we find

$$F = \frac{\beta_0^2 \sqrt{m}}{\alpha_0} (1 - \sqrt{1-e^2}).$$

To the elements I corresponds the classical development of the perturbative function according to the sines and cosines of multiples of the mean anomalies. The development of  $S$  according to excentric anomalies, which is required for the elements II, has been given by NEWCOMB in Vol III of the Astron. Papers of the Am. Eph. For the development in function of true anomalies, which is needed when using the elements III, the foundations have been laid down by HILL in the paper already quoted.

Case IV.  $\alpha = \alpha_0 = \text{const.}$ ,  $\beta = \beta_0 = \text{const.}$ ,  $\delta = \delta_0 = 0$ .

The third linear element is a function of  $\varkappa$ . It will be called  $M$ . We have

$$\mu = \frac{\partial \Phi}{\partial M} = \frac{d\varkappa}{dM} \int \frac{\partial R}{\partial \varkappa} dr = \frac{\beta_0^2}{\alpha_0} \frac{d\varkappa}{dM} \int d\mu.$$

Consequently we must take

$$\frac{dM}{d\varkappa} = \frac{\beta_0^2}{\alpha_0}$$

from which

$$M = \frac{\beta_0^2 \varkappa}{\alpha_0} = \beta_0 \varkappa \sqrt{a} = \alpha_0 \varkappa a. \quad (32)$$

The semi major axis  $a$  is constant, as it was in case III, and  $\varkappa$  is variable. The meaning of  $\varkappa$  is however different from that of  $\nu$  in formula (22). From (10) we find

$$M \sqrt{1-e^2} = G. \quad (33)$$

Here again the motion is described as a Keplerian motion in an ellipse with varying elements. The ellipse has a point of contact with the true orbit, and therefore belongs to the family of ellipses mentioned above. The body  $P$  in its orbit, and the fictitious planet in its ellipse, however, have not the same velocity, but the same momentum. Since they have different masses, they have also different velocities, agreeing only in direction.

The energy is now

$$IV. \quad H = -\frac{M^2}{2ma^2} + \left(\frac{M^2}{ma} - k\right) \frac{1}{r} - S \dots \dots (34)$$

and the living force

$$2mT = \frac{M^2}{a} \left(\frac{2}{r} - \frac{1}{a}\right) \dots \dots \dots (35)$$

If we put  $M = M_0 + \Delta M$ ,

$$M_0 = \frac{\beta_0 \sqrt{k}}{\alpha_0} \sqrt{m},$$

then the differential equations become

$$\left. \begin{aligned} \frac{d\mu}{dt} &= \frac{M}{am} \left(\frac{2}{r} - \frac{1}{a}\right) - \frac{\Delta M(2M_0 + \Delta M)}{amr^2} \frac{\partial r}{\partial M} - \frac{\partial S}{\partial M} \\ \frac{dM}{dt} &= \frac{\Delta M(2M_0 + \Delta M)}{amr^2} \frac{\partial r}{\partial \mu} + \frac{\partial S}{\partial \mu} \\ \frac{dg}{dt} &= -\frac{\Delta M(2M_0 + \Delta M)}{amr^2} \frac{\partial r}{\partial G} - \frac{\partial S}{\partial G} \\ \frac{d\mathfrak{G}}{dt} &= -\frac{\partial S}{\partial \mathfrak{G}} \end{aligned} \right\} (36)$$

In the same way as the systems I, II, and III, we can of course derive other systems of elements. A system in which, as in III, the semi major axis is constant, but with osculation, is obtained as follows. We take the same function  $\Phi$ , given by (5) or (9), but now we put

$$R^2 = z^2 \left(-a^2 + \frac{2\beta^2}{r} - \frac{\gamma^2}{r^2}\right).$$

The function  $R$  thus now contains four parameters. The elements I, II, III are derived as above by assigning to the fourth parameter a constant value  $z = r_0 = \sqrt{m}$ .

The equation (11) now becomes

$$\gamma = \frac{G}{\kappa} + \delta. \quad \dots \quad (29)$$

We have now, remembering that finally we will put  $\delta = 0$ .

$$\frac{\partial R}{\partial \kappa} = \frac{R}{\kappa} - \frac{G}{\kappa^2} \frac{\partial R}{\partial \gamma} = \frac{1}{\kappa} \left( R - \gamma \frac{\partial R}{\partial \gamma} \right) = \frac{1}{\kappa} \left( \alpha \frac{\partial R}{\partial \alpha} + \beta \frac{\partial R}{\partial \beta} \right).$$

By the aid of (10) and (14) to (16) we find easily

$$\frac{\partial R}{\partial \kappa} dr = \frac{\beta^2}{\alpha} (2dE - dM) = \frac{\beta^2}{\alpha} d\mu \quad \dots \quad (30)$$

Here an angle  $\mu$  has been introduced, of which the geometrical meaning is easily seen. If we take polar co-ordinates  $\varrho$  and  $\varphi$  with the second (empty) focus as origin, then  $\mu$  bears the same relation to  $\varphi$  as the mean bears to the true anomaly. Therefore, since

$$r^2 df = a^2 \sqrt{1-e^2} dM,$$

the equation connecting  $\varphi$  and  $\mu$  is similarly

$$\varrho^2 d\varphi = a^2 \sqrt{1-e^2} d\mu.$$

We have the formulas

$$\begin{aligned} \mu &= E + e \sin E \\ \varrho \cos \varphi &= a (\cos E + e) & \varrho &= a (1 + e \cos E) \quad (31) \\ \varrho \sin \varphi &= a \sqrt{1-e^2} \sin E & \varrho &= \frac{a(1-e^2)}{1-e \cos \varphi} \end{aligned}$$

The angle  $\mu$  is easily seen to be proportional to the "action", if for the mass we take  $\kappa^2$ . In that case the components of the momentum become  $y_i = \kappa^2 \frac{dx_i}{dt}$ , and

$$\int 2T dM = \alpha^2 \mu$$

I now take the fourth parameter  $\kappa$  as variable. We then have Here  $r = 2a - \varrho$  must be expressed as a function of the elements by (31).

$\Delta M$  is of the order of the perturbing masses. If  $S = 0$  the motion is Keplerian:  $M, G, \Theta, g, \vartheta$  are constants.

For use with the elements IV, for which I will not try to coin a name, a development of the perturbative function  $S$  according to the trigonometric functions of multiples of  $\mu$  would be required. This can be derived from the well known development in function of the mean anomaly by substituting  $\varrho$  for  $r$ ,  $\varphi$  for  $v$ ,  $-e$  for  $e$  and  $\mu$  for  $l$ .

**Mineralogy.** — “*On the pseudometeorite of Igast in Livonia*”.  
By Prof. Dr. A. WICHMANN.

In the afternoon of the 17<sup>th</sup> of May 1855 at about 6 o'clock a lady, Miss BECKMANN, standing on the stairs outside a country-seat 2 miles N.E. from Walk in Livonia, suddenly saw between the lime-trees on that spot a dazzling luminiferous phenomenon, at about 6 or 9 feet above the ground, whilst she heard at the same time a tremendous clap.

At about the same time the proprietor, Mr. FR. SCHULTZ, found himself in a rather high field situated at a distance of 1 werst (1.067 km.) from the country-seat. He, likewise, heard in an entirely cloudless sky a violent detonation, so strong that his saddle-horse and another horse, drawing a barrow, were frightened and threatened to bolt.

Assuming, on correct grounds, that a falling meteorite had exploded, the chemist L. BORNWASSER immediately made an investigation on the ground in the neighbourhood of the above-mentioned lime-trees, and collected two handfuls of peculiar mineral fragments which he supposed to proceed from that meteorite.

C. GREWINGK, to whom we are indebted for the report concerning this event, described those pieces as cellular melted masses of a slaggy nature, looking much like pumiceous lava. On some fragments he found moreover numerous particles of quartz and feldspar as it were fused together with them. From the analysis made by C. SCHMIDT appeared the enormously high percentage of 80,874 SiO<sup>2</sup> of that so-called meteorite<sup>1)</sup>. He could not identify the mass with any other earthly rock, and — on good grounds — rejects the possibility of a formation by lightning (fulgurites).

In 1881 F. J. WIK made a microscopic examination of the “meteorite” of Igast. He found larger individuals of quartz, orthoclase<sup>2)</sup> and plagioclase, a fine-grained groundmass, and moreover little colourless, allongated crystals with globulites which he regarded as ammonium chloride<sup>3)</sup>. At last he pointed out that, for a meteorite, the mineralogical composition was quite peculiar<sup>4)</sup>.

<sup>1)</sup> C. GREWINGK und C. SCHMIDT, Ueber die Meteoritenfälle von Pillistfer, Buschhof und Igast in Liv- und Kurland. Archiv für die Naturkunde Livlands, Ehstlands und Kurlands, III. Dorpat 1864, p.p 457—461, 482—483.

<sup>2)</sup> Read mikrokline.

<sup>3)</sup> Hereby were meant the plagioclase-lathes. Ammoniumchloride is not extant at all

<sup>4)</sup> Mineralogiska meddelanden VII. Ofversigt af Finska Vetensk. Ac. Förh 21, 1881—82. Helsingfors 1882, p. 63.

A short time after A. VON LASAULX published the results of his microscopic examination. Though at first sight the rock showed great similarity with a basalt rich in glass-basis in which numerous grains of quartz, microcline, and plagioclase were shut up in a groundmass, consisting of brown glass, numerous grains of magnetite, little lath-shaped crystals of plagioclase, besides yellowish green grains of ilmenite, he regarded it as an artificial product that was accidentally found at the very place where the fire-ball had been seen. He did not exclude however the possibility that it was a melting-product brought about by a flash of lightning, but he denied the possibility that it was a meteorite<sup>1)</sup>. In a report about VAN WIJK's treatise MIL COHEN likewise deemed the meteoric nature exceedingly doubtful<sup>2)</sup>. Afterwards he asserted even that the stone of Igast was doubtless a pseudo-meteorite<sup>3)</sup>.

In 1884 the rock was again described by STANISLAS MEUNIER. He acknowledged that it was quite different from all known meteorites, and pointed out its resemblance with volcanic rocks, viz. the "ponces ponceuses". Consequently the rock was classed with the "météorites volcaniques" by the name of "Igestite"<sup>4)</sup>.

H. MICHEL treated this subject most elaborately, he published a short time ago a description in which he entered into all details, and overlooked however the microscopic investigations of all his predecessors<sup>5)</sup>. The optical character of all the constituents of the rock were defined more exactly, but for the rest the results of his examination agree with those of the former investigators. At last he says:

"Wenn man weiter die ganzlich unmeteorische Oberfläche des Stückes, seine schlackige Beschaffenheit, das Fehlen der für alle Meteoriten bezeichnenden thermomorphischen Erscheinungen, das Vorkommen von groben Quarzkörneraggregaten neben Bestandteilen, die sonst basischen Gesteinstypen anzugehören pflegen, in Betracht zieht, kommt man wohl zu der Überzeugung, dass es sich wahrscheinlich um eine bei irgendeinem Glashütten- oder Ziegelbrennerprozess zufällig entstandene Schlacke handelt."

After what has been said before, we may no longer doubt, that

1) Ueber die Vermehrung der Meteoritensammlung des mineralogischen Museums. Zugsber. Niederrhein. Ges. f. Natur- und Heilkunde. Bonn 1882, p.p. 108—110.

2) Neues Jahrb. f. Min. 1883, I, p. 384.

3) Meteoritenkunde I. Stuttgart 1894, p. 215.

4) Météorites. Paris 1884, p.p. 293—294, 352 (EDM. FRÉMY, Encyclopédie chimique II. 2).

5) Zur Tektitfrage. Ann. k.k. Naturhist. Hofmuseum. 27. Wien 1913, p. 6—8.

the stone of Igast is a slag of artificial formation, and consequently the chemist BORNWASSER has missed the fragments of the real meorite. H. MICHEL has however not solved the problem of the origin of the slag. As far as I know, such like slags do not occur in tile-works, neither does the chemical composition agree with it. In glass-works one will likewise look in vain for similar slags, quite apart from the question, how such a by-product of industry can ever have reached the isolated country-seat of Igast. Neither does the comparison with fulgurites, made by A. VAN LASAULX, hold.

In my opinion a plausible explanation can be found if we regard the discovered fragments as proceeding from a rye-slag. C. GREWINGK described the product of combustion and melting of a rye-stack as a grey partly graphitic mass, having the appearance of lava or slag of the hardness  $6\frac{1}{2}$ <sup>1)</sup> and A. LAGORIO<sup>2)</sup> added to this, that according to the microscopic examination augite, graphite and orthoclase were secreted, and that the appearance reminded of certain glossy modifications of volcanic rock and of melting-products obtained by F. FOUQUÉ and A. MICHEL-LÉVY by an artificial process.<sup>3)</sup>

It is a striking fact, that H. MICHEL likewise compares the microscopic character of the stone of Igast with those products. The fact that inclosures of quartz, microcline and plagioclase that do not originally proceed from that slag, are found in the rock might be thus explained, that the slag, when still in its liquid state, has run over sand so that the grains of quartz and microcline were enclosed. I must however acknowledge, that the gramineous slags which I had an opportunity of examining, did not show any resemblance with the rock of Igast, neither did they show similarity with the slag examined by A. LAGORIO. The material proceeding from burnt hay-stacks, served instead. As these stood on a clay-soil it can easily be explained that the inclosed grains of sand were but few in number, but the secreted individuals of plagioclase, augite and magnetite were neither met with. In the thin sections could be discerned a light yellowish or greenish glass, in which locally numerous microlites and sometimes tridymite-aggregates were secreted. Of a similar nature was the slag formed by the combustion of great masses of straw belonging to the straw-board-works "Union"

<sup>1)</sup> Petrificirte Roggenkorner. Sitzungsber. Naturf. Gesellsch. Dorpat. 5. 2. 1879. Dorpat 1880, p. 220.

<sup>2)</sup> Zusammensetzung von Roggenschlacken. Ibid. p. 230.

<sup>3)</sup> Réproduction artificielle de feldspaths et d'une roche volcanique complexe (labradorite) pyroxénique, par voie de fusion ignée. Compt. rend. Acad. des Sc. 87 Paris 1878, p. 781.

at Oude-Pekela (prov. of Groningen) on the 30<sup>th</sup> of July last. It was like dark-green glass consolidated with white pumiceous particles. The usually rather homogenous glass contained only comparatively few colourless crystals.

All these slags correspond, with regard to their general character, with similar products described by CH. VÉLAIN <sup>1)</sup>

If we may now remind that the ashes of graminæ do not contain aluminium <sup>2)</sup>, then it is clear, that in their slags we should look in vain for feldspar, unless a compound of aluminium had, during the melting-process, been resorbed from the soil, and secreted at the refrigeration in the shape of feldspar.

At last in addition to the above we subjoin a description of a slag owing its existence to a similar event as the one at Igast. On the 8<sup>th</sup> of June 1898 a pupil of the gymnasium of the Hague had seen a meteorite in a glowing condition explode in a garden at Voorburg.



The fragments gathered by him, which I owed to the kindness of Prof. J. F. VAN BEMMELLEN, now at Groningen, were likewise nothing else than pieces originating from a swarthy slag.

<sup>1)</sup> Etude microscopique des vers résultants de la fusion des cendres de graminées. Bull. Soc. Min. I. Paris 1878, p. 113—124.

<sup>2)</sup> ALOIS VON HUBERT. Geschmolzene Heuschlacke. Berichte über die Mittheilungen von Freunden der Naturw. 4. Wien 1848, p.p. 64—66,

They were however more compact than those of Igast, and inclosed grains of sand could only be discovered at the outer side. In consequence of this fact an enormous difference presents itself between the microscopic character. As becomes immediately apparent from the figure above the slag is characterized by an excellent ophitic structure. The secreting products consist chiefly of more or less allongated phenocrysts of plagioclase varying in length between 0.05 and 0.6 mm. and in breadth between 0.01 and 0.04 mm. According to the extinction-direction this plagioclase belongs to labradorite. The intervening metastasis (in the figure black) consists of a globulitic glass, in which are found numerous magnetite crystals surrounded by a light halo. They are single octaeders of which the smaller ones are sometimes arranged in lines. Locally there are in the base still aegite individuals and very narrow plagioclase slags.

The origin of this slag could not be ascertained.

**Anatomy.** — “Contributions upon *Neurobiota vis.*” (The arrangement of the motor nuclei in *Myxine glutinosa* in *Cryptobranchus Necturus*, *Rana fusca* and *Bufo*). (From the Anatomical Institute in Berlin and the Institute for Brainresearch, Amsterdam)<sup>1</sup>.  
By Dr. P. RÖTHIG; Berlin. (Communicated by Prof. L. BOLK).

*Myxine glutinosa*<sup>2</sup>).

It is known (ANDERS RETZIUS, JOHANNES MÜLLER, GUSTAF RETZIUS, L. EDINGER et. al.) that the brain of *Myxine glutinosa* is very rudimentary. Some parts of it are compressed in a fronto-caudal, others in a caudo-frontal direction.

The study of complete frontal, horizontal and sagittal sections reveals — as far as the mixed and motor nerveroots are concerned — the presence of the Trigemini, Facialis and several (occipito-) spinal nerves. On the contrary there is no Oculomotorius, no Trochlearis, no Abducens and no Glossopharyngeus. Also GUSTAF RETZIUS<sup>3</sup> — in his

<sup>1</sup>) My sojourn in the Institute for Brainresearch in Amsterdam has been facilitated by a gift from the Preussische Akademie der Wissenschaften for which I want to express my thanks.

<sup>2</sup>) The specimens of *Myxine glutinosa* used for this research have been collected in Kristineberg in Sweden. They were fixed while still living and stained after various methods, chiefly after BIELCHOWSKY. They will also be used for a monograph which I intend to publish together with Dr. ARIENS KAPPERS (Amsterdam) on the central nervous system of this animal.

<sup>3</sup>) RETZIUS, Biologische Untersuchungen N. F. Bnd. V 1893, (Das Gehirn und Auge von *Myxine*.)

classic treatise on this animal — emphasizes the absence of these nerves. Whether the vagusroot is present has to be settled still by further research-work, in which also the periferal nervous system is considered.

Till now — only examining the central nervous system and the roots — it has been impossible to me to state the presence of this root while GUSTAF RETZIUS, thus confirming his father's opinion and that of JOHANNES MÜLLER, does accept a motor vagusroot, and — with some reserve though — also a sensory root of the same.

Renewed researches have made it probable to me that the roots which these authors consider as vagusroots have to be regarded as motor and sensory (occipito-) spinal nerves.

This results from the fact that the cellular column from which its rootfibres arise is the direct continuation of the column from which the ventral roots of the spinal cord originate. Moreover the more caudal spinal rootlets leave the cord in exactly the same way as this so-called motor vagal root.<sup>1)</sup>

The absence of the entire glossopharyngeus and first vagus root is mentioned also for *Bdellostoma Dombeyi* by J. B. JOHNSTON<sup>2)</sup>.

In fig. 2 I give a graphic reconstruction of the motor roots and nuclei of *Myxine glutinosa*, made after the method used by KAPPERS<sup>3)</sup>.

If we compare this with the sagittal reconstruction of *Petromyzon fluviatilis*<sup>4)</sup> (Fig. 1) we are struck by the peculiar character of *Myxine*.

The distance between the hind border of the entrance of the motor fifth's root and the front border of the VII<sup>th</sup>'s entrance is smaller in *Myxine* than in *Petromyzon*, which proves that these roots have approached each other in *Myxine*. The VII root is found already a few sections behind the V<sup>th</sup>.

The closest approach has, however, occurred between the

<sup>1)</sup> That the dorsal root corresponding to this ventral root has to be regarded as a vagus root is not very probable since it contains — as far as I can see — only sensory fibres. It is not a mixed root, as is always the case with the vagus. For the same reason it is improbable that both the dorsal and the ventral root should constitute together the vagus, on account of the fact that the vagus has always a mixed character, its sensory and motor rootlets leaving the brain either together or on a very short distance, while these are opposed as real dorsal and ventral roots.

<sup>2)</sup> J. B. JOHNSTON, Note on the presence or absence of the Glossopharyngeus Nerve in Myxinoids. *Anat. Record*, Vol. II, 1908.

<sup>3)</sup> KAPPERS, *Verhandelingen der Kon. Akad. v. Wetenschappen te Amsterdam* 1910, Tweede Serie, Deel 16, N<sup>o</sup>. 4.

<sup>4)</sup> From KAPPERS: *Folia Neurobiologica* Bnd. VI, Sommerergänzungs Heft, 1912.

 = III K. und W.  = IV K. und W.  = V K. und W.  = VI K  
 = VII K. und W.  = IX K  = X K  = Cerv. M., Spin. Occ. K. und XII K. und W  
 = VI W.  = IX W.  = Oliva sup.  = Nucl. paramed und Oliva inf.  
 ↓ = Calamus

EXPLANATION OF THE FIGURES.

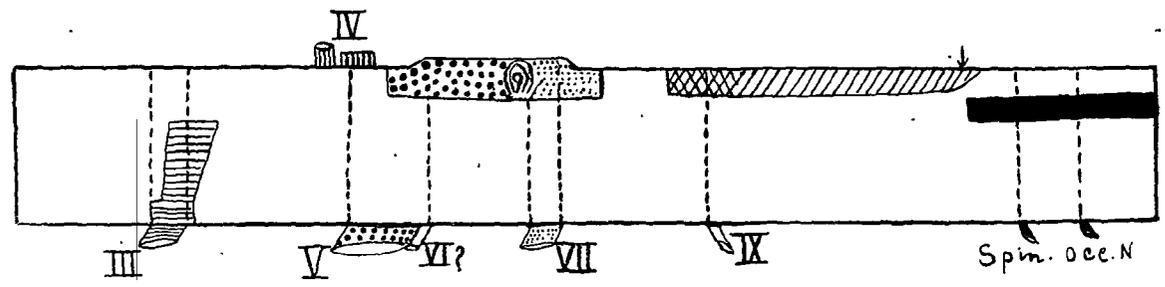


Fig. 1. Petromyzon.

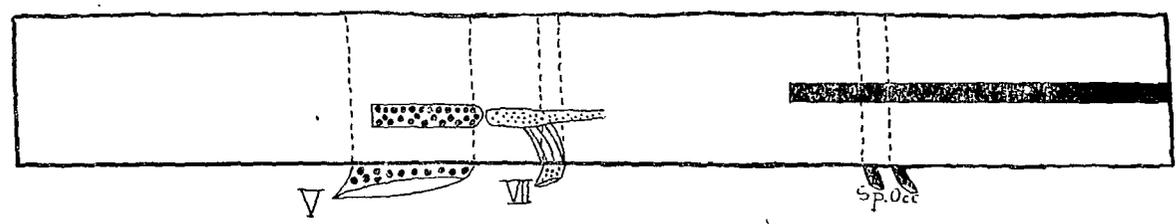


Fig. 2. Myxine glutinosa. Topographic relation of the motor nuclei and roots in Petromyzon and Myxine.

(occipito-) spinal rootlets and the VII, which is easily explained by the above mentioned absence of the IX (and the greater part of the X?) and the caudo-frontal compression of the oblongata that results from this.

If we compare in transverse sections the position of the V--VII column in *Petromyzon* (fig. 3) and *Myxine* (fig. 4) we find that the position of this nucleus in *Myxine* is a much more ventral one.

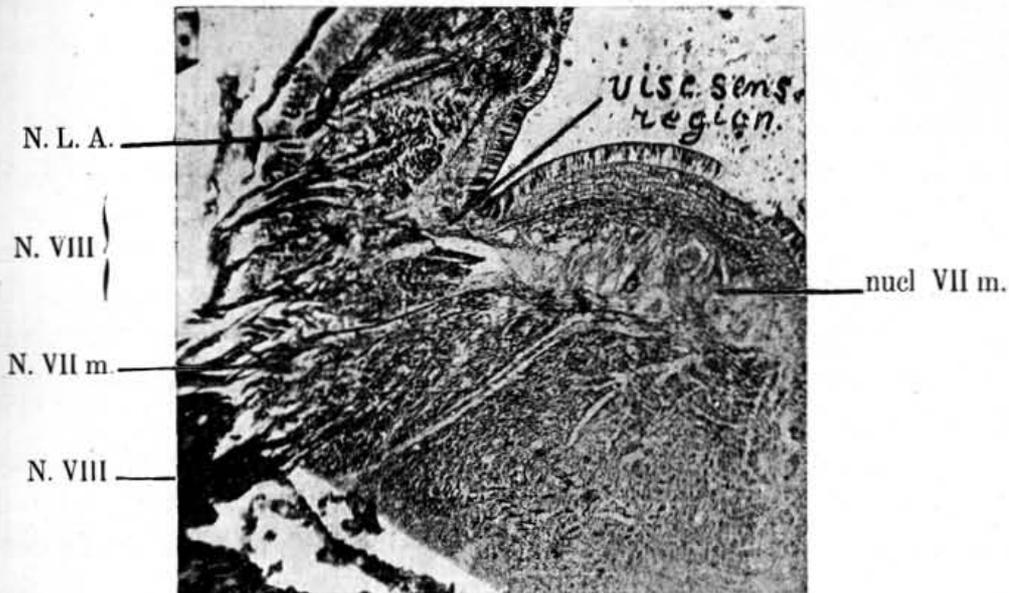


Fig. 3. VII-nuclei and root of *Petromyzon*.



Fig. 4 *Myxine glutinosa*

In *Myxine* the fairly large cells of this column are located in the most ventral part of the oblongata closely against the fibres of the descending V<sup>th</sup>. Similarly as in *Petromyzon* the V<sup>th</sup> and VII<sup>th</sup> nucleus

are practically continuous <sup>1)</sup>, and their fronto-caudal extension is about the same.

Some smaller cells continue the column in a backward direction equally as in *Petromyzon*, they seem not to be connected with rootfibres though.

As in *Petromyzon* also in *Myxine* the caudal shifting of the facialis nucleus to the level of the glossopharyngeus root — otherwise present in all fishes — does not take place. This is not strange though and can even be expected — since the caudal tastecentrum, which causes the shifting in other animals is hardly or not developed in this animal: The sensory IX<sup>th</sup> being absent while the sensory VII<sup>th</sup> is very small.

Moreover — most fibres of the sensory VII<sup>th</sup> in *Myxine* are no taste-fibres, but general sensory fibres as can be deduced from the fact that they join the descending V<sup>th</sup> and consequently are — according to our knowledge about other animals — of the same character as these (compare for the different components of the sensory VII<sup>th</sup> in Cyclostomes the important contributions of JOHNSTON: *Morphologisches Jahrbuch* Bd. 34, 1905 and *Anatom. Anzeiger* Bnd. 37, 1910).

Just the fact that even the sensory VII<sup>th</sup> is chiefly of the same character of the sensory V<sup>th</sup> and unites with it explains why the corresponding motor nuclei are attracted to the region of the descending V and VII<sup>th</sup> fibres, which constitute their chief, if not only reflectory centre, their periferal endings forming the sensory investment of the muscular apparatus of the V and VII (the lips and the so-called tongue or sucking apparatus). This determination of the V and VII nuclei through reflectory or neurobiotactic influences is the more striking, because the facial nucleus does not only lack the caudal displacement, but even shifts in frontal direction as appears from the fact that its root-fibres show a frontal course in the medulla (see fig. 2). The nucleus of the VII thus approaches still more the entrance of the sensory V<sup>th</sup> that dominates its functions.

<sup>1)</sup> Where the somewhat smaller cells of the VIIth nucleus touch the Vth nucleus, the column is less compact, has an indication of a gap. It is known that ТРЕТЯКОВ (Archiv. f. mikroskopische Anatomie Bnd 74, 1909, p. 713) supposes the VI nucleus of *Ammocoetes* (the young *Petromyzon*) to lie at the end of the Vth cells in the V—VIII column, because the root-fibres of the abducens accompany the Vth root to the oblongata and cannot be separated from them in the bulb. I do not know whether this opinion is right, but I only want to call attention to the fact that in *Myxine*, where certainly no VI nucleus is present, there is indeed a sort of a gap at the place where ТРЕТЯКОВ supposes the VI nucleus to be in *Ammocoetes*.

*Amphibia.*

Figures 6, 7, 9 and 10 demonstrate the topographic relations of the motor nuclei and nerve roots as found in my amphibian material.

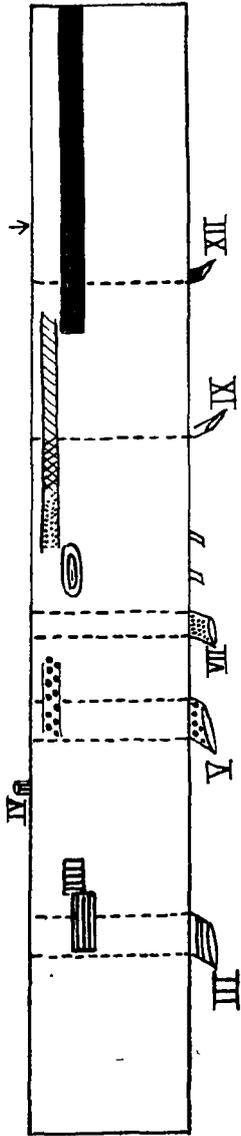


Fig. 5. Molge.

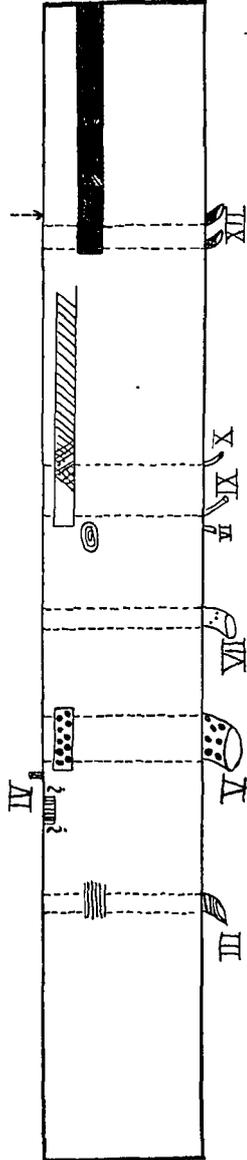


Fig. 6. *Cryptobranchus japonicus*.

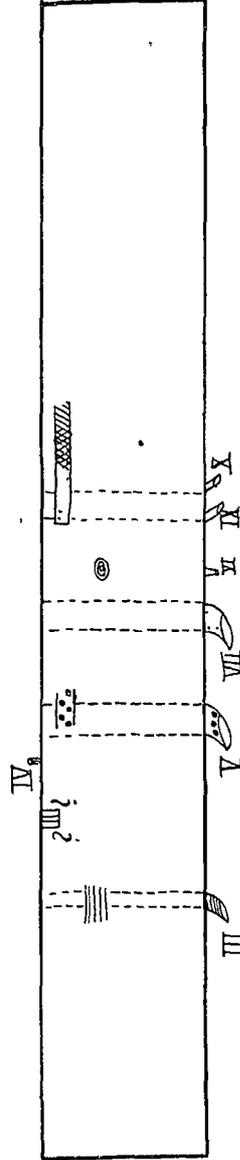


Fig. 7. *Necturus maculatus*.

They confirm the results obtained by KAPPERS <sup>1)</sup> in his urodele (Fig. 5) and anure amphibia (fig. 8) in so far as in both urodele amphibia

<sup>1)</sup> l. c. p. 46.

which I examined (*Necturus* and *Cryptobranchus*) just as in his urodela (*Siren* and *Molge*) the facial nucleus has shifted a good deal caudad from its root entrance to the level of the entrance of the glossopharyngeus root, where it constitutes a unity with the motor column of the glossopharyngeus and vagus, a condition which is the motor (reflectory) expression of the union of the sensory nerve roots of the VII and IX on the level of the IX<sup>th</sup> entrance.

On the contrary in my *Rana* and *Bufo* the nucleus facialis keeps its

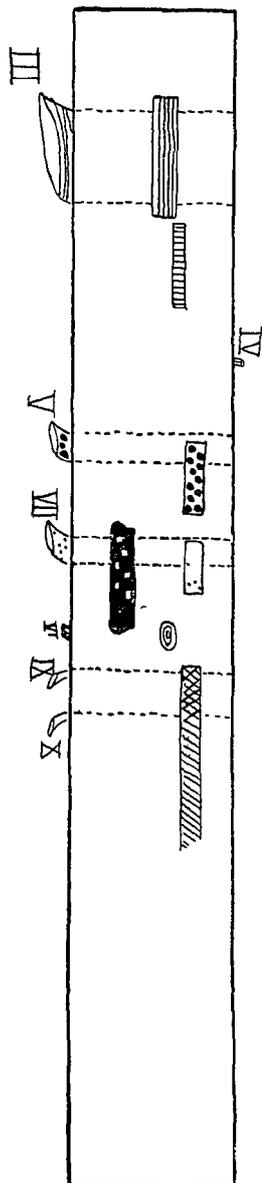


Fig. 10. *Rana fusca*.

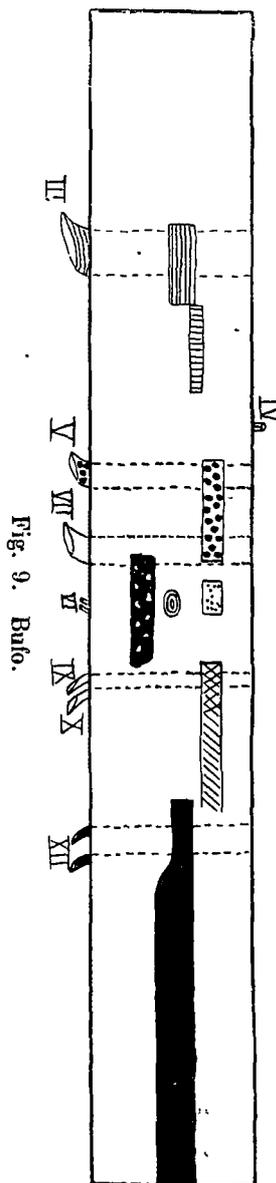


Fig. 9. *Bufo*.

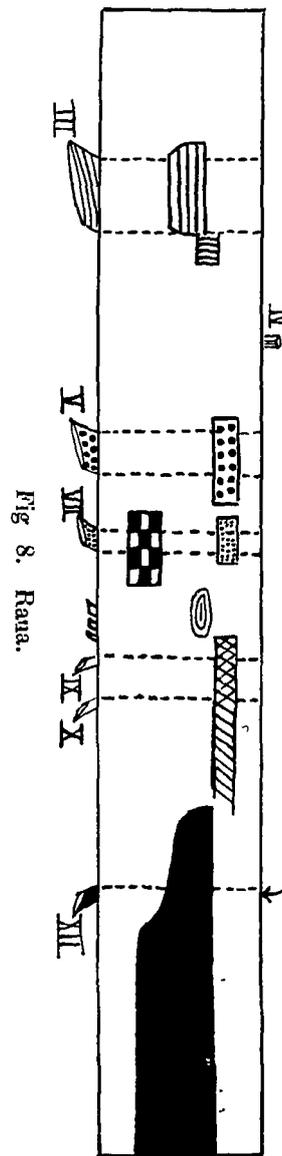


Fig. 8. *Rana*.

place on or near the level of its root entrance as has also been described by KAPPERS for his specimen of *Rana*. (fig. 8).

In connection herewith it is interesting to notice that the sensory VII<sup>th</sup> and consequently the caudal mixed VII—IX sensory nucleus is less developed in anura than in the urodela.

I further found that the abducens nucleus lies behind the root-entrance of the VII<sup>th</sup>, in *Necturus* and *Bufo* a little closer to the VII<sup>th</sup> than in *Cryptobranchus* and *Rana*.

The position and extension of the V and III nucleus, the size and arrangement of the III, IV, V, VI, VII, IX, X and XII roots, as also the slight variations which these exhibit are clearly demonstrated in the sagittal schemes.

My series of *Necturus* and *Rana* were not continued sufficiently backward to state the limit of the spino-occipital column and the position of the spino-occipital roots.

The relation found in *Bufo* however shows a striking resemblance to the condition represented in KAPPERS' *Rana*. In *Cryptobranchus* however this column does not extend as far frontally as in *Molge*.

The trochlear nucleus extends in my *Rana* and *Bufo* much more in a caudal direction than in KAPPERS' *Rana*.

This large backward extension of the IV nucleus induces me to add the following remarks concerning the phylogenetic development of this nucleus :

In *Petromyzon* this nucleus has a position dorsal to the ventricle (SCHILLING<sup>1</sup>), TRETJAKOFF<sup>2</sup>), HUET<sup>3</sup>), KAPPERS<sup>4</sup>)) in the velum anticum cerebelli frontally from but close to the level of the trigeminus nucleus at a great distance behind the oculomotor nucleus (compare fig. 1).

Contrary to this in most other mammals the nucleus has a much more frontal position, directly behind the oculomotor nucleus and ventrally from the ventricle.

The phenomena observed in the frontal shifting of another eye-muscle nucleus, the VI nucleus (KAPPERS, l.c. p. 118) prove that the first form in which this frontal shifting can take place consists in its elongation in a frontal direction. So does the abducens nucleus of *Chelone* and *Alligator* extend from the glossopharyngeus to the facialis level (l.c. fig. 105).

In the higher Reptilia (*Varanus* and *Lizard* e. g.) also the rest of

<sup>1</sup>) Abhandl. der Senckenb. Naturf. Gesellsch. 1907, Vol. 30, p. 441.

<sup>2</sup>) l. c., p. 713.

<sup>3</sup>) Proceedings of the Kon. Akad. v. Wetensch. Amsterdam, February 25, 1911.

<sup>4</sup>) l. c. p. 9.

the nucleus has shifted in a frontal direction and the whole of it has become more compact and shorter and is found in its totality on the level of the VII root. It is equally possible that the considerable elongation of the trochlear nucleus in my specimens of *Rana* and *Bufo* is a result of the originally more caudal position of the nucleus. In my *Rana* and *Bufo* the frontal shifting would thus be in its first stage: the elongation in the direction of the III<sup>d</sup> nucleus, while in higher animals the whole of the IV nucleus has attained the more frontal position and consequently the nucleus has become more compact and shorter again, having concentrated directly behind the III<sup>d</sup> nucleus. From this standpoint considered, the condition which KAPPERS found to be present in his *Rana* has to be explained as a case in which the shifting has reached already its second and last stage, the concentration of the whole IV nucleus directly behind the oculomotor one<sup>1)</sup> (see fig. 8).

In *Necturus* and *Cryptobranchus* I have not been able to determine the topography of the trochlear nucl., though the root of this nerve was fairly well developed and could be traced a good distance in the cerebrum.

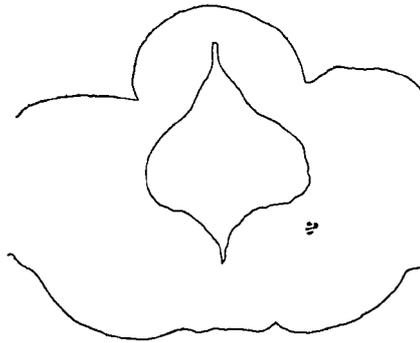


Fig. 11 *Cryptobranchus*  
Nucleus Trochlearis (1<sup>1)</sup>)

It is possible however that a small group of cells lying laterally (not ventrally as in anura) to the ventricle has to be considered as such (fig. 11). The fibres of the trochlear nerve can be followed easily in its vicinity.

The possibility of this is sustained by the fact that in the original condition (found in *Petromyzon*) the nucleus has a position dorsal to the ventricle (see fig. 1), the position under the ventricle having to be considered

as a secondary one and a transition between them is e. g. the location as found in *Varanus* ((KAPPERS l. c. fig. 56, p. 61) where a more lateral position is found.

<sup>1)</sup> The possibility that the difference in caudal extension between the trochlear nucleus in the *Rana* described by KAPPERS and my specimen might be due to inaccurate observation is excluded, because I have examined myself KAPPER'S *Rana*, which gave me the conviction that his topographic map is perfectly right and that the trochlear nucleus in his specimen is indeed much more compact

Similarly this cellgroup in *Cryptobranchus*<sup>1)</sup> can represent the trochlear nucleus in a transitional stage between the dorsal and ventral position.

The same cellgroup was found in *Necturus*. In both animals this group is not in contact with the III-nucleus, thus constituting a striking contrast with *Molge*, where the IV-nucleus has not only already attained its ventral position, but is also in close contact with the III<sup>d</sup> nucleus as can be easily demonstrated.

**Anatomy.** — “*Note on the size of the dorsal motor nucleus of the X<sup>th</sup> nerve in regard to the development of the stomach.*” By Dr. H. A. VERMEULEN Utrecht. (Communicated by Prof. BOLK).

If one compares the shape of a frontal section through the medulla oblongata in front of the calamus scriptorius in a horse, a cow, a pig and a dog, one is struck by the difference. In the horse and the dog the floor of the 4<sup>th</sup> ventricle is fairly level, whereas in the cow and the pig it has acquired the form of a split.

In the latter the sideparts of the floor have a bulging character, but in the horse it slopes down to the raphe, without any considerable protrusion, and in the dog it is nearly flat. With the exception of the dog these differences remain the same more frontally. The fossa rhomboidea of the horse is very long compared with the cow's (horse 49—51 m.m., cow 34—35 m.m.), but in the former the walls are less steep.

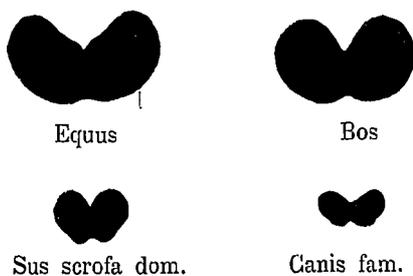


Fig. 1.

Form of the IV ventricle (caudal).

Also in the pig the stem of the brain is only short. In the dog the floor of the ventricle deepens again in frontal sections, but — as I said — in caudal regions it is very flat. These differences in the shape of the fourth ventricle appear to be related with the extension and the form of the nucleus motorius dorsalis vagi.

and shorter. On the other hand also my measures and topography in my *Rana* and *Bufo* have been controlled by KAPPERS, who found them to be right.

Perhaps the difference between the two *Ranae* has to be explained by the possibility that in one case *Rana fusca* (mihi) and in the other case perhaps *Rana esculenta* is used.

<sup>1)</sup> Another argument for the probability that it may be considered as trochlear nucleus is the fact that this lateral cellgroup was not present in *Rana*, nor in *Bufo*.

The material examined for this study has been fixed in alc. 95% and is embedded in paraffine. The stem of *Equus*, *Bos*, *Capra* and *Canis familiaris* has been stained with toluidine blue, that of *Sus scrofa dom.* with cresyl-violette.

*Equus caballus.* The dorsal motor nucleus of the X<sup>th</sup> extends over 520 sections of 18  $\mu$ . The calamus is found in section 214, counted in caudo-frontal direction. Consequently  $\frac{2}{5}$  of the nucleus is found in the closed part of the oblongata (see fig. 2) and  $\frac{3}{5}$  in the open part of it. In the closed part it is first a small group of cells, growing considerably in frontal direction.

The lateral part, which increases most, contains several large cells.

In consequence of the small size of the XII nucleus on this level the cells of the motor X come nearer to the central canal than those of the XII<sup>th</sup>. More frontally the XII<sup>th</sup> nucleus enlarges and the cells of the X<sup>th</sup> then are entirely dorsally and later dorso-laterally from it. In the middle of its length the dorsal vagus nucleus has acquired its greatest size. It then has a pyramidal form, the top of the pyramid being directed towards the ventricle. One section may show 80—100 cells. More frontally the top of the pyramid disappears so that the rest of the nucleus is entirely situated laterally to the XII<sup>th</sup>, on a somewhat deeper level.

In this series the dorsal vagus nucleus is found to extend still 28 sections more frontally than the caudal limit of the facial nucleus.

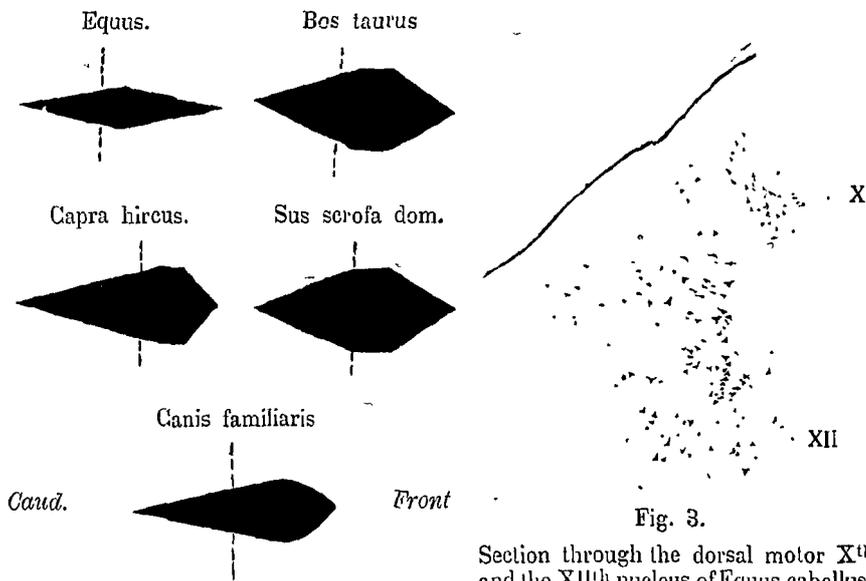


Fig. 2.  
Extension of the nucleus motorius dorsalis vagi (black) in regard to the Calamus scriptorius (dotted line).

Fig. 3.  
Section through the dorsal motor X<sup>th</sup> and the XII<sup>th</sup> nucleus of *Equus caballus*.

*Bos taurus.*

The dorsal motor nucleus of the X<sup>th</sup> covers 500 sections of 18  $\mu$ . The calamus is found in section 212, counted from the caudal pole of the nucleus, so that, similarly as in the horse,  $\frac{2}{5}$  of it are found in the closed part (caudally from the calamus) and  $\frac{3}{5}$  in front of it (comp. fig. 2).

It begins as a small group of cells, caudally from the hind pole of the XII<sup>th</sup>. It soon increases in size and is already a considerable mass of cells when the XII<sup>th</sup> nucleus appears in the sections, lying dorso-laterally from the latter. Already here the nucleus is much larger than in the horse. Forty sections behind the calamus the X<sup>th</sup> nucleus is twice as large as on the corresponding place in the horse.

Near the calamus the nucleus has acquired a considerable dorso-medial extension growing towards the floor of the ventricle. Soon after that it acquires also a pyramidal form, the top of the pyramid being directed towards the ventricle. In one section 200 cells were found. As a rule the cells are larger than in the horse and the number of the large type of cells has obviously increased, several of them exhibiting the large motor type (comp. fig. 3 and 4). The nucleus still increases gradually in size beyond the calamus and keeps its maximum of development as far as the frontal third of its extension, in which it gradually decreases again, first losing the top. It is however still a considerable nucleus when the XII has already disappeared.<sup>1)</sup>

In my series the vagus nucleus extends 75 sections in front of the hind pole of the VII<sup>th</sup>, thus exhibiting in every respect a greater size than in the horse.

*Capra hircus.* The dorsal motor nucleus covers a series of 290 sections of 15  $\mu$ . The calamus is found in section 185 counted from the caudal limit of nucleus. Consequently the relation between the parts contained in the closed region of the oblongata and that in the open bulb is reversed,  $\frac{4}{5}$  of it occurring in the spinal oblongata,  $\frac{2}{5}$  in the open region (see fig. 2). The nucleus begins 60 sections behind the caudal pole of the XII<sup>th</sup> as a small group of cells lying

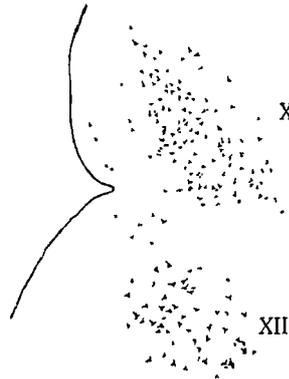


Fig. 4.

Section through the dorsal motor X<sup>th</sup> nucleus and the XII<sup>th</sup> nucleus of *Bos taurus*.

<sup>1)</sup> The nucleus XII of the cow seems to be less developed though than in horse, 20<sup>1</sup>

dorso-laterally from the central canal. Where the XII<sup>th</sup> nucleus appears in the sections the dorsal X<sup>th</sup> has already 25-35 cells, of a similar size as those of the XII<sup>th</sup>. More frontally this relation changes because the cells of the XII acquire a larger size.

Located originally dorsally from the XII it acquires — similarly as in the horse — a more perpendicular position after having increased in its lateral border. Then we find again the pyramidal form, also present in the other animals described till now, the top of the pyramid being directed towards the floor of the ventricle. The nucleus then lies dorso-laterally from the XII. For the rest its relation is very similar to that of the cow. Here also the nucleus extends several sections — 48 — in front of the caudal limit of the VII<sup>th</sup> nucleus.

*Sus scrofa domesticus.* The dorsal motor X<sup>th</sup> nucleus extends over 240 sections of 15  $\mu$ . The calamus is found in section 118, counted from the caudal pole, so that the spinal and bulbar division of the oblongata contain about equal parts of it (compare fig. 2).

The nucleus begins with some fairly large cells dorso-laterally from the central canal caudally from the hind pole of the XII<sup>th</sup> nucleus. The nucleus enlarges (contrary to the condition found in the foregoing animals) at its mesial border. This medial part increases considerably. The nucleus first lies entirely dorsally, then dorso-laterally from the XII (fig. 5) as a pyramid of which (contrary to the foregoing animals) the base is directed towards the floor of the ventricle. The greater number of its cells — amongst which a good many of the large motor type — is about 150 in one section.



Fig. 5.

Section through the dorsal motor X nucleus and the XII nucleus of *Sus scrofa domesticus*.

X<sup>th</sup> extends several sections — 42 — in front of the caudal limit of the VII nucleus.

The largest size is attained in the middle. This size is kept as far as the frontal third part of the nucleus in which the number of cells gradually declines.

Similarly as in the other animals described, the dorsal motor nucleus of the

*Canis familiaris.* The dorsal motor nucleus of the X<sup>th</sup> covers 278 sections of 10  $\mu$  in the dog. In section 125, counted from the hindpole, the calamus is found, so that a little less than the half of it is located

behind the calamus (see fig. 2). The first cells of the dorsal X<sup>th</sup> appear 62 sections behind the caudal limit of the XII<sup>th</sup>, dorso-laterally from the central canal. When the XII<sup>th</sup> nucleus appears the X is found dorsally from it. Near the calamus its cells protrude only a little laterally from the XII, which on this level has already required a considerable size. Only in the open bulb the increase of the nucleus becomes more developed, showing a similar form as in the pig: a pyramid, the base of which lies near the floor of the fourth ventricle.

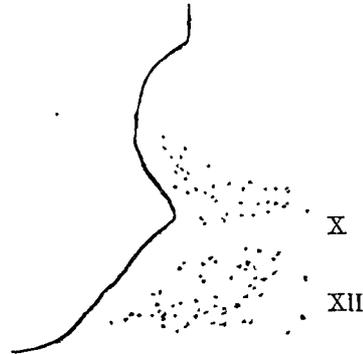


Fig. 6.  
Section through the dorsal motor X nucleus and the XII nucleus of *Canis familiaris*.

Approaching more and more the ependyma, the largest number of its cells is found to be 80. The large type of cells is however — similarly as in the horse — much less frequent than in the ruminantia and in the pig. The nucleus has its greatest size on a more frontal level than in other animals. Over several sections the nucleus keeps a considerable size and then first decreases at its dorsal border, while the rest of it remains on a lower level, lying laterally not dorso-laterally from the XII. The most frontal part as in the other animals extends a little beyond the caudal limit of the facial nucleus as has also been described by KAPPERS<sup>1)</sup>.

From the foregoing pages appears that, in our domestic animals, the dorsal motor nucleus of the X<sup>th</sup> has the least development in the horse, in which also the cells of large type are less numerous. The anatomical characteristics of oesophagus and stomach seem to be in accordance with this. KOSAKA<sup>2)</sup> has demonstrated that the dorsal vagal nucleus innervates the posterior part of the oesophagus, the stomach and the lungs. In the horse the cervical part of the oesophagus contains striped musculature, the thoracic part and stomach smooth musculature. Only microscopically vestiges of striped musculature can be traced in the latter<sup>3)</sup>. In this animal the size of the ventricle is relatively small and consequently there is not much smooth musculature and glands. In the cow, sheep, goat, pig, and dog this

<sup>1)</sup> C. U. ARIËNS KAPPERS. Weitere Mitteilungen über Neurobiotaxis, VII. Die phylogenetische Entwicklung der motorischen Kerne in Oblongata und Mittelhirn. Folia Neurobiologica, Ergänzt. Heft. Bnd VI 1912. S. 116. Fig. 102.

<sup>2)</sup> KOSAKA. Ueber die Vaguskerne des Hundes. Neurologisches Centralblatt No. S. 1909. S. 4 u. 5.

<sup>3)</sup> ELLENBERGER. Handbuch der vergleichenden Mikroskopischen Anatomie der Haustiere.

transition takes place further down the oesophagus. In the cow and the sheep it only takes place in the sulcus oesophagus, the continuation of the oesophagus in the stomach, in the goat, pig, and the dog near the cardia. But not only the oesophageal musculature, also and even chiefly the ventricular smooth musculature is immensely enlarged in the cow, where also the glandular surface is larger and it seems probable to me that these differences have to explain the small size of the dorsal motor X<sup>th</sup> in the horse and the small number of cells of the large motor type found in it.

Although the greater part of the oesophageal red musculature is striped and innervated by the IX, I should not be astonished if this considerable quantity of red musculature in the lower part of the oesophagus and stomach of the cow contained also a good deal of smooth muscles with a vagal innervation.

I have been able to control this in the bird, where the red musculature of the stomach appeared to be smooth. Moreover, among the several hundred horses which passed the section-room I found one in which the oesophagus was red also further down to the place where it pierces through the diaphragm. I examined the praecalamic part of the vagal nucleus (312 sections of 18  $\mu$ ), and I was struck by the fact that in this animal the shape of the oblongata near the calamus resembles more that of the cow and the pig than that of its own sort. Also here the floor of the ventricle protrudes much more in its lateral portion.

In comparison with my other series of 18  $\mu$  it appeared that the nucleus keeps its maximum-size also further frontally. Whereas in the normal horse the nucleus had lost its greatest size 120 sections in front of the calamus, in this horse the maximum of the nucleus was still found 190 sections in front of the calamus. Several cells of the large motor type are found in this nucleus and in many sections the top of the pyramid-shaped nucleus approaches the floor of the ventricle more than is the case in the normal horse.

Consequently it is very obvious that the vagal nucleus is the largest in those animals which have a large stomach. Already KOSAKA and YAGITA<sup>1)</sup> have explained the large size of the dorsal motor X nucleus in birds from the fact that these animals have several stomach compartments. I may add to this that one compartment, the so called muscular stomach of these animals has a considerably developed red musculature (which on microscopical examination appears to be smooth) and the dorsal motor nucleus of the X in birds has many large cells.

<sup>1)</sup> KOSAKA und YAGITA. Experimentelle Untersuchungen über den Ursprung des Nervus Vagus etc. Okayama-Igakwai Zasshi No. 188. 1905. S. 2.

The horse has a stomach which is decidedly small (8.15 L.) and a dorsal motor X nucleus which is equally small (comp. fig. 3), the ruminantia have an enormous stomach (cow  $\pm$  200 L.), which in some compartments is very rich in musculature and glands. In accordance we find a very large dorsal X nucleus in the cow (see fig. 4).

Also the pig is well provided in this respect if we consider the small size of its body (stomach 7.8 L.) and equally the dog. In the latter the stomach varies considerably according to the race, but as a rule is well developed (according to MENTZLAFF 8.26—29.31 % of the body-weight). Among our ruminant animals we find the difference that a ventricular compartment, which in the cow is very muscular is poorly developed in the goat and the sheep. Perhaps this explains the fact why in the latter the dorsal X acquires only its greatest size in its frontal third part, whilst in the cow the nucleus already acquires its greatest dimensions in the middle and keeps this maximum over a much longer distance than the sheep and the goat (see fig 2).

Now comparing the shape of the caudal part of the floor of the fossa rhomboidea with the above mentioned differences in the size and form of the dorsal motor nucleus, we understand why in those animals where this nucleus is more considerably developed and contains a great many motor cells the floor protrudes in the ventricle.

That this is not so in the dog may depend on the fact that this nucleus is only small directly in front of the calamus, and only acquires its greatest size in the frontal third part.

Finally I make use of this occasion to rectify a slip of the pen that has occurred in C. U. ARIËNS KAPPERS'S VII<sup>th</sup> communication on Neurobiotaxis, on p. 97. Dealing with the dorsal motor nucleus of the horse the author says: "Nur beim Pferd fand VERMEULEN ihn erheblich grösser, was er mit dem grossen Magen dieses Tieres in Verbindung bringt". This must be of course "nur beim Rinde".

**Anatomy.** — "*On the relation between the quantity of white and grey substance in the central nervous system.*" By Dr. A. J. HOVY, Utrecht. (Communicated by Prof. L. BOLK).

The relation between white and grey substance in the central nervous system has frequently puzzled the mind of neurologists. So authors (CHIARI, HESCHL, JELGERSMA and others) have alluded to it when dealing with the gyrated surface of the brain.

The quantitative relation has however rarely been measured with any amount of exactness. The greatest obscurity still exists as

far as this relation in regard to the evolutionary standpoint of mammals is concerned. It is even difficult to find a trustworthy method for measuring this relation and still more difficult to explain an eventual result. Doing so there would be a considerable chance to leave the field of exactness and to grasp in the darkness of theories.

The many factors that may act a part in this relation have been mentioned by ERNST DE VRIES <sup>1)</sup>.

Several other authors (SNELL <sup>2)</sup>, WEBER <sup>3)</sup>, DUBOIS <sup>4)</sup> have demonstrated that there exists a relation between brainweight and the place occupied by the animal in the evolutionary series, but specially between the weight of the brain and that of the body in such a sense that small animals have as a rule a greater relative brainweight than large animals of the same order.

From this appears that at least two factors, the evolutionary stage and the size of the animal have an influence on the mass of the brain.

Equally in the study of the relation of grey and white matter different factors have to be considered.

The author intended to study only one of these factors, viz. the influence of the size of the brain on the relation between white and grey matter.

This relation has very rarely been examined with exact methods.

The first who tried to obtain really exact results was DANILEWSKY <sup>5)</sup>, who made use of the physical method of ARCHIMEDES to define the quantitative relation of two constituents of a mixture, by measuring the specific weight of each of the constituents, and then the specific weight of the mixture.

With this method DANILEWSKY found the relation between grey and white matter in a dog's brain to be 50 : 50 in one case and

<sup>1)</sup> Dr. E. DE VRIES, Das corpus striatum der Säugethiere. Anatom. Anzeiger. 37ster Bnd. 1910. p. 386.

<sup>2)</sup> SNELL, Die Abhängigkeit des Hirngewichts und die geistigen Fähigkeiten. Archiv f. Psychiatrie. Bnd 23, 1892.

<sup>3)</sup> WEBER, M. Vorstudien über das Hirngewicht der Säugethiere Festschrift f. Gegenbaur 1896. WEBER, M. Over het Hersengewicht der Zoogdieren. Kon. Akademie v. Wetensch. te Amsterdam, October, 1896.

<sup>4)</sup> DUBOIS, E. Ueber die Abhängigkeit des Hirngewichts von der Körpergröße bei den Säugethieren Archiv. f. Anthropologie, Bnd 25, 1897.

<sup>5)</sup> DANILEWSKY. Die quantitativen Bestimmungen der grauen und weissen Substanzen im Gehirn; Centralblatt für die medizinischen Wissenschaften N<sup>o</sup>. 14, April 1880 p. 241.

The results here referred to were already mentioned by the author at the congress of naturalists in Charkow, 1878.

57:43 in an other. In the human brain DANILEWSKY found as an average result of several experiments this relation to be 39:61.

These results are highly interesting and it is a great pity that DANILEWSKY has not continued this work and that the only results which he mentions concern two subjects with such a different development of the nervous system. I will however call attention to the fact that in the larger of the two — man — the author found a much greater relative amount of white substance (11% more) than in the smaller.

Intending to examine only one of the factors that may influence the relation between white and grey matter: the size of the brain, I have thought it convenient to study corresponding regions in small and large representants of the same orders, thus avoiding as much as possible the influence that might be exercised by differences in evolution. I found the spinal cord to be the most fit for this purpose on account of the circumscript form of its constituents and since the cervical cord of a large amount of material was at my disposal in the Central Institute for Brain Research I have made use of this.

That the brain of large and small animals of the same sort shows a difference in the quantitative relation of the above mentioned constituents was remarked already by BRANDIS <sup>1)</sup> in 1893 and independently of this author by ERNST DE VRIES (l.c.)

The former found that in the spinal cord of a large bird (Anser) the white matter was not only absolutely, but also relatively larger than in a small bird (Regulus, see fig. 2).

It seemed useful to me to test this occasional remark by a larger amount of material chosen from all classes of vertebrates and from as many orders of mammals as were fit for this research. My material contained:

- Two sharks.
- Two chelonia
- Three lacertilia
- Four birds
- Three rodents
- Two ungulates
- Two carnivora
- Four platyrrhine apes
- One elephant.

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<sup>1)</sup> Untersuchungen über das Gehirn der Vögel. Archiv. f. mikr. Anatomie. Bnd. 41, 1893. pag. 177. Theil I.

In all these groups small and large representants were compared — except that there is no small proboscidean to be compared with the elephant<sup>1)</sup>. I have however taken into consideration also the latter because it shows so well the general law in the relation between white and grey matter as will be seen in my table (fig. 1).

The following method was used:

The sections coloured after WEIGERT—PAL were drawn in a projection-apparatus, in about the same size. Since it is only a question of relation the magnification is not of importance, and can only in so far act a part as a stronger magnification enables us to greater exactness in drawing the details of the circumferences.

These drawings were made on waxplates of constant thickness<sup>2)</sup>, and the circumference of the grey and white matter cut out.

The outcuts were weighed and their relation expressed in percents. They are represented in the table of figure 1. In each column the grey matter is represented by the black colour, the white substance by the white colour; the number under each column indicates the percentage of grey matter.

In those columns where a large and a small representant of the same order are compared, we constantly see that in the larger representant the relation is very much in favour of the white matter. Equally in the elephant the enormous prevalence of white substance is striking.

In two animals — *Hexanchus* and *Scyllium* — the grey substance is not very compact but shows a rather reticular arrangement, the openings of the reticulum being filled up with white substance. This made it very difficult to make trustworthy outcuts, for which reason I have omitted to reproduce the results — which however was not in contrast to the general rule.

Since the four platyrrhine apes did not all differ considerably in size, I have only represented the relation in the smallest and largest monkey.

The general rule expressed by my table for small and large adult material seems to be equally striking in the development of the central nervous system as appears from the interesting researches of R. STERN<sup>3)</sup>, who has pointed out that during the development of the spinal cord from infant to adult the white substance increases

<sup>1)</sup> The tapir might be used for comparison being nearest akin. This animal however has not been stained. It is fairly large moreover.

<sup>2)</sup> As used for waxreconstructions after BORN and PETERS' method.

<sup>3)</sup> R. STERN. Beitrag zur Kenntniz der Form und Grösze des Rückenmarks querschnittes. Arbeiten aus dem Neurologischen Institute der Universität Wien 1908, p. 367.

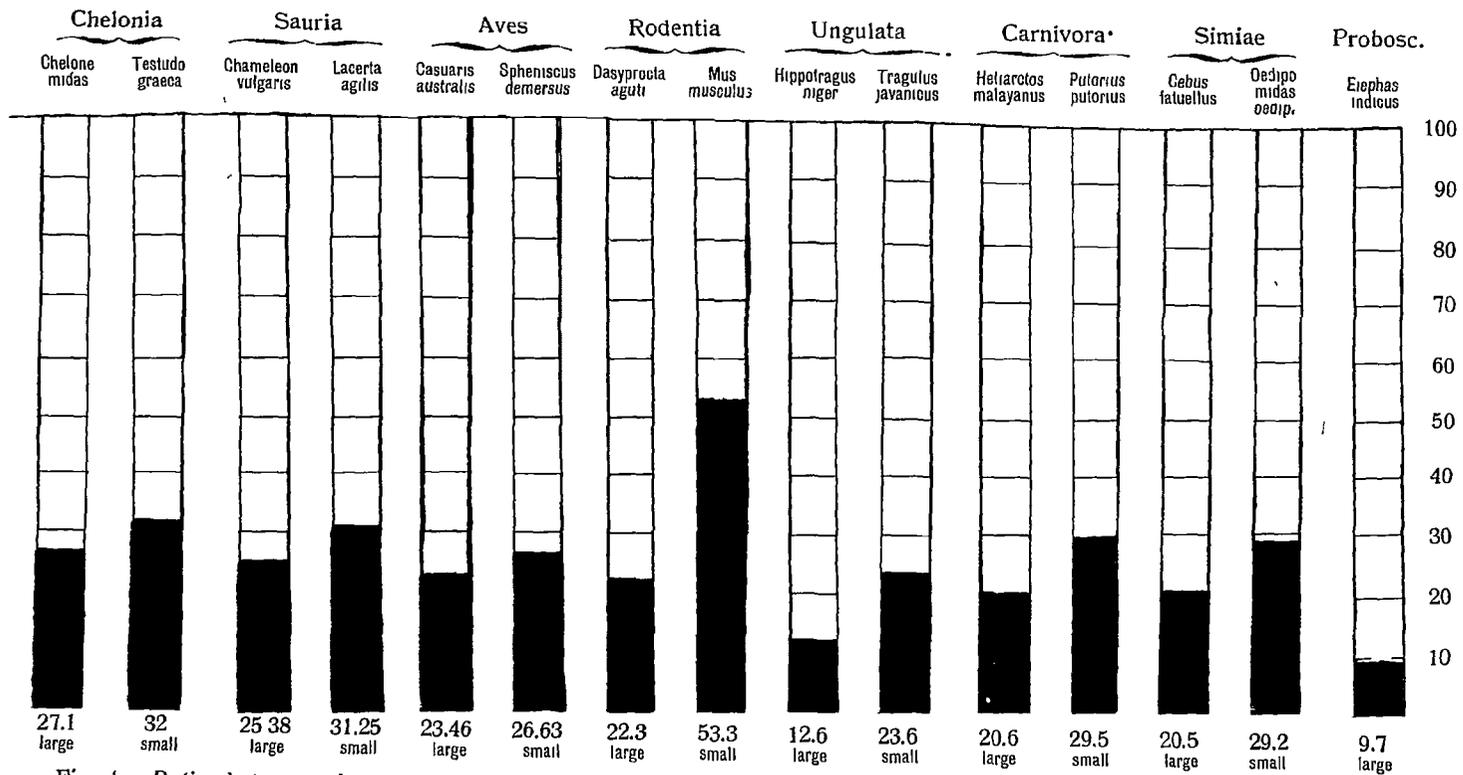


Fig. 1. Ratio between the grey (black) and white (white) matter in the cervical cord of small and large representants of the same orders,

much more than the grey substance (the difference being about 10%).

It seems to me that the rule demonstrated here has to be explained by the factors pointed out by ERNST DE VRIES viz. that if a brain increases in size, the number of myelinated fibres increases with the number of cells (that is with the grey substance) but since each fibre (each myeline sheath) becomes so much longer<sup>1)</sup>, the whole quantity of white matter increases in a higher degree than the quantity of grey matter.

Apart from the differences mentioned above, I found also a difference in the shape of the grey substance in small and large representants of the same orders (see fig. 2).

As a rule the butterfly-like figure representing the grey matter has a clumsy form in small animals whereas in the large ones it is much more gracile. Specially the grey commissure between the left and right horns becomes more gracile as is strikingly demonstrated by a comparison between the mouse and the elephant. It seems that the increase of white substance in the posterior and anterior funiculi causes an enlargement of the distance between the horns.

Finally I want to remark that also the form of the cervical cord as a whole seems to be modified in large animals in such a sense that in small animals this form is more round, while in large animals it is more oval (see fig. 2).

It may be possible that this difference has to be ascribed to a greater opportunity for bilateral extension in the cervical part of the vertebral canal in large animals. It is however equally, if not more possible that the increase of white substance in large animals does not take place in the same degree in all the funiculi of the cord and that special parts are favoured, so it may be that the considerable enlargement of the posterior and anterior funiculi, which causes the horns to lie at a greater bilateral distance of each other, causes at the same time an enlargement of the cord in bilateral sense.

I do not believe as yet that this phenomenon may be considered as a rule, but I wanted to call attention to it since R. STERN (l. c. p. 322) has pointed out the opposite during the growth of the human spinal cord, stating that the spinal cord of the infant has a more oval, the one of the adult a more circular form.

<sup>1)</sup> Moreover the longer myeline-sheaths are often a little thicker. This is however not of great importance relatively and may practically be neglected.

On the other hand the fact that in larger brains some cells are somewhat larger, as has been demonstrated still recently by OBERSTEINER for the Purkinje cells of the Cerebellum (Arbeiten a. d. Neurologischen Institut der Universität Wien Bnd XX, 1913), may be also neglected, since its influence on these relations is relatively unimportant.

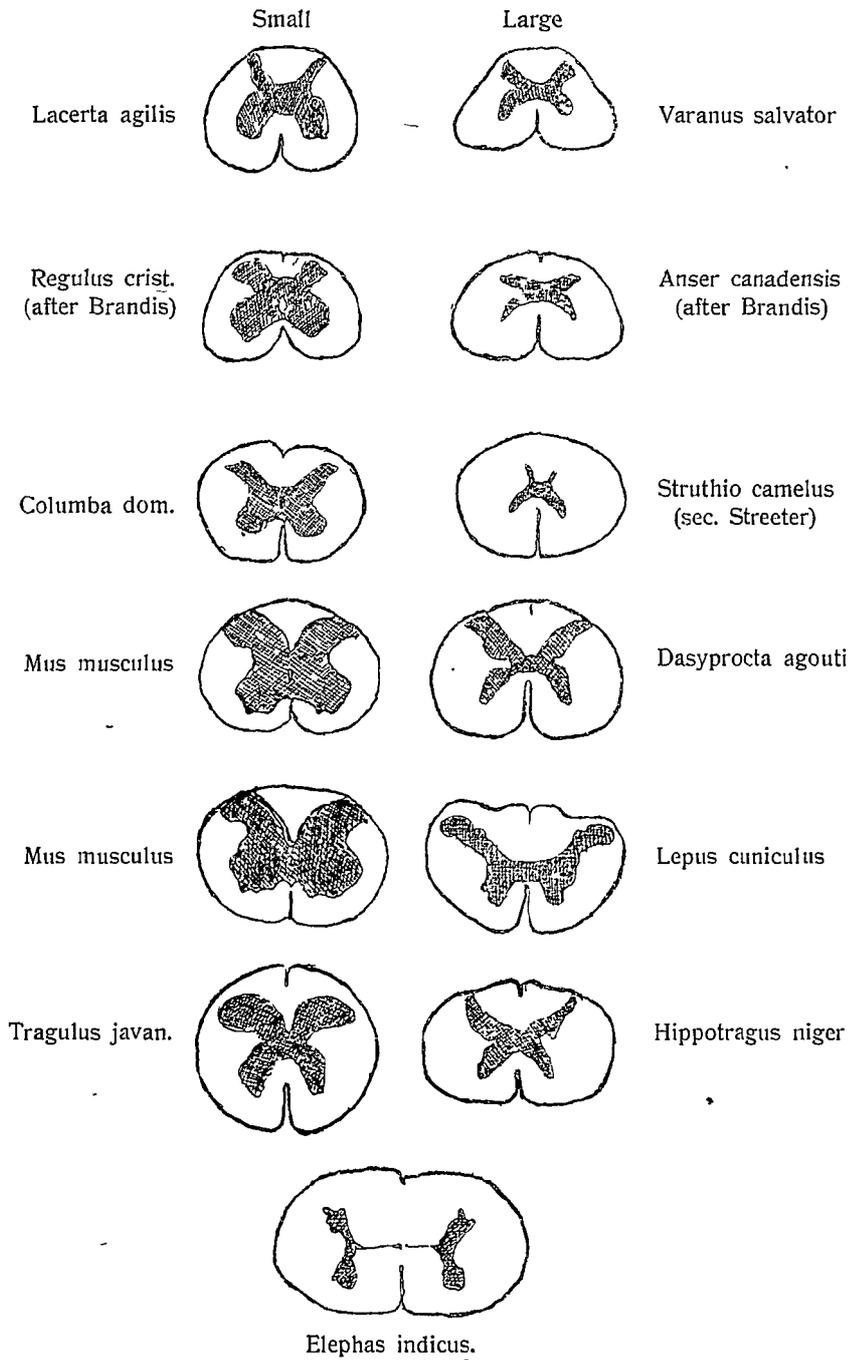


Fig. 2. Relation between grey (black) and white (white) matter in the cervical cord of small and large representants of the same orders. (The sections are drawn in the same size in order to show better the relative enlargement of white substance).

This observation of STERNS seems not to be applicable in a comparison of small and large adults.

Resuming my results, I may state the following conclusions:

1<sup>st</sup>. In the spinal cord of large individuals of the same order the relation of the white substance to the grey is much more in favour of the white than in small individuals.

2<sup>nd</sup>. This rule holds good for all the classes and orders examined.

3<sup>d</sup>. This phenomenon can be explained — and according to my opinion has to be explained — by the explication given by ERNST DE VRIES (vide supra).

4<sup>th</sup>. Also the shape of the grey matter shows a modification in large animals in so far as it becomes more gracile, which is chiefly demonstrated by the distance of and the grey connection between the horns.

**Physics.** — “*The magneto-optic KERR-effect in ferromagnetic compounds.*” IV. By PIERRE MARTIN of Geneva. (Communication from the BOSSCHA-Laboratory by Prof. H. DU BOIS.)

In a former paper<sup>1)</sup> I have given the dispersion curves of the KERR-effect for certain manganese and iron compounds. It should be particularly noticed that almost all of these curves, as has been further confirmed with new material, show an algebraic maximum and minimum between or near the limits of the visible spectrum. In the present research I have determined some new dispersion-curves and have also investigated in the case of a few substances the relation between the KERR-effect and the temperature.

For this purpose the material was cut into small discs of the same size as the pole-top (V, 7 mm.) face, and this entire system completely insulated from the pole-shoes by a layer of asbestos. The heating was accomplished by means of an ordinary Bunsen burner. Up to 300° the temperature was measured with a thermometer imbedded close to the mirror. For higher temperatures up to 450° a compressed nitrogen thermometer was used.

By regulating the flame the temperature could be kept constant to within about 5°. In order to prevent as much as possible oxydation and “tarnish colours” the mirror was constantly bathed with carbon dioxide which had been led over  $\text{KMnO}_4$ ,  $\text{SnCl}_2$ ,

<sup>1)</sup> P. MARTIN. These Proceedings 15, p. 138, 1912.

$\text{NaHCO}_3$  and  $\text{CaCl}_2$  <sup>1)</sup>). A few measurements were made at a low temperature, the whole system being imbedded in carbon dioxide snow.

Otherwise the experimental arrangement was the same as hitherto <sup>2)</sup> except that instead of the small half-ring a large DU BOIS full-ring electromagnet was used. With this all of the mirrors investigated were capable of saturation, since the strongest field was estimated at from 30 to 40 kilogauss.

The direct-vision high-luminosity monochromator <sup>3)</sup> was recalibrated at several points with the aid of a mercury vapour lamp. The observations proper were made exclusively with an arc lamp. The field was reversed each time to eliminate constant errors and the observed values corrected for the FARADAY-rotation in the air-path. In view of the smallness of the rotations it proved still impossible to determine the ellipticity.

As regards the material, it was found that most pulverized substances by moderate compression with or without binding material could also be worked up into pastils which were more or less capable of polish.

The present research aims principally at a general knowledge with regard to the magneto-optical properties. Especially is this true of the temperature curves the range and precision of which need still to be extended considerably.

In the following tables I denote as hitherto by:  $\lambda$ , the wave length of the light in question in  $\mu\mu$ ;  $\Delta$ , the double rotation on reversing the current as read off the scale in mm.;  $\pm d\epsilon$ , the mean error respectively in minutes or in percent.  $N$  is the number of readings made for each direction of the current, which varied according to the brightness of the mirror from 10 to 30;  $t$ , the temperature;  $\theta_0$ , the temperature at which the magnetizability vanishes.

To Geh. Rat. G. TAMMANN, Göttingen, Prof. P. WEISS, Zürich, Privatdocent Dr. S. HILPERT, Charlottenburg, and to the firm, Griesheim-Elektron, I am greatly indebted for kindly supplying valuable materials.

#### BINARY MANGANESE COMPOUNDS.

*Manganese Arsenide* (Mn As, HILPERT,  $\theta_0 = 45^\circ$ ). The rotation in

<sup>1)</sup> R. SIEDENTOPF Dissert p 8 Göttingen 1897.

<sup>2)</sup> Cf. ST. LORIA. These Proceedings **12** p. 835, 1910; **14**, p. 970, 1912.

<sup>3)</sup> H. DU BOIS, Ztschr. für Instr. Kunde **31**, p. 1. 1911.

the yellow amounted to about 1.5' and appeared to vanish in the orange.

*Manganese Antimonide* (Mn. 35. Sb. 65 = MnSb nearly, TAMMANN,  $\theta_0 = 265^\circ$ ). The dispersion curve is given in my first paper (l.c. Fig. 2). The temperature curve,  $\varepsilon = \varphi(t)$ , is represented in table 1. Below  $60^\circ$  the rotation remains constant. In the neighbourhood of  $80^\circ$  it begins to decrease and thereafter continues to decrease at a nearly linear rate. The zero point seems to lie at about  $265^\circ$ . After heating to  $205^\circ$  the rotation rose again to its former value on cooling and, therefore, does not show thermal hysteresis. A second heating gave the two last points near  $222^\circ$  and  $245^\circ$ . Further heating destroyed the mirror.

TABLE 1.

$\varepsilon = \varphi(t)$  Mn Sb (saturated)  $\lambda = 567 \mu\mu$

<i>N</i>	<i>t</i>	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$ (min.)	%
15	25°	— 124.6	— 17.4	0.05	0.3
15	50— 60°	— 125.0	— 17.5	0.05	0.3
15	97—103°	— 113.5	— 15.9	0.1	0.6
10	145—155°	— 71.4	— 11.0	0.2	2.0
10	185—193°	— 49.3	— 6.9	0.2	3.0
15	200—205°	— 40.7	— 5.7	0.05	1.0
12	215—220°	— 27.8	— 3.9	0.1	2.5
15	240—245°	— 14.3	— 2.0	0.1	5.0

## BINARY IRON COMPOUNDS.

*Iron Carbide I*, (Cementite HILPERT,  $\theta_0 = 235^\circ$ ). WOLOGDIN found for the transition temperature  $180^\circ$ , which with the apparatus used by him may represent a lower limit. MAURAIN observed in the case of high degree carbon steels irregularities below  $240^\circ$ . This was confirmed by SMITH, WHITE, BARKER and GUILD who ultimately extracted the cementite powder from their steel by the ARNOLD process<sup>1)</sup>. The

<sup>1)</sup> M. WOLOGDIN, Compt. Rend. 148, p 776, 1909; CH. MAURAIN, Compt. Rend. 150, p. 779, 1910; Ann. d. Chim. et Phys. (8) 20, p. 372, 1910; S. W. F. SMITH, W. WHITE, S. G. BARKER und G. GUILD, Proc. Phys. Soc. London 24, pp. 62, 342, 1912 und 25, p. 77, 1912; I. O. ARNOLD, Journ. Iron & Steel Inst. 1, p, 174, 1910.

final drop in the magnetization was found by them to lie between  $200^\circ$  and  $240^\circ$  for fields of about 10 gauss. First of all was available the sample I, which had been etched with  $H_2SO_4$ . Fig. 1 represents the temperature curve between  $-78^\circ$  and  $+220^\circ$ . The curve extended cuts the axis of abscissae near  $235^\circ$  in agreement with the results of the other observers just cited.

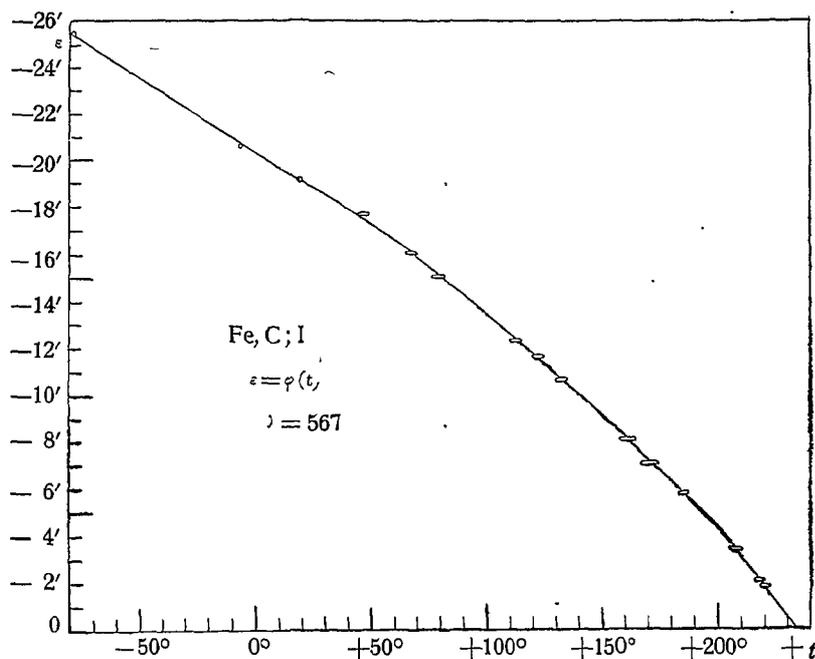


Fig. 1.

I received from Dr. HILPERT, also, two different pulverized cements which after pressing in the dry state could be polished fairly well. These, it should be noticed, gave entirely distinct dispersion curves, different from those for sample I, which moreover differed among themselves. While the latter shows a maximum and minimum of the rotation respectively in the violet-blue and in the green-yellow, these singularities are displaced in the case of samples II and III. All, however, gave strong negative rotations which will now be discussed more in detail.

*Iron Carbide II* (4.8% C, about 20% free iron, HILPERT) shows a powerful rotation (between  $-18'$  and  $-21'$ ) with a numerical maximum in the yellow and a minimum in the orange-red. (Fig. 2). The mirror, which had a distinct yellowish appearance, scarcely

reflected the blue light at all, so that it was impossible to use wave-lengths shorter than  $483 \mu\mu$ .

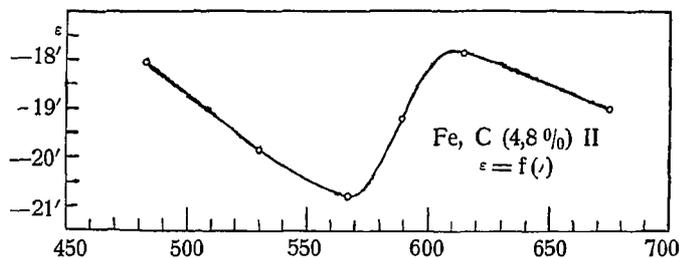


Fig. 2.

On heating, the surface near  $80^\circ$  lost its reflecting power. After repolishing this occurred again, so that no temperature curve could be determined.

*Iron carbide III* (15% C, HILPERT,  $\theta = 183^\circ$ ). Here the rotation was smaller (between  $-4'$  and  $-14'$ ) and showed a numerical minimum in the blue-green. Yellowishness of the mirror, however, prevented measurements in the blue below  $466 \mu\mu$ .

The dispersion curve is shown in Fig. 3.

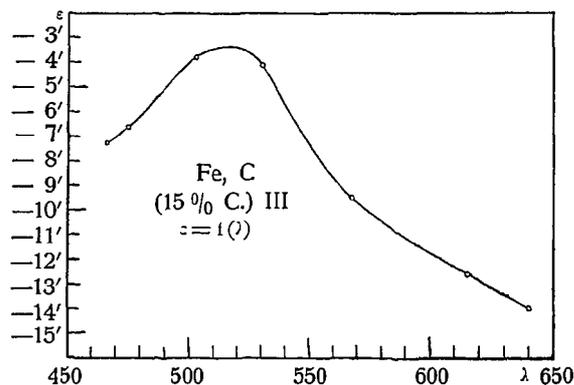


Fig. 3.

Above  $110^\circ$  the rotation decreased gradually and at a nearly linear rate up to about  $183^\circ$ . The reflected image finally became indistinct and during the cooling only a small rotation of  $1,5'$  could with difficulty be perceived. This observation was repeated. Gentle polishing, however, served to restore the original condition completely, so that the phenomenon cannot be regarded as thermal hysteresis.

The temperature curve is shown in Fig. 4.

The zero point agrees with that found by WOLOGDIN. According

to HILPERT the sample III contains free carbon together with a new higher carbide, possibly  $\text{FeC}_2$  or  $\text{FeC}$ . The diversity of the

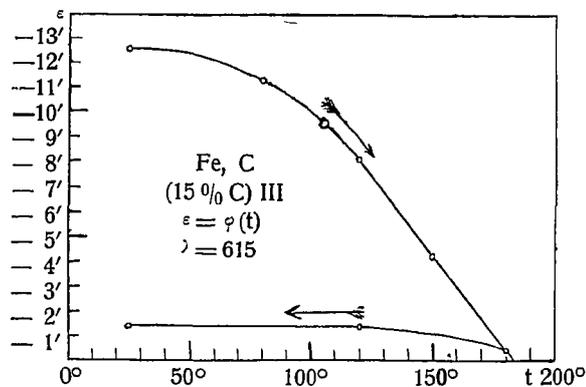


Fig. 4.

results may, therefore, be due to the presence of two or even three carbides or mixtures of the same, which is interesting from a metallurgical point of view.

*Ferrosilicon* (atomic percentage of Si 30, TAMMANN,  $\theta_0 > 450^\circ$ ) Conglomerate of mixed crystals. The saturated mixed crystal with 33,3 atom. perc. Si has the same composition as the compound, Fe, Si whose existence is still uncertain<sup>1)</sup>. The hard material could be finely polished. The substance is characterized by a powerful negative rotation increasing continuously from the violet to the red and by the absence of singularities in the dispersion curve. (Tab. 2).

T A B L E 2.  
Ferrosilicon (saturated) TAMMANN.

$N$	$\lambda(\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \sigma\varepsilon$ (min.)	%
20	435	— 93.9	— 13.18	0.04	0.3
20	450	— 101.3	— 14.22	0.04	0.3
18	483	— 111.1	— 15.58	0.03	0.2
20	530	— 119.5	— 16.75	0.02	0.15
25	567	— 123.2	— 17.27	0.01	0.06
30	615	— 126.0	— 17.65	0.01	0.06
20	675	— 128.0	— 17.91	0.02	0.1
17	703	— 129.1	— 18.05	0.03	0.2

<sup>1)</sup> G. TAMMANN und W. GUERTLER, Zeitschr. f. Anorg. chem. 47, p. 163, 1905.

The rotation, already somewhat smaller at 80°, decreases slowly and at a nearly linear rate up to 280° after which it falls off very rapidly and vanishes apparently at about 460°. The course of the observations was as follows. The mirror was heated gradually up to 300°. At 340° it began to tarnish. The freshly polished mirror was then heated as rapidly as possible, since the "tarnish colours" form only slowly, up to 305°. Here a few test readings were taken which were satisfactorily continuous with the previous ones. At 400°, however, the mirror began to discolour again, the rotation increasing gradually. Nevertheless, I was able to estimate the minimum value of the rotation at about 4°. The behaviour on cooling could not be determined on account of the tarnish. The temperature curve is given by Table 3.

TABLE 3.

 $\epsilon = \varphi(t)$   $\lambda = 615 \mu\mu$  Ferrosilicon (saturated) TAMMANN.

$N$	$t$	$\Delta$ (mm.)	$\epsilon$ (min.)	$\pm \delta\epsilon$ (min.)	%
30	25°	- 126.0	- 17.65	0.01	0.06
15	87°	- 121.1	- 16.96	0.02	0.1
14	120°	- 115.3	- 16.16	0.02	0.1
15	160°	- 107.5	- 15.05	0.03	0.2
17	202°	- 101.0	- 14.15	0.04	0.3
15	243°	- 92.8	- 12.99	0.04	0.3
20	295°	- 82.7	- 11.56	0.02	0.2
10	305°	- 75.4	- 10.6	0.1	1
	405°	- 28	- 4		

*Ferrocobalt*; ( $\text{Fe}_2\text{Co}$ , WEISS and VON FREUDENREICH,  $\theta_0 = 987^\circ$ ). This substance was investigated by PREUSS<sup>1)</sup>; its intensity of magnetization at saturation, as is well known, is about 10% greater than that for pure iron. It shows, accordingly, throughout the entire spectrum the most powerful rotation yet observed and a clearly distinguishable ellipticity. The curve has a sharp minimum in the violet, then rises rapidly in the green and less rapidly in the red where the maximum rotation amounts to about - 34°.

<sup>1)</sup> A. PREUSS, Dissert Techn. Hochschule. Zürich 1912.

T A B L E 4.  
 $\varepsilon = f(\lambda)$  Fe<sub>2</sub>Co (saturated) WEISS.

<i>N</i>	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$ (min.)	%
30	435	— 156.3	— 22.11	0.04	0.2
25	458	— 153.2	— 21.67	0.04	0.2
30	475	— 155.6	— 22.00	0.03	0.25
10	503	— 170.0	— 24.05	0.04	0.15
25	530	— 189.8	— 26.85	0.02	0.08
20	567	— 211.7	— 29.94	0.01	0.03
25	615	— 223.9	— 31.69	0.02	0.06
20	675	— 235.6	— 33.33	0.04	0.12
25	695	— 239.6	— 33.89	0.05	0.15

*Ferronickel* (Fe<sub>2</sub>Ni, WEISS and VON FREUDENREICH<sup>1)</sup>). The dispersion curve belongs to the general type showing a numerical maximum in the yellow and a minimum in the red. (Tab. 5). The rotation is, however, greater and the form of the curve different than for the nickel iron alloys (25.4, 27 and 36 percent nickel) investigated by LORIA<sup>2)</sup>. As regards the effect of temperature, the rotation increases on heating from — 78° at first slowly and then more rapidly (Tab. 6). Owing to the “tarnish colours” it was impossible to make measurements above 250° at which point the rotation had decreased to about one half its initial value.

#### METAFERRITE SERIES.

In these compounds, whose composition has been determined by HILPERT<sup>3)</sup> and which are related structurally to ferroferrite, the iron oxyde acts as the acid radical and as the seat of the ferromagnetic properties. Available were calcium-, ferro-, ferr-, cobalto-, cupri-, and zincferrite, all of which are more or less magneto-optically active. They are arranged in the following in the order of the atomic weight of the basic component.

<sup>1)</sup> Cf. F. HEGG, Diss. Techn. Hochschule Zürich 1910.

<sup>2)</sup> ST. LORIA, l. c. As a matter of fact the compound, Fe<sub>2</sub>Ni, behaves differently and forms an exception to the general nickel steel series; cf. S. HILPERT and E. COLVER-GLAUERT, Zeitschr. f. Electrochemie 17, p. 760, 1911.

<sup>3)</sup> S. HILPERT Verh. D. Phys. Ges. 11, p. 293, 1909. Ber. D. Chem. Ges. 42, p. 2248, 1909.

TABLE 5.

 $\varepsilon = f(\lambda)$  Fe<sub>2</sub>Ni (saturated) WEISS

<i>N</i>	$\lambda(\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min)	$\pm \delta\varepsilon$ (min.)	%
20	435	— 125.3	— 17.56	0.05	0.25
15	483	— 141.9	— 19.88	0.05	0.25
20	530	— 154.8	— 21.69	0.03	0.15
18	567	— 160.9	— 22.55	0.03	0.14
13	589	— 159.1	— 22.29	0.03	0.14
18	615	— 145.2	— 20.30	0.03	0.15
20	640	— 133.0	— 18.61	0.02	0.11
20	675	— 138.1	— 19.33	0.03	0.15
20	703	— 142.9	— 20.00	0.05	0.25

TABLE 6.

 $\varepsilon = \varphi(t)$   $\lambda = 567 \mu\mu$  Fe<sub>2</sub>Ni (saturated) WEISS

<i>N</i>	<i>t</i>	$\Delta$ (mm)	$\varepsilon$ (min)	$\pm \delta\varepsilon$ (min.)	%
30	— 78°	— 131.7	— 18.46	0.02	0.1
20	+ 20	— 126.4	— 17.70	0.02	0.1
12	+ 88—93°	— 112.0	— 15.68	0.04	0.25
15	+ 117—122	— 106.5	— 14.91	0.03	0.2
15	+ 158—163	— 96.0	— 13.44	0.04	0.3
17	+ 200—205	— 86.3	— 12.08	0.03	0.25
15	+ 240—245	— 74.8	— 10.47	0.03	0.3

*Calcium ferrite.* (CaO . Fe<sub>2</sub>O<sub>3</sub>, HILPERT,  $\theta_0 = 156^\circ$ ). The rather hard brittle material could be nicely polished. The failure of LOMIA to obtain an effect with this same substance was probably due to an accidental selection of those points in the spectrum at which the rotation is either zero or very small. It is exceedingly minute, to be sure, throughout. Nevertheless, I was able to determine a curve. This is of the general type with an algebraic minimum in the blue,

maximum in the green and zero points near  $510 \mu\mu$  and  $590 \mu\mu$ . (Fig. 5  $\times$  points).

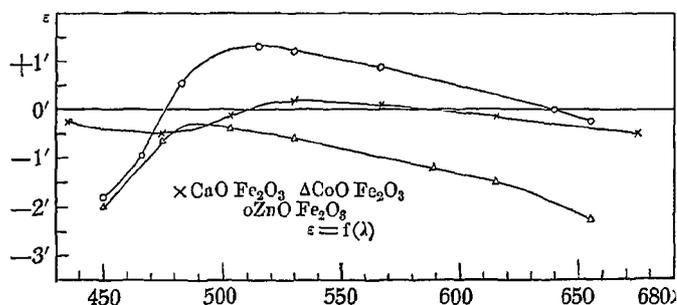


Fig. 5

The rotation was too small for the determination of a temperature curve.

*Titanium ferrite* ( $\text{Ti}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3$ , Ilmenite, regular). The same mirror as used by LORIA without result gave no measurable effect ( $\epsilon < 0,1'$ ).

*Ferroferrite* ( $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ , magnetite electrode of the firm Griesheim-Elektron,  $\theta_0 > 500^\circ$ ). The dispersion curve is very similar to those found by LORIA for a natural octahedral surface and by WEISS for calcined amorphous  $\text{Fe}_3\text{O}_4$ . The maximum  $\pm$  rotations are, however, somewhat less. The singular points of the three curves are located as follows:

Ferroferrite	Zero-point	Maximum
Natural Octahedral Surface	464 $\mu\mu$	ca. 575 $\mu\mu$
Calcined Amorphous	492 „	„ 615 „
Magnetite Electrode	496 „	„ 600 „

The position of the flat maximum is, of course, more or less uncertain. The agreement is, therefore, much better than e.g. with the cementite samples.

On heating the decrease in the rotation begins before  $200^\circ$  and continues nearly linearly up to  $430^\circ$ . A straight line extrapolation of the curve cuts the axis of abscissae near  $510^\circ$  (Tab. 8). On cooling the point near  $200^\circ$  was again observed and at ordinary temperature the values of the rotation agreed with those before heating.

*Ferriferrite* [ $\text{Fe}_2\text{O}_3 \cdot 2\text{Fe}_2\text{O}_3$ , martite, pseudomorphous with octahedral magnetite, from Twin Peaks, Utah]. The above form of the

TABLE 7.

 $\varepsilon = f(\lambda)$  Magnetite Electrode (saturated) GRIESHEIM.

$N$	$\lambda$ ( $\mu\mu$ )	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm d\varepsilon$ (min.)	%
20	435	- 20.6	- 2.91	0.12	4
20	450	- 17.9	- 2.53	0.10	4
20	466	- 15.4	- 2.17	0.05	2.5
15	483	- 7.7	- 1.10	0.06	5.5
20	493	- 3.0	- 0.43	0.02	4.5
15	503	+ 5.1	+ 0.70	0.04	6
10	530	+ 19.3	+ 2.69	0.08	3
25	567	+ 30.6	+ 4.27	0.01	0.2
12	589	+ 32.4	+ 4.54	0.05	1
15	615	+ 31.8	+ 4.44	0.03	0.7
30	675	+ 25.2	+ 3.53	0.02	0.6
15	695	+ 22.4	+ 3.14	0.10	3
20	712	+ 19.7	+ 2.76	0.15	5.5

TABLE 8.

 $\varepsilon = \varphi(t)$   $\lambda = 589 \mu\mu$  Magnetite Electrode (saturated) GRIESHEIM.

$N$	$t$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm d\varepsilon$ (min.)	%
12	20°	+ 32.4	+ 4.54	0.05	1
17	135-140°	+ 31.5	+ 4.40	0.03	0.7
15	200-205°	+ 27.9	+ 3.91	0.05	1.3
20	305-310°	+ 18.0	+ 2.52	0.04	1.6
15	425-430°	+ 7.3	+ 1.02	0.05	5

chemical symbol is in accordance with the theory of HILBERT which supposes that in the case of magnetic iron oxide the basic and acid properties are united in one and the same molecule. It is, however, conceivable that the very slight activity of the acid radical may be due to an admixture of foreign basic oxide in the mineral.

In any case, I was able using a polished surface to measure with tolerable precision an exceedingly minute rotation. ( $\varepsilon < 0,2'$ ). This increases somewhat toward the blue and seems to weaken at the end toward the red. The form of the curve is, of course, very uncertain. (Tab. 9).

TABLE 9.

$\varepsilon = f(\lambda)$  Martite (saturated) TWIN PEAKS

<i>N</i>	$\lambda(\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$ (min.)	%
25	466	+ 3.4	+ 0.45	0.05	11
20	503	+ 1.7	+ 0.22	0.04	18
15	530	+ 0.8	+ 0.10	0.03	33
25	567	+ 1.3	+ 0.18	0.03	11
18	615	+ 0.6	+ 0.08	0.03	37
15	640	0.0	- 0.01	0.04	
30	640	+ 0.6	+ 0.08	0.03	37

The smallness of the rotation did not permit a determination of the temperature curve.

*Ferriferite* ( $Fe_2 O_3 \cdot 2Fe_2 O_3$ , haematite, hexagonal, from Elba,  $\theta_0 = 645^\circ$ ). The same as above holds for the natural specular ore<sup>1</sup>). From an excellent crystal a mirror was cut parallel to the principal axis. LORIA was able for this direction to give only an upper limit for the rotation,  $0,2$ . In view of the positive results with martite it seemed that the rotation with haematite could perhaps also be measured. This proved to be the case, the rotations lying in the neighbourhood of the above limiting value and being likewise positive. The increase toward the violet appears to be less marked than with martite, but little weight can be attached to the exact form of the curve. (Table 10).

A beautifully reflecting mirror cut parallel to the base gave, in agreement with LORIA's result, absolutely no rotation. The base is, therefore, a "ferromagnetic plane". It was out of the question to determine the temperature curve.

<sup>1</sup>) T. KUNZ. (Neues Jahrb. f. Mineral. etc. p. 86 1907) determined for simple normal haematite  $\theta_0 = 645^\circ$ ; the optical constants were measured by G. FÖRSTERLING, loc. cit. Beil. 25, p. 344, 1907.

TABLE 10.

 $\varepsilon = f(\lambda)$  Haematite (saturated) ELBA

$N$	$\lambda(\mu\mu)$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$ (min.)	%
20	450	+ 2.1	+ 0.27	0.1	37
20	483	+ 0.8	+ 0.10	0.05	50
18	530	+ 1.0	+ 0.14	0.02	14
20	580	+ 0.7	+ 0.09	0.01	11
25	615	+ 0.1	+ 0.01	0.02	
30	648	+ 0.9	+ 0.13	0.03	23

*Cobaltoferrite* ( $\text{CoO} \cdot \text{Fe}_2\text{O}_3$ , HILPERT,  $\theta_0 = 520^\circ$ ). The material, a black powder, yielded a sufficiently reflecting mirror. The rotation is throughout the entire spectrum negative and reaches a numerical minimum in the blue green. (Fig. 5). Up to  $250^\circ$  I was unable to detect any decrease in the rotation.

*Cupriferrite* ( $\text{CuO} \cdot \text{Fe}_2\text{O}_3$ , HILPERT,  $\theta_0 = 420^\circ$ ). LORIA has determined the dispersion curve (l.c. p. 897). On heating, the rotation remains constant up to  $200^\circ$ . It then decreased at first slowly and then somewhat more rapidly up to  $420^\circ$  where it vanished. On cooling, the rotation regained its original value. (Table 11).

TABLE 11.

 $\varepsilon = \varphi(t)$   $\lambda = 475 \mu\mu$  Cupriferrite (saturated) HILPERT

$N$	$t$	$\Delta$ (mm)	$\varepsilon$ (min.)	$\pm \delta\varepsilon$ (min)	%
15	$25^\circ$	+ 12.8	+ 1.75	0.03	2
20	$212-217^\circ$	+ 12.5	+ 1.71	0.02	1
15	$280-287^\circ$	+ 11.5	+ 1.51	0.03	2
15	$347-353^\circ$	+ 6.7	+ 0.91	0.04	4
15	$385-393^\circ$	+ 3.4	+ 0.50	0.04	8
20	$410-415^\circ$	+ 1.0	+ 0.16	0.03	19

*Zincferrite*. ( $\text{ZnO} \cdot \text{Fe}_2\text{O}_3$ , Franklinite, from Franklin, New Jersey,  $\theta_0 = 62^\circ$ ). The sign of the rotation changes twice within the

spectrum. It is positive in the green and negative at the two ends. The zero points are near  $477 \mu\mu$  and  $640 \mu\mu$ . The form of the curve, also, indicates a minimum in the ultra-violet. (Fig. 5,  $\circ$  points).

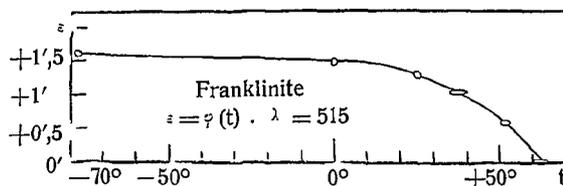


Fig. 6.

The rotation decreases very slowly from  $-78^\circ$  to  $0^\circ$ . It then falls off rapidly, vanishing between  $60^\circ$  and  $65^\circ$ . (Fig. 6). In agreement with this WOLOGDIN found  $61^\circ$  for the transition temperature.

**Physiology.** — “*On the TYNDALL-phenomenon in gelatin-solutions.*”

By L. ARISZ. (Communicated by Prof. H. ZWAARDEMAKER).

(Communicated in the meeting of June 28, 1913).

In watching the TYNDALL-phenomenon in a 1% gelatin-solution Prof. ZWAARDEMAKER observed a greater intensity of the diffused light after the change from sol to gel than before the gelatification.

This prompted me to investigate the TYNDALL-phenomenon more closely.

For a determination of the intensity of the light a method was adopted that has been suggested by HARTMANN<sup>1)</sup>. My mode of procedure was the following: A series of photographs were taken of the TYNDALL-phenomenon at right angles to the incident pencil and the intensity was calculated every time from the grade of blackness of the picture. This estimation was based on the principle, that when a number of plates, as uniform as possible, are exposed under precisely the same conditions of time, temperature, development and further treatment, the density of the negative will depend only on the intensity of the light.

Different portions of a plate being successively exposed at various known distances to the same constant light-source for an equal space of time, afford a suitable scale of various grades of blackness. For

<sup>1)</sup> Zs. f. Instrum. 19. 97. 1899.

a measurement of the intensity of the light we have only to compare the density of the image of the TYNDALL-cone with this scale.

A small NERNST-lamp I found to work very well as a light-source; by means of some lenses its light was focussed to a well-defined pencil, which was sent through a closed glass cuvette with smooth walls and filled with the solution to be examined. In order to regulate the temperature the cuvette was placed on a thermostat, a cover of asbestos preventing as much as possible the influence of the temperature of the surroundings. The cover was removed only while the pictures were being taken. This arrangement as well as the photographic apparatus was unaltered during the whole series of exposures, so as to yield perfectly comparable results.

In order to obviate any deteriorating influence of an occasional inconstancy of the NERNST-lamp or of some error in our procedure, an exposure was made together with the TYNDALL-phenomenon on the same plate, of a surface, lighted directly by the lamp. The density of this comparison surface must be the same on the various plates of a series in order to draw conclusions from the differences in the pictures of the TYNDALL-cones<sup>1)</sup>.

After some preliminary experimentation with an aqueous gelatin-solution, demonstrating that a fall of the temperature causes a considerable rise of the intensity, I invariably used solutions of gelatin in glycerin, because a previous investigation of some other properties, especially the viscosity, had proved how their condition is influenced by the temperature. An advantage of these solutions is that, in closed vessels, they keep very long without any alteration attributable to evaporation or to micro-organisms. For the solution I used commercial glycerin containing about 30% of water and gelatin, which had been washed long enough, to remove the salts and had then been dried again. After careful filtration the solution was put in the cuvette. Then it still contained a large number of air-bubbles, which could be removed in vacuo at 70°.

In all gelatin-solutions that were examined, the incident pencil generated a beautiful cone. In diluted solutions nearly the same intensity is observed over its whole length; in more concentrated solutions (10 %) the intensity diminishes rapidly but evenly, as the

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<sup>1)</sup> For the pictures I used the very sensitive plates of Lumière ("étiquette violette"). Time exposure 30 sec. Development with oxalate of iron after EDER for 2 minutes. Fixation in a hyposulphite solution. Development with oxalate of iron is preferable since it yields perfectly black tints, whereas organic developers often act upon the tone of the image.

pencil penetrates farther into the solution. The colour of the diffused light is white and, as in all other cases, the light, emerging perpendicularly on the incident pencil, is highly polarized.

In experimenting upon the TYNDALL-phenomenon I was guided by the knowledge of the changes in gelatin-solutions, obtained in studying the viscosity in the selfsame solutions. Before long I intend to discuss this point at length. With a view to elucidate the experiments reported in this paper, it is necessary to preface them with a short survey of my experience just now alluded to.

The properties of a gelatin-solution, whether this be a sol or a gel, are, in a condition of equilibrium, completely determined by the concentration, the temperature and the pressure. Most often, however, the solution worked with is not in equilibrium. Therefore, even under constant outward circumstances alterations are to be noted in the solution, which bring it nearer to the equilibrium. This approximation occurs rapidly at 60° or at a higher temperature, when the equilibrium is established in a few minutes. Lower temperatures slacken this process. At 40° it takes some days even; at 20° an equilibrium cannot be noted even after three weeks and at 0° the progress of the process is imperceptible.

In order to find the value of a variable in the equilibrium at a given concentration, temperature and pressure, I took the equilibrium to be the limit of all the changes that occur in the solution. Therefore, the preceding treatment was conducted in such a way, that when the desired temperature was reached, the value of the variable was either too high or too low, so that while the temperature remained the same, it was respectively reduced and augmented. By prolonging the experiment we can get as near to the equilibrium as we like.

Now it appeared that the intensity of the TYNDALL-cone evinced changes similar to those described here. We publish an experiment in which the phenomenon was faint soon after the required temperature was reached and was gradually intensified; a 2% gelatin-glycerin solution, after being heated for five minutes to 70°, was at once cooled in cold water. As soon as the room-temperature was reached pictures were taken at regular intervals of an hour. The images obtained, showed that the intensity of the light had increased continuously. In the meantime another change had taken place in the solution, viz. the viscosity had increased slowly and after 2 hrs the solution had been solidified; even then, however, the intensity was increasing; this was proved by an exposure made after 12 hours.

We give a summary of our results in the following table <sup>1)</sup>.

2% gelatin-glycerin solution cooled to 16° after heating to 70°					
Readings after	0 hr	1 hr	2 hrs	3 hrs	12 hrs
Consistence	fluid	viscous	nearly solid	solid	solid
Intensity	0,25	1	1,4	1,4	2,8

The conversion from sol to gel is not sudden.

In another experiment the initial intensity of the TYNDALL-phenomenon at the temperature of the experiment was greater than when the solution reached the equilibrium, determined by this temperature, so that, as the test proceeds a reduction of the intensity is to be looked for. The experiment was performed with a 1% solution that had been kept at room-temperature for some time and had subsequently been warmed to 50°. *At this temperature the solution was fluid always.* At intervals of 24 hrs three determinations were made, demonstrating a slow and slight diminution of the intensity of the light.

1% gelatin-glycerin after 10 days at 16°—18°, warmed to 25°.

Readings after:	1 day	2 days	3 days
Consistence:	fl.	fl.	fl.
Intensity:	5,6	4	4

After heating to 70° the intensity was rapidly reduced to 0,5 and then remained constant. Experiments such as these can be repeated at will on the selfsame liquid. The results will ever be the same. They are in keeping with the above survey, so that we are justified in concluding that the intensity of the TYNDALL-phenomenon always approximates its equilibrium value and that in that state it is a function of the temperature.

Hereafter we were eager to know, whether the changes of the TYNDALL-cone occur only when the solution passes from sol to gel or whether they are not dependent on this conversion. To ascertain this a series of experiments were carried out with a 1% solution, that had been heated beforehand to 70°. They were continued for 12 days, in which time the viscosity was highly increased, but a conversion to gel was out of the question. At first an exposure was made every 24 hrs, later on every 2 × 24 hrs. It appeared that after 12 days no equilibrium had been established; from the 1<sup>st</sup> to the 8<sup>th</sup> exposure (on the 12<sup>th</sup> day) a set of negatives was obtained,

<sup>1)</sup> The values recorded apply to the most intense portions of the cone. They are calculated from ratios for which the unit was arbitrary.

illustrating a growing intensity of the TYNDALL-phenomenon ; the rate of the growth, however, was gradually reduced.

1% gelatin-solution cooled to 16°—18° after heating to 70°.

Readings after: 0 d. 1 d. 2 d. 4 d. 6 d. 7 d. 9 d. 11 d.  
consistence: fl.  
Intensity: 1 2 2 2,5 4 4 5,6 5,6

We are in a position to record also another experiment carried out at 20° with a 2% solution and started a few hours after the solidification of the solution. For four days the changes were noted. Here also an alteration took place, which was most marked in the first 12 hours and then became less conspicuous.

2% gelatin-solution cooled to 20° after heating to 70°.

Readings after: 0 d. 1/2 d. 1 d. 1½ d. 2 d. 3 d.  
consistence: solid  
Intensity: 1,4 4 5,6 5,6 5,6 (4)<sup>1)</sup>

The last two experiments yielded two series of plates that were very much alike inter se. It is impossible to determine whether they had been taken from a sol or from a gel. The TYNDALL-cone does not enable us to tell the one from the other any more than the naked eye does.

The changes in the 1% and the 2% solutions are not so conspicuous at high temperatures as at the temperature of the above experiments. At 40° no change could be made out, and if we compare the intensities at 40° and at 70°, the difference seems to be nihil. We take it therefore, that beyond 30° the temperature has only little, if any, influence on the intensity and that the increase commences only below 30°.

Additional experiments were made with 5% and 10% solutions. As for the latter we can but say, that changes presumably did occur at various temperatures, but that they could not be clearly demonstrated by our method of working<sup>2)</sup>.

The 5% solutions yield results similar to those of the 1% and the 2% solutions. Here also different values of the intensity of the light correspond to the various temperatures; changes only appear at lower temperatures. Contrary to the 1% solution, an obvious difference is to be noted in the 5% sol. between the intensity at 40° and 70°, as shown in the following table:

<sup>1)</sup> In this exposure the comparison surface was not equal to that of the other plates of the series.

<sup>2)</sup> The rapid reduction of the intensity of the diffused light as the pencil penetrates farther into the solution, renders it difficult to determine the differences in the absolute intensity.



KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
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*Secretary:* Prof. P. ZEEMAN.

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**Physiology.** — “*Rolling movements, and the ascending vestibular connections. (Fasciculus Deiters Ascendens.)* By Dr. L. J. J. MUSKENS<sup>1)</sup>. (Communicated by Prof. J. K. A. WERTHEIM SALOMONSON).

(Communicated in the meeting of April 25, 1913).

By rolling movements we intend to have understood, the complex of symptoms that I described under the name<sup>2)</sup> of rolling movements, so that this forced movement was reckoned to be present, as long as the head was rotated around the bodily axis (cervical spine) and there is still present an apparent tendency to lie down on one side, and inclination to fall down on that side. We deal here therefore with a locomotion, or tendency to locomotion, in a vertical plane, standing vertical to the long axis of the body.

I have arranged a great number of experiments, about the N. vestibularis especially on cats, after the anatomical lesions, found with the MARCHI method after death.

In a first group the cases, where the vestibular root itself was wounded by the instrument, or was found degenerated at least to such a point (by stretching, cerebral haemorrhage) in such an intensity that a very serious lesion of the root either partial or total must have been present. The supposition of this serious lesion of the vestibular nerve when finding compact degeneration of the root gains in probability, as soon as one compares the duration of the rolling movements in this group with the duration of this movement after other lesions, as also with the duration of the circuscumovement in a former publication.<sup>3)</sup> Then one is struck by the far longer duration of the forced movements, after direct lesion of the vestibular nerve, i.e. in the cases with anatomically certified degeneration as above was alluded to. Practically in cats only after direct lesion of the vestibular nerve during weeks rolling movement can be found; after lesion of the vestibular nuclei, and a fortiori of the ascending systems only the formerly described minor conditions of the forced movements can be found.

If we study up this first group, at once we are struck with the fact, that without exception the rolling movement is performed, in the same direction i.e. in such a way, that the locomotion always

<sup>1)</sup> (In this paper. a translation of the one that was communicated April 25, 1913, the author has introduced considerable additions and alterations).

<sup>2)</sup> Journal of Physiology XXXI, 1904 p. 204—221.

<sup>3)</sup> The posterior longitudinal fascicle and the circuscumovement. These Proceedings 26 Oct. 1912, and Neuraxe 1913, p 727.

takes place, to the side of the lesion.<sup>1)</sup> Usually shortly after the operation a rotation of the eyeballs around their anteroposterior axis in the same direction is present and also mystagmiform movements of the eyeballs, slow in the sense of the rotations and rapidly back to the normal position (loc. cit.).

In the latter stages the only symptom recalling the movements is a tendency to lie down on the operated side, or even a slighter resistancè, if one tries to push the animal on that flank.

All this is in accordance with the older experiments of FLOURENS, SCHIFF and CYON and the more recent ones of EWALD, WINKLER, BARTELS etc. about lesions of the semicircular apparatus and section of the N. acustico-vestibularis.

As soon as the rolling movements are completely compensated, it is easy by blindfolding the animal, by causing an emotion or by the dropping experiment of MAREY (the normal animal lift up by its feet and dropped unvariably comes down on its feet) to bring about again the original rotation. Also in epileptic fits the rotation may reappear. It is peculiar that in ether-narcosis sometimes a rotation in the inverse sense was noted.<sup>2)</sup>

All this being the rule for experimental animals, whether it be exclusively the vestibular root, or also the acoustic nerve, the tuberculum acusticum, the corpus restiforme and the crus medium cerebelli, are simultaneously hurt, for the anatomical connections of the N. Vestibularis those individuals especially have value, whereby — more or less by accident — exclusively the vestibular root was partly or totally degenerated.

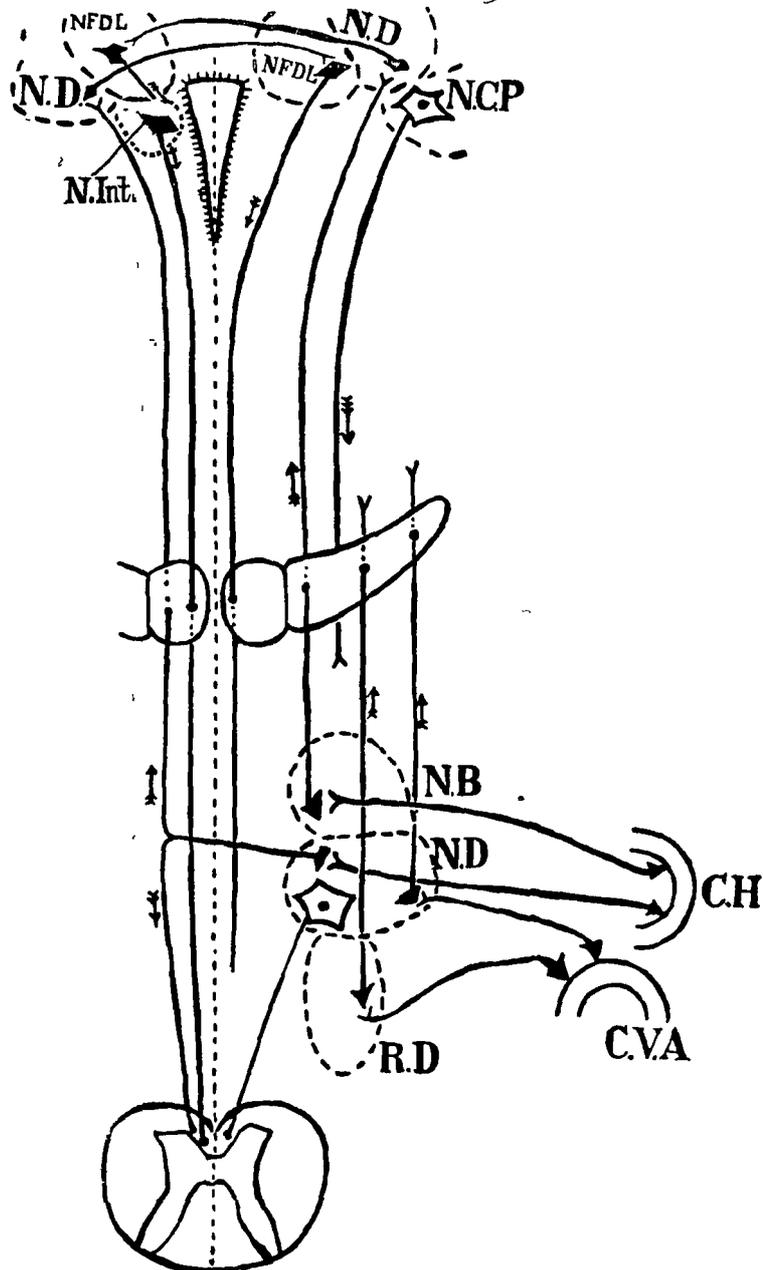
Here I must mention rabbit V, where the pars petrosa cerebelli was extirpated and as an exclusive associated lesion the N. Vestibularis happened to be hurt. Here we could follow up the degenerated nerve-sheaths pre-eminently to three celgroups: to the triangular part of the DEITERS Nucleus and its descending Ramus, to the

<sup>1)</sup> The direction of the locomotion associated with the forced movements, is judged by the original position of the animal itself. As also this does not preclude the mixing up of these conditions (e.g. a sick person, lying in bed on the back-side, presents negative geotropy, compared with all other mammals), the primary position of the animal is always reduced to that of the simplest vertebrate with the simplest forced movements, viz of fishes. This detail will prove of importance as soon as we proceed from the analysis of the forced movements towards that of the various pathological conditions of the ocular movements and towards that of the various pathological conditions of the ocular movements, conjugated deviations and other neurological syndroms.

<sup>2)</sup> Compare RISIEN RUSSELL, Phil Transaction CL XXXV, p. 837, 1894 and ROTHFELD PFLÜGER'S Archiv. Vol. 49, p. 440 1912.

medio-dorsal group and to the region of the Nucleus BECHTEREW- and the Nucleus Tecti.

In none of the animals of this first group degeneration was found,



either ascending or descending, into the area of the P. L. B. (Posterior Longitudinal Bundle) its lateral wing, the so-called F. D. A. (Fasciculus DEITERS Ascendens).

In the second group we bring the cases, where there was possibly some lesion of the N. vestibularis, recognisable by a less compact degeneration in that nerve and certainly not caused by a direct lesion, but by an indirect one as shifting of the cranial contents, vicinity of an malacial hearth and also by retrograde degeneration. In this it strikes us, that the N. Vestibularis appears not only to be exposed to an associate lesion after an operation in the posterior cerebral cavity, but that also the vulnerability of this cerebral nerve is observed after lesions of some distant structure.

We have to stand still with the three cases (107, 108, 109) where the region of the posterior commissure was wounded.

In these cases the forced movements cannot be considered as having the same origin. In cat 108 the dependence of the rolling and circus movement to the left on the degeneration found in the vestibular nerve is most conspicuous, because in this case no degeneration in the secondary vestibular system was found. On the other hand we find in 107 a slight, even doubtful, degeneration in the L. vestibular nerve, which cannot be considered responsible for the long lasting circus movement to the R. nor for the long lasting rolling movement to the L. As we saw in a former publication<sup>1)</sup> the descending degeneration of the most medial segment of the P. L. B. on the operated side is most common<sup>2)</sup> in animals, where a lesion of the region of the posterior commissure was performed and circus movement ensued to the operated side.

For some time I considered the rolling movements to the L. dependent on the centrifugal degeneration of the bundle, lateral to the P. L. B. (PROBST)<sup>3)</sup> particularly because also one of KARPLUS and ECONOMO's<sup>4)</sup> animals had shown after a similar lesion rolling movement (and the position in that sense) to the normal side; equally in this animal this bundle was found degenerated.

Later experience however leads me to doubt whether this bundle has anything to do with the forced movements. Also regarding the bundle that degenerates within the area of the P. L. B. from the interstitial nucleus far down the spinal cord (interstitio-spinal bundle) I am not in the position to deny nor to affirm its relation to the vestibular system, and physiologically spoken to the forced movements. The fact, that in 2 cats (107 and 108), which performed

<sup>1)</sup> Comp. Transactions Royal Dutch Academy 26 Oct. 1912 p. 727.

<sup>2)</sup> Compare Boyce. Neurologisches Centralblatt. 1894. p. 467.

<sup>3)</sup> Jahrbücher für Psychiatrie und Neurologie 1903. Vol. 23. p. 17 and Deutsche Zeitschr. f. Nervenheilk. 1900. Vol. 17. p. 156.

<sup>4)</sup> Archiv für Psychiatrie Vol. 46 page 393.

during the longest period rolling movements, tends to throw some doubt on the interpretation, presented above, viz. that the secondary lesion of the vestibular roots might alone be responsible for these disturbances. It suggests the possibility, that this interstitial-spiral bundle, descending low down the cord, might represent the efferent tract for the rolling movement, as we saw the commissuro-medullary bundle did for the circling movements. The vulnerability of the vestibular nerve to distant lesions renders the analysis, of this sort of functional disturbances viz. rolling in their relation to the anatomical findings extremely delicate. Not only in lesions of the Mesencephalon and of the Cerebellum but also after a lesion caudal to the exit of the 8<sup>th</sup> nerve (as in cat 145) this nerve root may be indirectly hurt.

These indirect lesions (by shifting of the cranial contents etc.) produce functional disturbances of the same order as those observed after direct lesion of that nerve. This is proved by the fact that practically only rolling movements ensue, which take place towards the side on which the black particles are found, particularly in the fan-like part of the intra-medullary course of the vestibular nerve, after having passed the narrow passage between the corpus restiforme and the descending 5<sup>th</sup> Nucleus. It is remarkable that in all cases the indirect vestibular lesion was found on the contra-lateral side of the primary lesion.

The duration of the forced movements after indirect vestibular lesion, is naturally far less than after a primary lesion<sup>1)</sup>.

Finally it is interesting to know that in my lesions of the region of the posterior commissure only in 109 some slight degeneration in the lateral part of the Fasciculus Deiters Ascendens (LRWANDOWSKI, WINKLER) was found. I think it allowed to infer from this fact that solely in this case also Deiters Nucleus had undergone some secondary changes, of which some black particles in that structure give evidence.

I also think we may infer that the vestibular nerve itself is far more vulnerable, than its nuclei and ascending connections, independent of the fact, that — as I have proved — the forced movements (rolling) observed after direct vestibular lesion are of a far more vehement character than after a lesion of its secondary connections.

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<sup>1)</sup> It is probable, that in human pathology a good part of the most common symptoms of increased cerebral pressure (dizziness, reflectory disturbances of the ocular movements, falling sideways) will prove to be the result of a similar indirect vestibular lesion, this nerve being after these experimental results far more vulnerable than its secondary intra-cerebral connections.

Rabbit I in group 2 of VAN VALKENBURG is interesting. The brain was stained after WEIGERT-PAL. Besides the atrophy of GUDDEN's nucleus, on the side of the lesion, described some time ago, in a reconsideration of the series of slides this author and myself could convince us of a decided diminution in size of the same sided P. L. B.-formation, in the pontine and medullary region. This case, therefore seen the decided tendency to roll to the right side, as noted down by Dr. VAN VALKENBURG, comes in the line, I think, of experiments 107 and 108, in suggesting the possibility, that the tr. interstitio-spinalis might represent the descending limb of the reflex-mechanism, dealing with the rolling to the intact side; in the same way as, after my former communication (October 1912) the commissuro-medullary bundle represents the descending limb of the reflex-mechanism, controlling the circus movement to the side of the lesion.

Next follow in my table three cases; where the region of DEITERS Nucleus was wounded and at the same time the vestibular radiation on one or on both sides was not found free from degeneration <sup>1)</sup>. The rolling movements, observed in these cases (in its rudimentary manifestations lying on one side, falling to one side, rotation of the head around the neck to one side) agree with those observed after lesion of the vestibular nerve.

As in these cases we have to deal with a gross lesion of the nuclei, the secondary ascending DEITERS-connections are not found free from degeneration. Again, for the anatomical-physiological analysis these cases are of little use, as such complicate lesions do not allow of any safe conclusion.

After my former communication about the circusmovement, which disturbance in its pure form was never observed by me as a result of direct lesion, we cannot but ascribe the circus movement to the right side in 113 and 118 to the lesion of DEITERS Nucleus on the right side and the degeneration in the crossed ascending P.L.B.-Bundle.

Complicated lesions we find also in group 3. It cannot be said that in any animal one cellgroup only, of DEITERS Complex was hurt. Solely in VIII and 99 we find a lesion limited to the Ramus Descendens of the Vestibular Nucleus. Here it is remarkable, that both animals, notwithstanding important differences in extension of the lesion; yet have shown the same type of rolling movement, viz. to the *normal* side. Here it must be recalled, that in none of my experiments with direct or indirect lesion of the nerve itself this

<sup>1)</sup> This is the reason why it is not possible to attempt in this sort of experiments the physiological analysis of the different parts of DEITERS-Complex.

rolling to that side was observed. Also it strikes us that in both cases, no trace of degeneration in the P.L.B., and the F.D.A. was found. Also in an other experiment the degeneration is found in the Ramus descendens and also this animal made in the latter days of its life rolling movements to the healthy side.

Also after sagittal lesions, immediately lateral to the P. L. B., I observed a tendency to fall on the normal side. In this point case 146 and 158 complete each other very well. In 158 the extensive sagittal lesion cuts off the whole of the DEITERS Complex from the raphe; in 146 the smaller and more caudal sagittal lesion begins exactly distally from the striae acusticae (MONAKOV). In both cases during a longer (158) and shorter (146) period a tendency to fall to the normal side was noted. Only in the proximal lesion we find the degeneration in the medial part of the F. D. A. In 146 nor in the Ramus descendens nor in the F. D. A. a sufficient degeneration is found, to be held responsible for the "Slight tendency to fall to the right side" as was noted some days after the operation. It may be supposed, that the sagittal haemorrhage on the lateral side of the P. L. B. by mechanical compression should have interfered with the function of the Ramus descendens and the Nuc. DEITERS, irritating it, but not causing the dissolution of medullary sheaths. In the case of 158 in accordance with the crossed ascending vestibulo-mesencephalic bundle in the P. L. B. during 9 days circus movement to the normal side was noted; in 146 only during a few days some tendency to it. That the crossed ascending vestibulo-mesencephalic bundle not exclusively must be limited to the areal of the P. L. B. proper, we find confirmed not only in 158, but also in 113.

The cases, which we have combined in group IV, (direct lesion of the P. L. B. system) can be divided after the physiological data into 2 subgroups. The first subgroup contains 7 animals, which during several days performed rolling movements to the *side of the lesion*. In all these animals the F.D.A. was either directly hurt by the lesion or was found in a decided state of degeneration, viz. as a result of lesion in the region immediately oral to the DEITERS-complex. The black granules as a proof of an intense ascending degeneration (descending fibres are never found in the F.D.A.) we find only in 92, 93 and N<sup>o</sup>. 3 (Series of Besta) spread over the whole area; in the other cases exclusively the lateral half of the F.D.A. is found degenerated, in 3 cases as a result of direct traumatical destruction of that part. Very instructive is in this regard 150, where exclusively the most lateral part of the F.D.A. was hurt about the Corpora quadrigemina posteriora, together with parts that

have certainly nothing to do with forced movements and secondary vestibular connections. Very instructive is furthermore the comparison of 90 and 92; in both cases both P.I.B. are cut through, but in one case simultaneously the right F.D.A., in the other one the left F.D.A. is severed. The rolling movements in all these animals were to the side of the F.D.A. that was degenerated, in toto or in the lateral part.

All lesions in this undergroup, are found in the F.D.A. between the proximal part of the DEITERS-Complex to the oral termination of the F.D.A., lateral to the trochlear nucleus. A destruction of the distal parts of DEITERS-complex (95) causing no degeneration of this area, I hold that the fibres of the F.D.A. arise in the medial and proximal cellgroups of DEITERS nucleus. LEWANDOWSKY and C. WINKLER also indicate, that the Fasc. DEITERS Ascendens exhausts itself in the 4<sup>th</sup> and 3<sup>d</sup> nuclei.

For comparison also 139 is placed in this series, because in this animal, exclusively the left posterior longitudinal bundle was cut, resulting in uncommonly long lasting circusmovement to the right side (10 days). There was however no trace of rolling movements. In the second undergroup (group IV) four animals are brought together, in which rolling movements to the *normal side* were observed after direct lesion of the F.D.A. Also in these animals it could be practically excluded, that the N. vestibularis or its Nuclei were hurt and could be held responsible for the forced movements, observed during life. As in these animals (158, 91, 68, 221 and also 5 (ECONOMO and KARPLUS)) we find exclusively degeneration of the medial part, of the F.D.A., I think we may infer that in this part of the areal fibres are abundant, which represent the ascending connections of the Ramus descendens Nuc. Vestibularis. It will be recalled, that a lesion in this latter cellgroup causes equally rolling movements to the *normal side*. It is interesting that in cat 68 a maximal rotation of the head towards the *normal side* was observed, being a result, I consider, of the haemorrhage, that was located in the middle part of the F.D.A.

In a scheme I have tried to render conspicuous the results of this investigation. If we compare these data of the physiological analysis of the ascendent connections of DEITERS-complex, with what we know from FLOURENS, SPAMER, CYON, EWALD, BARANYI, CAMIS and others about the function of the semicircular canals, there can be hardly any doubt, that for the rolling movements, we have to look to the anterior vertical canal as its source of centripetal impulses. As we have found two bundles in the F. D. A. of which a lesion causes

either rolling to the affected or to the normal side, it seems not very risky, to admit 2 connections from this canal to separate cellgroups in DEITERS-complex. As Marchi-preparations do not allow a further analysis of the nuclei, we can only suppose, that the Ramus descendens Nuc. Vestibularis controls the rolling to the normal side, the more proximal part of DEITERS-complex the rolling to the affected side.

Equally for the circus-movement a similar arrangement can be recognised. An important difference is only this detail, that one of the two ascending connections of the cellgroup, that controls the circus-movement to the affected side, crosses the raphe.

The whole of the posterior longitudinal bundle together with its lateral wings (F. D. A.), we find thus composed by 2 descending and four ascending systems of fibres. The two innermost bundles are descending ones from the nuclei of the posterior commissure, the medial one degenerating to the medulla, the lateral one to far down the spinal cord. The first one (commissuro-medullary bundle) is found degenerated after the lesions in the region of the posterior commissure, that had caused circus-movement to the affected side. The second bundle (f. interstitio-spinalis) has probably nothing to do with the forced movements.

The middle part of the entire P. L. B. system is composed of two ascending bundles, originating in DEITER's complex. The innermost, more voluminous one, contains crossed fibres, F. vestibulo-mesencephalicus cruciatus, the lateral one homolateral fibres (F. Vestibulo-mesencephalicus homolateralis).

After section (and ascending degeneration) by a lesion of the DEITERS' complex of either of these bundles circus-movements to the normal side are performed.

The outmost part of the P. L. B.-system is composed of two ascendent bundles either of them originating in the DEITERS' complex and terminating in the tegmentum little beyond the level of the trochlear nucleus. The outmost of these two bundles (probably from the proximal parts of DEITERS' complex) elicits by its ascending degeneration rolling movements to the affected side (F. vestibulo-tegmentalis lateralis), that of the innermost one (probably arising from the Ramus descendens) rolling movements to the normal side (F. vestibulo-tegmentalis medialis).

As far as I can judge, the relative situation of these bundles is pretty constant, but the ascending fibres intermingle more than the descending ones. Not rarely the bulky crossed vestibulo mesencephalic bundle holds in the cross-section an area far beyond the P. L. B. proper.

If we compare from the physiological standpoint the duration and the degree of the circus- and rolling-movements after lesions of the peripheral organ (semi-circular canals), the vestibular nerve, of its nuclei and of the ascending connections, we are struck by the difference in the results. Vehement forced movements and, peculiarly enough only rolling movements to the affected side, are exclusively found after lesion of the vestibular nerve. Especially so in the lower vertebrates as the rabbit and cavia. A lesion of the nuclei is followed by less vigorous forced movements, mostly of mixed type, rolling-movements combined with circus-movements. According to the nuclei involved, all combinations may occur, together with the corresponding conjugated deviation of the eyeballs.

After a lesion of the ascending connections, it is due to the anatomical arrangement, that circus-movements to one side and rolling-movements to the other side combined, will prevail. Although in a measure the degree and duration of the forced movements and concomitant symptoms (falling aside, conjugated deviation), is dependent on the quantity of the fibres degenerated, it appears, that the compensation is arrived at the more early, the more central the lesion is situated.

In so far the extraordinary sensitiveness of the vestibular trunk cannot cause astonishment, as from clinical experience there is sufficient reason to expect an uncommon irritability of that nerve (HIDZIG'S vertigo by galvanisation of the head, the frequency of dizziness in cases of tumour cerebri not only of the posterior fossa cerebri but also far distant).

From my experiments I conclude, that the forced movements are the result of an irritation, caused by the degeneration of the medullary sheaths. If an haemorrhage occurs in the area of the P. L. B. system, the forced movements show an uncommon vehement character and last longer; but finally, after complete destruction of the nerve fibres and after the process of compensation is set in action, all traces of spontaneous forced movements disappear and can only be elicited after certain measures (blindfolding, narcosis, mutilation of the cerebral hemispheres).

Although the 2 types of forced movements, which until now (viz. locomotion in the horizontal plane and in the plane vertical to the long axis of the animal) show many points of comparison, they cannot be looked upon as quite similarly arranged mechanisms. Not only is there disagreement in anatomical arrangement of the ascending bundles, but we also failed to find a distinct centrifugal bundle in the P. L. B. system, whose descending degeneration causes

rolling movement. It will be recalled, that for the forced movement in the horizontal plane (circus-movement) the Commissuro-medullary bundle fills up that gap. In this bundle we can recognize SHERRINGTON's "final common path", by whatever reflex-arrangements the circus movement (with the conjugated deviation of head and eyes) is provoked.

As a general result it may now be safely concluded, that my supposition of 1902<sup>1)</sup> proved right, that the P. L. B. system plays an important rôle in the physiology of the forced movements, in the horizontal plane (circus) and in the vertical plane, standing vertical to the bodily axis (rolling). Long before this BLEULER, DUVAL and LABORDE, CAYGAL, EDINGER HELD, BOYCE<sup>2)</sup> et al. had hinted to such a relation; BLEULER had directly urged the need of experimental work on the P. L. B., which as far as I am aware till now has been neglected. Advancing knowledge of anatomical connections has, for many years, made it probable, that ascending vestibular neura split up in particular divisions of the Oculomotor Nuclei (WALLENBERG<sup>3)</sup>). Descending fibres in the P. L. B. were demonstrated by VAN GEHUCHTEN<sup>4)</sup> GEE and TOOTH<sup>5)</sup> and KOHNSTAMM<sup>6)</sup> down to the lumbar region. PROBST, SPITZER, L. KAPLAN and L. FINKLENBURG<sup>7)</sup> proved, that the ascending fibres were of vestibular origin and thence declared their function, to be of equilibratory character. MONAKOW, FERRIER and TURNER, LLOYD THOMAS, LEWANDOWSKY, WINKLER and VAN GEHUCHTEN added materially to our knowledge of the anatomical analysis of the P. L. B. formation. PROBST discovered that from BECHTEREWS nucleus most ascending fibres are homolateral and WALLENBERG succeeded in showing in birds, that the innermost fibres in this structure are derived from the contralateral vestibular nuclei. Yet, the physiological analysis of this region made very little progress. As to the descending tracts to DARKSCHEWITCH<sup>8)</sup> BOYCE, REDLICH<sup>9)</sup> we owe details about the grey masses about the posterior commissure, but no special research was reported about the accurate relation of these nuclei and the descending fibres in the P. L. B., as far as I am aware. It may be observed that only recently CAYAL's accurate description of this region in the chicken and FUSÉ's detailed account, from MONAKOW's laboratory, on the vestibular nuclei, as also HORSLEY and CLARKE's researches have cleared the road for the physiological analysis.

1) Transactions Royal Dutch Academy 1902.

2) Philosophical Transactions 1898. Vol. 186. P. 325.

3) SCHMIDT's Jahrbüchen. 1899.

4) Academie royale de Belgique. 1895.

5) Brain. 1898.

6) Monatschrift f. Psychiatrie und Neurologie. 1900. Vol. VIII.

7) Monatschrift f. Psych. u. Neur. 1900. Vol. VIII. P. 210.

8) PFLÜGER. Archiv. Vol. 36. P. 639.

9) Monatschrift f. Psych. u. Neurol. 1899. Vol. V. P. 119.

Now it is interesting to note, that in this latter period fresh additions to our knowledge of the physiological function of this important structure (P. L. B. formation) came from quite other quarters, viz. from clinical anatomy. —As I wish to reserve a detailed account of these data for another occasion, I will confine myself to stating, that the wellknown symptom of conjugated deviation — being a subphenomenon of the symptom of circus movement — appeared to stand in a direct relation to a lesion of the P. L. B. in such a way that destruction of the right P. L. B. caused conjugated deviation to the left. As we saw in a former publication <sup>1)</sup>, by purely physiological and anatomical methods practically the same conclusion was arrived at for circus-movement in the cat. It cannot be denied, that both lines of thought complete each other very nicely. The old law of SCHIFF-PROBST (“A hemisection of the pons causes circus movement to the normal side; of the mesencephalon to the affected side”) had, so it appeared, to be read in this way: a section of a P. L. B. results in circus movements to the non-sectioned side; a lesion of the posterior commissure results in circus-movements to the affected side”.

The further physiological analysis of the lateral wings of the P. L. B. formation in cats, as we have attempted in this paper, discloses at all events the important fact, that this part of that structure holds fibres of equally vestibular origin, but of different function. The degeneration of these tracts brought about either by direct lesion or by a lesion of its nutrient grey matter, results in forced movements in another plane, viz. rolling-movements, and the allied conjugated deviation, the MAGENDIE-HERTWIG squint. Here the relation between the ascending and descending tracts, controlling these movements, became not so transparent, as was the case with those controlling the circus-movement.

For the latter we found, that the gray matter near the posterior commissure was at the same time the endstation of the ascending tracts and the origin of the descending tract. For the rolling-movements it was proved, that the ascending bundles terminate in the tegmentum near the IV Nucleus, whereas we could only hesitatingly indicate one or two paths, that might be considered as the corresponding efferent tract. In another publication I intend to deal with those ascending vestibular connections, whose lesion causes forced movements in a third plane (the vertical plane, that coincides with the long axis of the body) viz. staggering and culbutation. Proof will be forthcoming, that they run in entirely different structures as those, dealt with in this and the former papers.

<sup>1)</sup> Transactions Royal Dutch Academy. 25 Oct. 1912 and Neuraxe 1913.

Physics. — "*The virial-coefficient B for normal butane.*" By Prof. J. P. KUENEN and S. W. VISSER.

(Communicated in the meeting of September 27, 1913).

Determinations of the vapour density of normal butane have enabled us to calculate the virial-coefficient  $B$  in the empirical equation of state as established by KAMERLINGH ONNES<sup>1)</sup>. In the course of these calculations anomalies appeared which may be explained by the presence of a small quantity of a lighter admixture: a confirmation of this supposition was obtained by determinations of the boiling point and from the critical temperature.

The vapour density was determined by weighing. For this purpose a glass bulb of about .4 litre was used, provided with a stopcock and ground joint by means of which it could be connected to a butane-reservoir, a mercury pump, and an open mercury manometer.

The volume of the bulb was determined by weighing with air. First the weight of the bulb was determined after having been exhausted as completely as possible by the mercury pump. In all the weighings a tarra-bulb of about the same external volume was suspended from the other arm of the balance: the reading was not taken until the equilibrium had become constant.

The pressure of the air and afterwards of butane was first of all taken equal to the atmospheric pressure, the temperature being that of the room. For this purpose a tube some metres long with a stopcock was attached to the filling-apparatus. The gas was admitted to a pressure of about 1 m.m. above the atmospheric: by opening the tap at the end of the long tube for a moment, the excess pressure could be let off without appreciable change of temperature and without fear of outside air penetrating into the bulb. Immediately after closing the bulb the temperature and pressure were read. The bulb was then weighed. In filling the bulb with butane vapour it was three times washed out with the vapour and exhausted.

The barometric pressures were reduced to 0° and in the weights at temperatures above 0° a correction was applied for the expansion of the glass.

In the same manner a determination with butane was made at 0°, the bulb having been kept in ice for at least half an hour. During the operation the butane-reservoir was also placed in ice to

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<sup>1)</sup> Leiden Comm. Suppl. 23; § 36; p. 114, sqq.

NUMBER OF EXPERIMENT	LESION	VESTIBULAR ROOT	POSTER. LONGITUDINAL FASCICLE				CIRCUS MOVEMENT	DURATION	ROLLING MOVEMENT AND ALLIED CONDITIONS	DURATION	FASC. DEITERS ASCENDENS		AREAL OF P.L.B. AND FASC. DEIT. ASC.	REMARKS ABOUT OTHER DEGENERATIONS
			Ascending		Descending						Ascending	R.		
			L.	R.	L.	R.								
<b>GROUP I. Direct lesion of the Vestibular nerve.</b>														
235.03	Acutro-vestibular region on R. side	R.: Wounded, entirely degenerated.	Little degeneration L > R.	Little L > R.	Head turned to R.	25 days	Rolls and falls to R.; lies on R. side	28 days		Degenerated			Degeneration on R. side: Tr. vestibulo-spinalis: descending Ramus V and VIII; V and VIII root; corp. trapezoid, striae acust. (Moukoff, Held), Nuc. Delters, Corp. restif. anterior and med. crus, nuc. dentat.	
Rabbit V	L.: Excision of so called flocculus	L.: degenerated	0	0	0	0	Head rotated and bent to L.	30	0	0			N. aquat. and corp. trapezoid, free of degeneration. Vestibular fibres followed up to: nuc. Ram. desc. VIII, Nuc. triang., dorsal colliculus and nuc. sedi. Middle third part of L. Cr. ant. cerebelli.	
42	R.: Acutro-vestibular cut	R.: entirely degenerated	0	0	0	0	Vehement rolling to R. with eye-ball rotation	35					R.: Corp. restiforme, corp. trapezoid, striae acustic. Held. On both sides R > L: descending V and VIII root and medial and lateral fillet.	
67	Destruction R. N. Vestib. and ganglion ventrale; proximal end of incision in lateral part of Fasc. Delt. asc.	R.: destruction	0	0	0	0	Vehement rolling to R. with eye-ball rotation	30					R.: Corp. trapezoid, corp. restif. (moderately); nuc. Bocheverov (?) nuc. test. nuc. central. and crus ant. Ram. desc. V and VIII free of degeneration.	
<b>GROUP II. Indirect, intramedullary, slight lesion of N. vestibularis, by shifting of cranial contents or vicinity of a malaciae head.</b>														
107	R.: Nuc. commiss. post., corp. quad. ant., corp. gantic lat.	L.: little degeneration (oral part)	0	0	0	med. dorsal	Circus to R.	8 days	Head rotated to L.	8 days	0	0		R.: Descending tract lateral to P.L.B. (Protz, Besta); nuc. nuc. (ventro-lateral part) and Fasc. intertr. spinal. (slight); L.: Subrospinal and pyram. tract.; nuc. triangul.
108	R.: lateral to nuc. commiss. post. (nuc. interstitial) cavity	L.: middle and proximal part degenerated	0	0	0	fasc. inter-tr. spinal	L.	1 day	Tendency to fall to L.	9	0	0		R.: Mesencephalic V root, corp. quad. ant., lemniscus lat., tract. opt., commissura post. L.: Monakow's, pyramidal and tecto-spinal tract., nuc. triangul.
106	Incision from L. ganglion haben. bil. R. corp. quad. ant.	L.: little degeneration (oral part)	0	0	0	little	R.	1	0	0	0		L.: Tecto-spinal (bil.) Pyramidal tract (diffuse) owing to lesion of medial part of caps. int. R.: Mesencephalic V root and commiss. post.	
134	R.: Excision of ant. lob. cerebell. (nuc. glob. folius)	L.: little	some fibres	0	0	0	Tendency to L.	3 days	Rolls over L. side	1 day	0	0		R.: Retrograde degeneration in area of spinocerebellar tracts and corp. restiforme; medio-lateral part of crus ant. L.: flocculus basalis (Rosenz-Thomson).
113	R.: Nuc. triang. VIII. nuc. intravest. and medull. groups (Fasc.)	R.: ventral part	lateral	0	med. ventral	lateral	Circus to R.	8	Head rotated to R.	8 days	0	0		R.: Mesencephalic vestibulo-spinal bundle, corp. restif., motor. V nuc. lemniscus, crossing of cerebellar tracts (ventral part) lemniscus med. and Protz's commissure. L.: Pyramid. tr.
116	R.: Dorsal magnocellular part of nuc. Delt. (also med. group and nuc. triang.)	R.: oral part	little	0	med. ventral	lateral	R.	1 day	Falls to R.	7	0	0		R.: Vestibulo-spinal and pyram. bundle, striae Monakow, rubro-spinal bundle, motor. V-root, saccul. reticul. lemnisc., medial fillet.
95	R.: Nuc. Bocheverov and nuc. bacilli pontis sup.	R.: oral part	0	0	0	lateral-ventral	L.	7 days	0	0	0		R.: Rubro-spinal b.; corp. trapezoid, (oral part); descend. V nuc.; V roots (not and sens) and medial fillet. (Crus cerebelli ant. posterior and lemniscus weakened. Delters nuc. free.	
Rabbit I	L.: Commiss. post. and nuc. interstitialis (V. Valkenberg?)	?	diffuse	diffuse	diffuse	diffuse	Spine bent to L.	4	Falls to R., with eye-ball rotation	6	0	0		R.: Crus cerebelli ant. posterior and lemniscus weakened. Delters nuc. free. Weigert-Pal stain; L.: Nuc. Gundersen atrophied. A.L. B. atroph. E4 medial. region. Also mes. fillet. Weigert-Pal stain.
<b>GROUP III. Extensive lesion of vestibular nuclei. Under this head, strictly taken probably no one animal can be presented, except VIII. Practically however may be regarded as such 113, 116, and 95, because the slight degeneration of the vestibular root can hardly be considered responsible for the symptoms. Also 99, 91, 92, and 83, and the slight lesion in the vestibular region (106 and 189) may be consulted.</b>														
VIII	R.: Cyst in caudal part of Ram. desc. nuc. VIII	0	L > R	little	L > R	little	0	Rolls to L., head and eyes rotated to L.	2; 4 d.	0	0		R.: Rubro-spinal and vestibulo-spinal b.; fibre arboriformis int., desc. V nuc., lateral X nuc., corp. restif., striae acust. (Mon.), crus ant. and Gowers b. L.: medial fillet.	
99	L.: Ramus desc. nuc. VIII, nuc. triang. and Bocheverov full of degenerated fibres.	0	0	little	0	little	L.	11 days	Head little rotated to R.	9 days	0	0		L.: Vestibulo-spinal b.; lateral fillet. Most of ascending P. L. B. fibres stop in pons.
145	R.: Sagittal lesion: caudal medial of nuc. Delters and transection of cord (P 4)	0	little	0	little	little	Some tendency to swing to L. side.	some days	Some tendency to fall to L.	some days	0	0		R.: Vestibulo-spinal b.; Gowers and Flechsig b., hilus olivae and medial fillet; corp. trapez. R. and L. Goll's tract. L.: Pyram. tr.
138	L.: Sagittal lesion: Delters complex completely cut off raphe and L. frontal pole removed.	R. and L.: little	diffuse	little	lateral	lateral	medial	9 days	Falls to R.	11 days	0	0		R.: Middle part of nuc. V desc.; nuc. corp. quad. post. R. and L. corp. trapezoid, hook bundle, crus med. cerebelli. (L > R). L.: Pyram. and direct vestibulo-spinal b., nuc. dent. (L. crus ant. free), lemn. med. and nuc. lemn. lat.
<b>GROUP IV. Lesion of longitudinal fibres, ascending from vestibular complex, between nuc. VI and nuc. IV, except 114 and 139.</b>														
92	Both P. L. B. + L. Fasc. Delt. asc.	L. nuc. Bocheverov cut off from raphe.	Total	Total	Total	Total	0	Falls to L.; eyes rotated to L.	4 d.; 12 d.	Degenerated			L.: Rubro-spinal tract; nuc. IV, R. and L.; Nuc. Delters and Bocheverov, in their oral parts, cut off from raphe; lateral fillet. R.: crus med. cerebelli.	
30	Both P. L. B. + R. Fasc. Delt. asc.		Total (oral part)	Total and strong	Total	Total	Circus to R.	9 days	Head rotated to R.	9 days	Medial part	Total		Haemorrhage on L. P. L. B. R. and L.: Crus cerebelli ant. posterior (deep layer). R.: crus cerebelli ant. (medial part); L.: lateral fillet.
23	Incision in R. crus cerebelli. ant. and F. Delters asc.	Lesion of R. nuc. Bocheverov and triangulatis	0	little	0	little	Tendency to walk to L.	6	Rolls to R.; falls to R.	4 d.; 22 d.	0	Lateral and medial		R.: F. vestibulo-spinal, corp. restif., nuc. globosus, crus cerebelli med. and ant.; format. reticul. pontis and mesencephalic V root.
82	Incision in R. crus cerebelli. ant. and F. Delt. asc.		0	0	0	0	0	0	Rolls to R.	6 days	0	Lateral		R.: Monakow's and Gowers' bundle; nuc. testif., crus cerebelli med. and ant. (with descending collicularis, Thomas, Protz). Haemorrhage in nuc. mol. V.
304	R.: Fasc. Delters asc., near nuc. IV		0	0	0	0	0	0	Rolls to R.	5	0	Lateral		R.: Motor and mesencephalic V root; rubro-spinal and lateral part of pyramidal tract; lateral fillet. R. and L.: nuc. testif. and middle third part of descending V nucleus.
79	Rabbit (Kohnstamm?) R.: Fasc. Delt. asc. (lateral part)		0	0	0	0	0	0	Head rotated to R. (thin to L. and upward)	4	0	Degenerated		R.: Gowers' and rubro-spinal bundle; crus cerebelli ant. and med. (oral part); nuc. of P. L. B. contains many degenerated cells; also both IV nuclei and L. nuc. angularis.
Series III V	(Besta?) Cat. Ablation of L. cerebellum		Degenerated	moderately (det. total)	Total	Total	0	0	Rolls with inclination to L.	4	Degenerated	0		R.: Middle (superficial layer) and anterior (total) crus cerebelli; nuc. Bocheverov (?). R. and L. hooklike bundle. L. nuc. reticularis.
114	Both P. L. B., oral to IV nuc. and Werneck's commissure		0	0	0	0	0	0	Sings: Falls to R. in epileptic fit.	—	Total destruction	Total destruction		R.: Rubro-spinal and lateral part of pyramidal bundle, medial fillet, Werneck's commissure; medial part of corp. quad. post. L.: nuc. rab. and dorsal parts of III nuc.
135	Extensively R. P. L. B. and substantia reticularis		0	strong (lateral)	little	Ventro-medial	Circus to L.	9	0	0	0	0		R. and L.: Middle crus cerebelli (slight prof.); proximal part of corp. trapezoid and olivae sup. (oral to VI nuc.); Protz's commissure. R.: medial fillet.
68	R.: Lateral half of post. haemorrhage on R. Fasc. Delters asc.	Proximal part of R. vestibular root	0	0	0	0	0	0	Lies on L. side	last days	Middle part	Haemorrhage on middle third part		R.: Rubro-spinal, Gowers' and medial part of pyramidal tract, descending V and VIII nuc.; corp. restif. (lateral part); ant. and middle crus cerebelli. Oral parts of Delters and Bocheverov nuclei within malacia.
91	L.: P. L. B. and medial part of Fasc. Delt. asc.	On R. side a little	Total	little	Total	little	Circus to R.	8	Falls on R.; lies down on R. side	14 days	0	0		R.: Pyramidal bundle, nuc. triangul., crus ant. cerebelli (moderate); L.: Rubro-spinal and hooklike bundle. Werneck's commissure. Purkinje infection.
221	3 figures in proximal part of vestibular nuclei ant. L. Fasc. Delters asc.		Lateral	0	Medial	little	Head bent to L.	1 day	Tendency to lie down on L. side	15	0	0		R.: Crus cerebelli ant. (with descending collicularis — Thomas, Protz). R. nuc. IV fall of degeneration.
5	(Economo and Karplus?) Cat. R.: Pes pedunculi and P. L. B.		0	0	0	0	0	0	Falls to L.	5 days	0	0		R.: Pyramidal and mesencephalo-olivary tract; crus ant. cerebelli and lemniscus. — Both rubro-spinal tracts.

Underlined in this table are the tracts, degenerated, which — after our present knowledge — probably determine the functional disturbances (equally underlined).

1) Proceedings Royal Dutch Academy. 1912. P. 1118.  
 2) Journal f. Psychologie u. neurologie XVI. 1910. Bdz. 93.  
 3) Archiv. f. Psychiatric. Vol. 50. 1912. P. 373.  
 4) Archiv. f. Psychiatric. Vol. 48. 1916. P. 311.

prevent distillation of liquid into the bulb. After the weighing the weight of the empty bulb was determined a second time as a test.

Subsequently determinations at room temperature were made at pressures of  $\frac{1}{2}$  and  $\frac{1}{4}$  atm. The pressure was in this case read on the mercury-gauge.

It appeared necessary to determine the contraction of the bulb by the diminution of the internal pressure. For this purpose the weight of air contained in the bulb at a pressure of  $\frac{1}{3}$  of an atm. was measured.

Finally two weighings were made with butane-vapour at  $0^\circ$  and at  $\frac{1}{2}$  and  $\frac{2}{3}$  of an atm.

#### MEASUREMENTS <sup>1)</sup>.

*Empty bulb.* The tarra-bulb + 8 grammes made equilibrium with the empty bulb + .84036 grms. A later weighing gave .84033, a third .84036. The mean of these is .84035. This weight is in error by an amount  $x$ , owing to the change of the external volume by exhaustion.

*Bulb with dry air.* At  $18^\circ.58$  and  $76.738$  cms. the weight of the air was found to be .47370 grms; a second weighing gave .47735 grms. at  $16^\circ.88$  and  $76.805$  cms. For the weight at  $0^\circ$  and  $76$  cms. they give .5009 grms and .5014 grms. the mean of which is .5012 grms. This figure has to be increased by the amount  $x$  mentioned above.

*Bulb with dry air at lower internal pressure.* At a pressure of  $26.816$  cms and a temperature of  $16^\circ.71$  the air weighed .16596 grms. The weight of the air contained in the bulb at  $0^\circ$ , and  $76$  cms would have been .49899 grms. It is easily proved, that the error of this figure owing to the change of external volume is approximately equal to  $x$ . The difference between .5010 and .49899 is therefore independent of  $x$  and represents the diminution of weight due to the diminution of internal volume at the lower pressure: as the diminution may be taken proportional to the change of pressure, it follows that the diminution of weight for 1 atmosphere would be .00333 grms. The external change of volume being approximately equal to the internal change, this latter weight is equal to the correction  $x$ . The weight at  $0^\circ$  and 1 atm. is thus  $.5012 + .0033 = .5045$  grms. From this weight the volume is found by dividing by the normal density of air. The measured weights of butane have

<sup>1)</sup> The calculations as given here differ slightly from those in the Dutch edition owing to a correction which had been overlooked.

also to be corrected by amounts proportional to  $x$  and to the pressure expressed as a fraction of 76 cms.

*Bulb with butane vapour.*

The following table gives the results of the 6 weighings.

	Temp.	Pressure	Weight.	Weight corrected.	Volume.
I.	16°.63	76.08 cm.	0.98219 Gram	0.98513	390.1 cm.
II.	0 .00	75.68	1.04400	1.04733	390.1
III.	21 .02	40.42	0.50339	0.50469	388.9
IV.	19 .94	18.57	0.22935	0.23016	388.1
V.	0 .00	23.48	0.31244	0.31347	388.3
VI.	0 .00	48.89	0.66184	0.66398	389.2

#### EMPIRICAL REDUCED EQUATION OF STATE.

The equation of state was taken in the form (Comm. Leiden, Suppl. 23)

$$pv = A \left( 1 + \frac{B}{v} + \frac{C}{v^2} + \frac{D}{v^3} + \frac{E}{v^4} + \frac{F}{v^5} \right) \dots \dots (1)$$

where  $p$  is the pressure in atmospheres at 45° latitude,  $v$  the volume of 1 gramme expressed in the theoretical normal volume as unit, further :

$$A = RT; \quad B = \frac{RT_k}{p_k} \mathfrak{B}; \quad C = \frac{R^2 T_k^2}{p_k^2} \mathfrak{C}; \text{ etc.}$$

$\mathfrak{B}$ ,  $\mathfrak{C}$ , etc. represent the "reduced virial coefficients", quantities which depend on  $T$  only and must be equal for different substances, except for small individual deviations.

$D$  and the subsequent coefficients may be neglected for pressures smaller than  $\frac{1}{2} p_k$ .

By introducing  $p$  as the independent variable instead of  $v$  equation (1) assumes the form.

$$pv = RT \left( 1 + \frac{B}{RT} p + \frac{C - B^2}{R^2 T^2} p^2 \right) \dots \dots (2)$$

The theoretical normal volume of pure butane is

$$22412 : 58.08 = 386.0$$

where 22412 is the normal volume of one gramme-molecule and 58.08 the molar weight of butane. When the constants were calculated on this basis, large deviations from the reduced equation of state were found. This finds a ready explanation in the fact, that

the butane was not absolutely pure. It seemed therefore preferable to treat the theoretical normal volume as an unknown quantity and deduce it together with the other constants from the observations. It was for this purpose, that the above weighings at  $0^\circ$  at three different pressures were made.

Substituting in (2)  $p_1, v_1$  and  $p_0, v_0$  respectively and dividing the two resulting equations, we obtain the relation

$$1 - \frac{p_1 v_1}{p_0 v_0} = \frac{B}{RT} (p_1 - p_0) - \frac{B^2}{R^2 T^2} (p_1 - p_0) \left\{ p_1 + \left( 1 - \frac{C}{B^2} \right) (p_1 + p_0) \right\}. \quad (3)$$

In this equation we may take for  $v_1$  and  $v_0$  the volumes of 1 gramme in ccm. The term containing  $C$  is of minor importance:  $C$  may therefore be calculated with sufficient accuracy from the reduced coefficient  $\mathfrak{C}$ , which is known from measurements on a number of other substances.

From equation (3) was found  $B = -.0430$

In the same manner the second and sixth weighings gave  $B = -.0431$ ; as the mean was taken .0431.

The theoretical normal volume of the butane used may now be calculated from equation (2): it becomes 388.1.

The difference of this figure from the value for pure butane (386.0) gives an indication as to the amount of the impurity: it points to the presence of a lighter admixture. The difference is .5%.

Using the normal volume found in this manner we may now deduce the virial coefficients  $B$  in the measurements at other temperatures.

$t$	$B$	$B$ calculated.
$0^\circ$	-.0431	-.0465
16.63	381	393
19.94	371	382
21.02	359	376

In the last column are given the values of  $B$ , as calculated from the mean reduced virial coefficient  $\mathfrak{B}$  for a number of substances. The correspondence is satisfactory considered the degree of accuracy of the method by which  $B$  was here determined. An error in the fraction on the left side of equation (3) appears in  $B$  one hundred times enlarged; an error of 5% in  $B$  corresponds to an error of observation of  $\frac{1}{2000}$ .

Moreover a complete correspondence can in any case not be expected, as the equation of state is after all only an approximation

owing to the mutual deviations of the various substances with regard to the law of corresponding states. This is shown by the following table containing various values of  $\mathfrak{B}$ .

Reduced temperature .644.		
mean reduced virial-coefficient $\mathfrak{B} = -1.12$ .		
	$t$	$\mathfrak{B}$
ammonia <sup>1)</sup>	$-12^{\circ}$ C.	$-1.22$
methyl chloride <sup>1)</sup>	$-5$	$-0.961$
isopentane <sup>2)</sup>	$23.7$	$-1.02$
n. butane <sup>3)</sup>	$0.0$	$-1.04$ .

*Test of the impurity.* The theoretical normal volume found 388.1 leads to a molar weight of 57.77. If we assume the admixture to be ethane, its amount may be calculated from the molar weights of ethane (30.05) and butane (58.08): the amount of ethane would appear to be 1%.

The above result respecting the nature of the admixture finds confirmation in the boiling point of our butane. This point ( $-1^{\circ}.0$ ) <sup>4)</sup> was derived from determinations of the vapour pressure in the neighbourhood of  $0^{\circ}$ :

temp.	press. (atm.)
12.0	1.6
0.00	1.049
0.00	1.046
$-6.2$	0.79

Owing to the presence of a more volatile admixture (ethane) the boiling point will be too low. In order to remove it to a certain extent the butane was cooled in solid carbon dioxide and vapour was pumped off. After this operation the vapour pressure at  $0^{\circ}$  was again measured; it was now 1.035 atm. The boiling point has therefore actually been raised: it now becomes  $-0.8^{\circ}$ . In repeating the same operation a large portion of the vapour coming off was collected in the bulb of the mercury pump. The pressure above the small quantity of liquid left, appeared to have diminished to 1.027 atm.,

<sup>1)</sup> For these data we are indebted to Mr. G. HOLST, whose results, which were worked out in the Leiden Laboratory, will shortly be published as a thesis at Zürich.

<sup>2)</sup> Calculated from S. YOUNG's data.

<sup>3)</sup> Deduced from the above value of  $B$ .

<sup>4)</sup> In Comm. 125 p. 4 by a clerical error the boiling point was given as  $-0.1^{\circ}$ .

which means a further rise of the boiling point: the final value may be taken at  $-0.6^{\circ}$  C.

A further confirmation of the presence of an admixture like ethane is afforded by the value of the critical temperature ( $150.8^{\circ}$ ). When for the various saturated hydrocarbons a graphical curve is drawn with the molar weights as abscissae and the corresponding critical temperatures as ordinates, the value found for butane seems to be a little too small. By representing the critical temperatures of ethane ( $305^{\circ}.3$ ), pentane ( $470^{\circ}.3$ ), hexane ( $507^{\circ}.9$ ), heptane ( $539^{\circ}.95$ ) and octane ( $569^{\circ}.3$ ) as an arithmetical series of the fourth order, we find for propane  $370^{\circ}.25$  instead of the experimental value  $370^{\circ}.1$  and for butane  $424^{\circ}.94$ , i.e.  $1^{\circ}.04$  higher than what was obtained by us. This result also points to a deviation of the critical temperature owing to the presence of a more volatile admixture.

**Physics.** — "*The viscosity of the vapour of normal butane*". By J. P. KUENEN and S. W. VISSER.

(Communicated in the meeting of September 27, 1913).

For the determination of the viscosity of butane vapour RANKINE's <sup>1)</sup> transpiration method was used; a method which is very simple and requires very little vapour, and in which the vapour comes into contact with glass and mercury only.

The apparatus consists of a long *O*-tube placed vertically and capable of being turned over on a horizontal axis. One arm of the *O* is capillary, the other one a wider tube. The vapour is forced through the capillary by a falling drop of mercury in the wide tube. When the drop has arrived at the bottom of the tube, the apparatus is simply turned upside down, and the drop now drives the gas through the capillary in the opposite direction. The time is measured between the moments at which the mercury passes two marks on the fall-tube. The whole tube is mounted in a glass jacket, where the temperature is kept constant.

In order to be able to work with a long capillary without making the apparatus unwieldy by its length, a capillary is used which is twice bent round: hereby it becomes almost three times as long as the wide tube.

<sup>1)</sup> A. O. RANKINE, Proc. Roy. Soc. London A 83, 265, 516; 1910.

The apparatus is provided at the top and the bottom with side-tubes which serve for the purpose of cleaning and filling and are sealed off before the measurements. At both ends the tube has a slight enlargement for collecting the mercury.

When the tube is used for relative measurements, the formula to be used is

$$\eta_1 : \eta_2 = t_1 : t_2$$

where  $\eta_1$  and  $\eta_2$  are the viscosities of both vapours,  $t_1$  and  $t_2$  their times of flow.

A correction has to be applied for gliding by means of the relation

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \frac{1 + \frac{4G_1}{R}}{1 + \frac{4G_2}{R}} = \frac{t_1}{t_2} \left\{ 1 + \frac{4G_2}{R} \left( \frac{G_1}{G_2} - 1 \right) \right\}$$

where  $G_1$  and  $G_2$  are the mean free paths of the two vapours and  $R$  is the radius of the capillary. When  $\frac{G_2}{R}$  is known, a rough approximation for  $\frac{G_1}{G_2}$  is sufficient.

The kinetic theory gives  $\eta = \frac{1}{3} dG\bar{V}$  and  $p = \frac{1}{3} dV^2$ , where  $d$  is the density,  $\bar{V}$  the square root of the mean velocity square,  $p$  the pressure. Eliminating  $\bar{V}$  we find  $\eta = \sqrt{\frac{1}{3} p d G}$  and therefore

$$\frac{G_1}{G_2} = \frac{\eta_1}{\eta_2} \sqrt{\frac{d_2 p_2}{d_1 p_1}}$$

*Critical velocity.* REYNOLDS' criterion for liquids also holds for gases<sup>1)</sup>. For our viscosimeter,  $\frac{Ddv}{\eta} = 146$  for air (admissible limit is 2000)  $D$  was .0358 cm.;  $d = .001293$ ;  $\eta = .000181$ ; the volume 2.246 ccm.; the time of flow 57 seconds.

#### CORRECTION FOR THE CAPILLARY ACTION OF THE MERCURY DROP.

In consequence of the difference in curvature of the two surfaces of the mercury drop, a correction has to be made in the pressure which may be different for different gases and different temperatures. This correction was determined by RANKINE by measuring the time of flow for several mercury drops of different length. The relation between the mass  $m$  of the mercury and the time of fall  $t$  may be represented by the equation

<sup>1)</sup> RUCKES, Ann. Phys. 25, p. 983, 1908.

$$m = a + \frac{b}{t}$$

where  $a$  is the unknown correction and  $b$  a constant, which is equal to the product of the corrected mass and the time. From a series of measurements with different  $m$  the constants  $a$  and  $b$  may be calculated.

In order to avoid the use of different masses which involved opening, refilling and reclosing the tube, an attempt was made to determine the correction in a different manner. By dividing a given quantity of mercury into a train of drops which fall down together the capillary action is multiplied <sup>1)</sup>. If the influence of each separate drop is the same, the correction must be proportional to the number of drops. Calling the number of drops  $x$ , RANKINE's equation becomes

$$m = xa + \frac{b}{t}$$

$a$  and  $b$  may thus be calculated from several measurements with different  $x$ ,  $m$  being known. If  $m$  is taken as unknown, the ratios  $a/m$  and  $b/m$  may be found. Calling these ratios  $a_1$  and  $b_1$  the equation takes the form

$$a_1x + b_1 \frac{1}{t} = 1$$

$b_1$  is thus the time for  $x=0$  i.e. the time corrected for the influence of capillarity. According to this equation the graphical relation between  $x$  and  $\frac{1}{t}$  should be a straight line.

In the application of this method some unexpected difficulties made their appearance.

To begin with the constants  $a$  and  $b$  were derived from three observations by RANKINE's method.

RANKINE's method	$m$	1.86	1.31	1.01	grms
	$t$	57.1	84.5	114.2	seconds.
	temp.	14.5°.			

These results give:

$$a = .160 \quad b = 97.10.$$

The observations with air were now repeated by the drop-method.

<sup>1)</sup> By providing the wide tube with a small contraction on the inside of the curve near one of the bulbs, it is easy to divide the mercury column into two or more drops.

*Drop-method. 1<sup>st</sup> series. m* 1.09.

<i>x</i>	1	2	3	4	5
<i>t</i>	102.7	119.7	143.3	174.3	216.9

temp. 15.5°.

These points do not lie exactly on a straight line. The deviation is very small for the first three drops; the fourth point is too high and the fifth deviates still more in the same direction. The first two drops give

$$a = .135 \qquad b = 97.99.$$

As this result does not agree with the former result as regards  $a$ , a further investigation of the method was made with air after the completion of the observations with butane. In this case three quantities of mercury were taken, each of which was used in a different number of drops.

The results were as follows.

*Drop-method 2<sup>nd</sup> series. x*

	1	2	3		
<i>m</i>	2.11	<i>t</i> 49.0	54.4	62.0	temp. 19.8.
<i>m</i>	1.53	<i>t</i> 69.1	80.1	97.9	temp. 19.5.
<i>m</i>	1.06	<i>t</i> 103.6	129.9		temp. 19.5.

From this set the influence of capillarity for one, two or three drops may also be calculated by RANKINE'S method.

The first column gives  $a = .121$   $b = 97.59$  for one drop.

„ second „ „  $a = .306$   $b = 98.31$  for two drops.

„ third „ „  $a = .533$   $b = 97.97$  for three drops.

The capillary effect per drop thus becomes:

$$.121 \qquad .153 \qquad .178.$$

it seems therefore to become greater as the number of drops increases.

The value of  $b$  is practically constant: the deviations are 0.4% and remain below the errors of observation.

In the calculation by the drop-method (combination of the results in the same row) the third point appears to deviate downwards this time.

The first row gives for  $x=1$  and  $x=2$ ,  $a = .192$   $b=94.1$  for  $m=2.11$

„ second „ „ „  $a = .185$   $b=93.1$  „ 1.53

„ third „ „ „  $a = .179$   $b=91.6$  „ 1.06.

The deviation from RANKINE'S method of calculation is also in the opposite direction. The differences between the constants  $b$  are again much smaller than those between the  $a$ 's.

The conflicting results of the two series of observations make it

probable, that the differences between the two methods are accidental, due to small differences in purity of the mercury and of the walls of the tube. A further investigation is therefore desirable, as the drop-method, if found trustworthy, is much preferable to the method which depends on the use of different masses.

For high temperatures with air and for all temperatures with butane the drop-method was the only one that could be used. It appeared advisable to use the constants  $a$  and  $b$  as derived from the first series of the above determinations, because in the measurements at  $100^\circ$  and with butane the same quantity of mercury was used.

After the first series of determinations with air the time of flow for air in steam of boiling water was measured. In order to get an even temperature it was found necessary to admit steam by means of two flasks one at each end of the vapour jacket. A side-tube in the middle allowed the steam to pass off. When the apparatus was reversed the condensed water could flow out through the same tube.

As mentioned above the constants  $a$  and  $b$  were determined according to the drop-method. As the results for air at ordinary temperature were found somewhat uncertain, the following results must also be considered to be only approximately correct.

Observations at

	100.1°		$m = 1.09$
$x$	1	2	3
$t$	121.9	139.4	161

The deviation for  $x = 3$  is upwards.

From  $x = 1$  and  $x = 2$  follows

$$a = .122 \quad b = 118.1.$$

The constants  $a$ , .135 at  $15^\circ.5$  and .122 at  $100^\circ$ , thus appear to differ but little, compared to the differences between the observations with a different quantity of mercury.

We thus find

$$\frac{\eta_{100.1}}{\eta_{15.5}} = \frac{118.1}{97.99} = 1.205.$$

Corrected for gliding 1.205.

BREITENBACH<sup>1)</sup> gives  $\eta_{15} = .0001807$ , RANKINE<sup>2)</sup>  $\eta_{15.5} = .0001803$ ; MARKOWSKI<sup>3)</sup>  $\eta_{99.6} = .0002212$ ; SCHIERLOCH<sup>4)</sup>  $\eta_{99.9} = .0002218$ .

<sup>1)</sup> Ann. Phys. 5, 166; 1901.

<sup>2)</sup> A. O. RANKINE l. c.

<sup>3)</sup> H. MARKOWSKI, Ann. Phys. (4) 14; 1904.

<sup>4)</sup> J. F. SCHIERLOCH, Diss. Halle 1908.

These values which have been selected from several which differ considerably give:

$$\frac{\eta_{100}}{\eta_{15.5}} = 1.228.$$

#### DETERMINATION OF THE VISCOSITY OF BUTANE VAPOUR.

The viscosimeter was connected to the butane-reservoir, and two or three times washed out with the vapour. Finally it was filled with vapour, while the reservoir was cooled to  $-8^{\circ}$  C. At the temperature of the room the vapour is then so far removed from saturation, that irregularities owing to condensation in the capillary need not be feared.

Again the results may contain a small error owing to the uncertainty of the drop-method used.

$$m = 1.09 \text{ grms.}$$

$x$	1	2	3	4
$t$	46.6	52.5	59.3	68.9
temp.	14.7.			

The deviations from the straight line were much smaller than in all the other determinations.

Calculation gives

$$a = 11 \quad b = 45.69.$$

In steam

$$m = 1.09 \text{ grms.}$$

$x$	1	2	3	4
$t$	60.4	67.7	76.5	86.5.

The deviations are again upwards and more pronounced than in the previous determination.

$$a = .11. \quad b = 59.40.$$

Second observation at room-temperature.

$$m = 1.09$$

$x$	1	2	3	4
$t$	47.0	53.4	60.8	68.3
temp.	16.0.			

The deviations have increased and agree in magnitude with those in the other observations

$$a = .12. \quad b = 45.74.$$

The differences in the two sets of measurements at room-temperature also point to accidental changes of the capillary action, possibly due to the formation or disappearance of a layer of vapour on the wall of the tube.

The relative viscosity follows from the equation

$$\frac{\eta_1}{\eta_2} = \frac{t_1}{t_2} \left\{ 1 + \frac{4G_2}{R} \left( \frac{G_1}{G_2} - 1 \right) \right\},$$

where the indices 1 and 2 refer to butane and air of 15.°5 respectively, while

$$\frac{G_1}{G_2} = \frac{\eta_1}{\eta_2} \sqrt{\frac{p_2 d_2}{p_1 d_1}} \text{ and } \frac{4G_2}{R} = \frac{.00001}{.02} = .0005.$$

These equations give for the viscosity of butane vapour relatively to that of air at 15.5°

at 14.7°	$\frac{\eta_1}{\eta_2} = .4661.$
at 16.0°	.4666.
at 100°	.6059.

The viscosity of air at 15.°5 is given by RANKINE equal to 0.0001803. The viscosity of normal butane thus becomes

temp. 14.7	$\eta$ .00008404
16.0	08413
100.0	1092

Of the other saturated hydrocarbons the only ones that we found mentioned are

methane temp. 0°	.0001040	GRAHAM <sup>1)</sup>
20°	1201	
isopentane 100°	08851	RAPPENECKER <sup>2)</sup>
212°.5	1164	

SUTHERLAND's formula which gives a connection between the temperature and the viscosity of the vapour is

$$\eta_1 = \eta_0 \frac{T_0 + C}{T_0^{3/2}} \frac{T_1^{3/2}}{T_1 + C}.$$

For isopentane RAPPENECKER deduces from his observations  $C = 500$ ; for normal butane we find from the above data  $C = 349$ . GRAHAM's data for methane give a negative  $C$ .

Isopentane at 100.0° C. corresponds with normal butane at 70.°0 (reduced temperature  $t = .809$ ). SUTHERLAND's formula gives for the

<sup>1)</sup> GRAHAM, Phil. Trans Lond. III, p. 573; 1864.

<sup>2)</sup> RAPPENECKER, Zs. Ph. Ch. 72, 695; 1910.

viscosity of butane at this temperature .0001005. In order to compare the two results at  $t = .809$  we have calculated for these vapours the constant  $\eta^{-1} M^{1/2} T_k^{-1/6} p_k^{2/3}$ , which KAMERLINGH ONNES <sup>1)</sup> has given for liquids. For comparison we have added the values calculated for methyl chloride, benzene and nitrous oxide, with data taken from LANDOLT's Tables (4th edition).

$t = .809$	$C \times 10^7$	$T$	$M$	$T_k$	$p_k$	$M^{1/2} T_k^{-1/6} p_k^{2/3}$	$\eta^{-1} M^{1/2} T_k^{-1/6} p_k^{2/3}$	
n. butane	349	1005	343.1°	58.08	423.9	37.5	31.15	$310 \times 10^3$
isopentane	500	885.1	373.1°	72.10	460.9	32.9	31.37	$354 \times 10^3$
methyl chloride	454	1082	366.6°	50.48	416.1	66.0	42.47	$393 \times 10^3$
benzene	700	1249	455.0°	78.05	562.4	47.9	40.25	$323 \times 10^3$
nitrous oxide	313	1342	249.6°	44.02	308.5	75.0	45.38	$388 \times 10^3$

The agreement as regards the hydrocarbons is not so near as for the liquids. For the rest the numbers do not diverge more than for the liquids, the data for which are given below for comparison. In the computation we have used for butane <sup>2)</sup> our own determination, for the saturated hydrocarbons the data of THORPE and RODGER <sup>3)</sup>, for the remaining substances the figures given by M. DE HAAS <sup>4)</sup>.

		$\eta \times 10^5$	$\eta^{-1} M^{1/2} T_k^{-1/6} p_k^{2/3}$
$t = .60$	n. butane	250	12460
"	n. pentane	270	11600
"	n. hexane	287	10950
"	n. heptane	301	10470
"	n. octane	322	9747
"	isopentane	263	11940
$t = .58$	benzene	420	9700
"	toluene	334	11720
"	methylchloride	288	14790
"	butyl iodide	533	11250
"	ethyl ether	286	11720

<sup>1)</sup> Comm. Leiden Suppl. 23, p. 85.

<sup>2)</sup> Comm. Leiden, 136.

<sup>3)</sup> THORPE and RODGER, Phil. Trans, 185A; 440; 1894.

<sup>4)</sup> Comm. Leiden 12, p. 12; 1894.

**Botany.** — W. H. ARISZ: "Positive and negative phototropism of the apex and base in oat-seedlings (*Avena sativa*)."  
(Communicated by Prof. F. A. F. C. WENT.)

(Communicated in the meeting of September 27, 1913).

(Preliminary communication).

OLTMANN<sup>1)</sup> has been able to show very convincingly that in the sporangiophores of *Phycomyces* a weak illumination produces positive curvatures and a strong illumination negative ones. BLAAUW<sup>2)</sup> confirmed these results and determined the quantity of light-energy necessary to produce these phenomena. In the case of Phanerogams also in the course of time negative curvatures have been seen, but except in the case of some roots, the communications are very vague and doubtful. OLTMANN and before him N. J. C. MÜLLER<sup>3)</sup> saw negative curvatures in seedlings of *Lepidium sativum*, while PRINGSHEIM<sup>4)</sup> saw faint inclinations of the apex in those of *Avena*.

Nevertheless very clear negative phototropic curvatures can easily be obtained in seedlings of *Avena sativa* when they are illuminated with only just that quantity of energy necessary to produce the phenomenon. I have endeavoured to show in an earlier paper<sup>5)</sup> that the reaction which occurs after the application of a certain quantity of light (this is true for 1—100 C. M. S.<sup>6)</sup>) has a constant strength. The reaction will increase in strength in proportion as the quantity of energy, used for stimulation, is greater.

With a short duration of stimulus the stronger reaction after more powerful stimuli is shown by the earlier occurrence of the curvature: that is to say, *the reaction-time*<sup>7)</sup> is a function of the

1) Flora Bd. 83 1897.

2) Recueil d. Trav. Bot. Néerl. Vol. 5 1909.

3) Botanische Unters. 1872.

4) COHN's Beitr. Bd. 9 1909.

5) Proceedings Roy. Acad. Sc. Amsterdam, March 1911.

6) The usual abbreviation for candle-metre seconds.

7) By reaction-time must here be understood the time which elapses from the beginning of stimulation to the moment at which the curvature becomes macroscopically visible.

The lengthening of the reaction-time after weaker stimuli, when the duration of stimulus ( $t$ ) is very short and constant (energy  $i \times t$  not constant) is by no means comparable to the lengthening of the reaction-time which BACH (Jahrb. f. wiss. Bot. Bd. 44 1907) and Mrs RUTTEN-PEKELHARING (Rec. Tr. Bot. Néerl. Vol. 7 1910) found by stimulation with weak centrifugal forces during the presentation time ( $i \times t$  constant). Here the lengthening of the reaction-time is

amount of light-energy used as stimulus. (Thus at 50 C. M. S. the reaction-time is 30 minutes, at 1 C. M. S. it is nearly 2 hours.)

Also the maximum curvature which is reached, is a function of the quantity of light-energy used as stimulus.

The degree of curvature, which is reached after a certain time, gives therefore (within these limits) a measure, by which conclusions as to the magnitude of the stimulus may be drawn.

These experiments have been continued further with greater amounts of light and have yielded the results that might have been expected. The reaction, which follows on stimulation with a definite amount of light-energy, is constant for that quantity of energy, only when the stimulus is applied for a comparatively short time. If the quantity of energy is applied for a longer time, then so-called tone-phenomena occur, which I intend shortly to discuss in greater detail.

If the stimulus is more than 100 C. M. S. the degree of curvature remains about the same. If however it is made considerably more, as for example 1200 C. M. S. at 23° C., then the resulting curvature is notably smaller; this continues up to 6000 C. M. S. when a new phenomenon appears, *the negative curvature*, which reaches a maximum at about 18000 M. C. S. From the paper of VAN DER WOLK<sup>1)</sup> and the recent one of WILSCHKE<sup>2)</sup> it has been shown that with these quantities of light positive curvatures from the base were to be expected and since it further seemed desirable to exclude such an influence, light was prevented from reaching the base. To this end there was placed round each seedling a black copper tube, which

entirely due to the longer presentation-time with weak centrifugal forces. For this case MAILLEFER (Bull. Soc. Vaud. Vol. 48 1912) has *mathematically* deduced the formula  $i(t-k) = \text{constant}$  (the reaction-time equals the presentation-time + a constant value.) This agrees with BACH's table 34, not with Mrs. RUTTEN—PEKELHARING's table 27.

The lengthening of the reaction-time on stimulation during the whole reaction-time is more complicated, because in that case neither the strength of the stimulus ( $i \times t$ ), nor the duration ( $t$ ) is *constant*. For this case TRÖNDLE (Jahrb. f. Wiss. Bd. 48 1910) has put forward the *empirical* formula  $i(t-k) = \text{constant}$ .

This formula is not supported by the tables which TRÖNDLE adduces as proof. Nor does BACH's table 33 according to TRÖNDLE give true values, whilst BACH's table 32 gives *constant* reaction-times for which  $t = k$ .

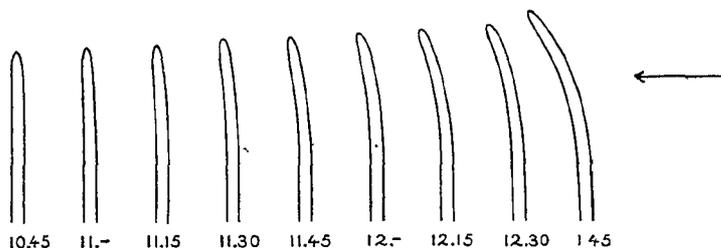
In BACH's tables 34 and Mrs. RUTTEN—PEKELHARING's table 27, as has already been pointed out, stimulation was not continued during the whole reaction-time.

<sup>1)</sup> Publications sur la Physiologie végétale, Nimègue 1912.

<sup>2)</sup> Sitzungsberichte K. Akad. Wien, Bd. 122, 1913.

rested on the ground and which could give no occasion for contact curvatures, because it could at no point touch the coleoptile. The phenomena, which are here discussed, are therefore exclusively the result of illuminating the apical zone of 1–2 mm. length.

The negative curvature can be observed very distinctly, but is much more developed, when after illumination the plant is rotated on a clinostat round a horizontal axis, so that no geotropic influence can counteract the curvature. In the same way as formerly I now also used an intermittent clinostat<sup>1)</sup> in which the positions of rest were separated by 180°. In each of these positions the plant remained for 2 minutes, so that there was enough time to trace the image of the seedling projected on to transparent paper by means of a lens and in this way to obtain a complete survey of the course of the curvature. The drawings were of course made by red light.



Negative curvature of an *Avena sativa* seedling.

At 10.15 the apical zone of 2 mm. was illuminated from the right with an intensity of 340 c. m. s. After stimulation on the intermittent clinostat temp. 25°.

The strength of the curve which is now reached, is found to be by no means inferior to that of a positive curvature, whilst, because only the uppermost zone of the apex is illuminated, there is here also a *conduction of stimulus* towards the basal zones.

*Apart from the direction of the curvature a negative curvature is in no single respect distinguishable from a positive one.*

Very remarkable and probably of some importance from a theoretical standing-point are the complicated curvatures which occur with illumination of about 9000 C. M. S. applied during 30 seconds.

In this case a positive curvature first takes place, later a negative one is visible and this, although only a length of 1 mm. of the apical zone, is illuminated. *It is evident from this that positive and negative curvatures are perceived and find expression independently of one another.*

<sup>1)</sup> Prof. MOLL in Groningen was so good as to allow me to make use for these experiments in his laboratory of the clinostat of VAN HARREVELD.

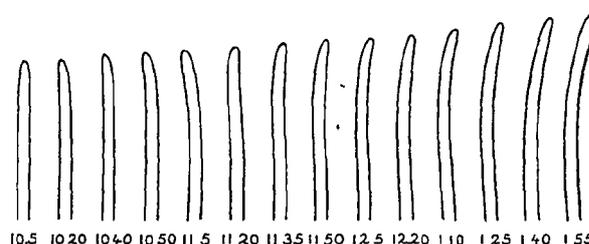


Fig. 2

Course of the curvature of an *Avena sativa* seedling. Illuminated from the left with an intensity of 340 C. M. S at 9.30 during 30 secs. Only an apical zone less than 1 mm. illuminated. Up to 11.8 a *positive* curvature, which afterwards passes into a strong negative one. After illumination on an intermittent clinostat; temp. 25°.

If the stimulus is more than 18000 C. M. S., the negative curvature then decreases again and generally no curvatures at all are observed. The remarkable phenomenon takes place however, that after the very strong stimulus of 400.000 C. M. S. during 4 seconds, weak positive curvatures are seen, which again disappear under the strongest illumination I have been able to apply, namely 1.600.000 C.M.S.

Following these observations of curvatures, which arise after illumination of the apical zone, I am able to give here some results with regard to the sensitiveness of the base.

VAN DER WOLK has stated that positive basal curvatures begin to occur at 20000 C. M. S. and are strong at 60000 C. M. S. VON GUTTENBERG and WILSCHKE have confirmed this. VAN DER WOLK and VON GUTTENBERG surrounded the apex with little caps of tin-foil. WILSCHKE thinks this method is wrong and makes use of a very pretty arrangement, by which the light falling through a slit illuminates a definite zone.

Nevertheless — and WILSCHKE himself shows this in his paper — this method of using little caps is not as he thinks to be dismissed as wholly useless, because the sensitiveness to contact-stimuli is particularly slight with small caps. WILSCHKE's method has the drawback that only very little of the material can be used at a time, and this is probably the reason why the phenomena, which will be described here, have escaped his notice.

I therefore used in my experiments little caps of tin-foil, which were so wide that they could be placed over the coleoptiles without friction. The little caps were completely light-tight and to make this perfectly sure were surrounded above with sealing-wax: this had at the same time the advantage of making them very easy to handle. They were removed immediately after illumination.

Nevertheless experiments were extremely difficult, especially at high temperatures, owing to nutation and contact curvatures. It is found absolutely necessary to use only those plants, which at the beginning of the experiment stood *completely* upright. For this reason about 80% to 90% of the cultivated material had to be unquestionably condemned.

It is now found that at 25° C., and it seems very desirable to choose such a high temperature for these experiments, very slight basal curvatures already occur at 100 C. M. S., when the upper 5 m.m. of the plant are covered with a cap. On applying more energy these curvatures increase and are clearly visible, 2 hours after the beginning of the illumination with 300 to 1200 C. M. S. They begin to be macroscopically visible after about half an hour.

If more light is applied in each case with very short duration of stimulus then the results are very uncertain. Sometimes very faint positive curvatures, at other times negative ones occur. The variability of the phenomenon is however so great and the curvatures are so complicated by the fact that sometimes first a positive and then a negative curvature arises, that it has not been possible to fix the amount of energy of which it can be said with certainty that the effect is positive or negative. The complications are probably due in great measure to the fact that the different portions of the base are not all equally sensitive, and various effects are thus superimposed.

A further investigation with only a small zone illuminated might be able to give an explanation of this. It is certain that with the application of 30000 C. M. S. during a short period no strong phototropic curvatures of the base occur. It need cause no surprise that VON GUTTENBERG, VAN DER WOLK and WILSCHKE all give these values since they did not apply this amount of energy as I did in a *short* period of time, but in much longer ones (VON GUTTENBERG, e. g. in an hour). Then the tone-phenomenon also occurs for the base and a large amount of energy applied over a considerable time no longer yields a negative but a positive effect.

To gain an idea of the sensitiveness of the most basal zones, the quantity of light was determined, which applied in a short time so as to eliminate tone, produced positive curvatures when the uppermost 12 mm. of the coleoptile had been covered with a cap. This limit was found to lie at about 400 C. M. S. The curvatures at 500 C. M. S. were the strongest, at more than 800 C. M. S. they were weaker, whilst from 1000 to 2400 C. M. S. even negative ones occurred.

If a comparison is now made of results which have been obtained

by illumination of the apex and of the base, it is found that in order to obtain a positive curvature of the apex a smaller amount of light is sufficient than for one of the base. The negative influence in the base and especially in the most basal zones is however visible with smaller amounts of light.

It is most remarkable that also the negative geotropic curvature, which JOST and R. STOPPEL<sup>1)</sup> found at high centrifugal forces were strongest in the more basal zones. Whether this is due to the greater rate of growth in the basal zones in comparison with the apex can only be decided by future investigations.

The results described point to the possibility of explaining the aberrant results obtained by VON GUTTENBERG and VAN DER WOLK. VAN DER WOLK held that illumination of the base makes the apex more sensitive to an illumination from the opposite side, whilst VON GUTTENBERG observed a smaller reaction of the apex. I also have been able to confirm VON GUTTENBERG's result. He applied 40000 C. M. S. in one hour, obtained therefore a strong positive basal curvature and then concludes from the decreased apical curvature that there is a conduction of stimulus towards the apex. Unfortunately it is impossible to repeat the experiments of VAN DER WOLK, because he did not state what quantity of energy he used for illumination and in what time this was applied. If however this was in a short time, then the assumption is obvious, that he was dealing with a zone in which negative curvatures arose, which superimposed on an apical curvature caused by illumination of the apex from the other side, produced a stronger effect in this direction, thus giving rise to the impression that the apex through the previous illumination of the base had become more sensitive. Experiments carried out in this direction have not led to a conclusive result, although a basal illumination of the base with 20000 C. M. S. and an apical illumination from the opposite side with 15 C. M. S. indeed produce apical curvature sooner and often rather more strongly than in plants without basal illumination<sup>2)</sup>. I have not obtained such striking results as those described by VAN DER WOLK, although the possibility is by no means excluded that taking a somewhat different length of the illuminated part and some other amount of energy, applied perhaps during a longer time, the phenomenon may show itself more markedly.

*Utrecht, Botanical Laboratory.*

<sup>1)</sup> Zeitschr. f. Bot. Bd. 4 1913.

<sup>2)</sup> If 120000 C. M. S. in 60 sec. is applied to the base then the apical curvature is noticeably slighter, because in this case a positive basal curvature predominates.

**Chemistry.** — “2.3.4.6-Tetranitro-phenylmethyl- and ethylnitramine.”

By Prof. VAN ROMBURGH and Dr. J. H. SCHEPERS.

(Communicated in the meeting of September 27, 1913).

Many years ago appeared a communication<sup>1)</sup> from one of us (v. R.) on tetranitrophenylmethylnitramine. This substance was the first aromatic nitramine with four nitro-groups in the nucleus, three of which were placed vicinally, causing a peculiar mobility of one of those groups. Thus it was shown that water, alcohol and amines readily react with it at the ordinary or at a slightly elevated temperature. As, since the publication of the above paper on this nitramine, nothing more has been published about it, save an occasional reference, it did not seem out of place to continue the research in different directions.

In the first place attempts have been made to improve the method of preparing the nitramine and we have been entirely successful by taking advantage of the fact that the tetranitrophenylmethylnitramine is *insoluble* in concentrated sulphuric acid, whereas the trinitro-compound is *soluble* therein. After a number of experiments, undertaken with the object of finding the most favourable conditions for obtaining the largest possible yield, we can recommend the following method.

10 grams of dimethylaniline are dissolved in 200 grams of strong sulphuric acid. When cold, a cooled mixture of 60 grams of sulphuric and 12 grams of nitric acid (D 1.51) is added drop by drop with vigorous stirring, the whole being cooled in ice and salt so as to keep the temperature at  $-2^{\circ}$ . Particularly at first the temperature rises strongly after each drop added. The liquid soon turns an orange-like colour. After the first half of the acid has been added, the remainder may be added more freely as there will be no further rise in temperature. After standing for half an hour in the ice and salt mixture, 100 c.c. of nitric acid (D. 1.51) are added. The liquid is then cooled for one day in ice or water and then left at rest for some days at the ordinary temperature.

After one or two days the liquid is congealed to a thick mass of crystals. A continuous evolution of carbon dioxide<sup>2)</sup> takes place, not accompanied, however, by brown vapours, because the nitrous acid formed combines with the sulphuric acid. After the lapse of a week the crystals are collected, by filtering, on glass wool and washed

<sup>1)</sup> Rec. 8, 282 (1889).

<sup>2)</sup> It contains traces of carbon monoxide

with strong sulphuric acid in order to remove the trinitrophenylmethylnitramine formed as a by-product. The mother liquor was poured into ice-water and yielded 2,4,6-trinitrophenylmethylnitramine.

The drained crystals of tetranitrophenylmethylnitramine are washed with gradually more diluted sulphuric acid and then with water until the filtrate gives no reaction with barium chloride. This product, having a melting point of  $140^{\circ}$ — $145^{\circ}$ , is pure enough for most purposes, but it may be further purified by dissolving in nitric acid (D 1.5) adding a little strong sulphuric acid, so as to protect the nitro-group in position 3, heating on a water-bath to  $70^{\circ}$  and, when cold, precipitating with strong sulphuric acid. After a day or two the mass is collected on glass wool, washed with sulphuric acid and treated further as described. The compound is now perfectly pure and melts at  $146$ — $147^{\circ}$ . The yield mounted to 18 grams.

From the mother liquor were obtained 6 grams of the *trinitro*-compound. After being dissolved in nitric acid and heated to  $70^{\circ}$ , the solution was allowed to cool and then poured into ice water. The product then melted at  $127^{\circ}$ .

An experiment made with absolute nitric acid gave no higher yield of the *tetra*-nitro-compound. Considering the conditions under which we operated, sulphuric acid, which according to REVERDIN<sup>1)</sup> can convert nitramines into nitrosamines will not be able to exert an unfavourable influence.

#### *Interaction of alcohols on tetranitrophenylmethylnitramine.*

The fact mentioned previously that tetranitrophenylmethylnitramine is attacked by boiling methyl and ethyl alcohol and gives an odour of nitrous ethers, invited a further research. In the first place it might be possible that in addition to nitrous esters nitrohydrocarbons were formed and further it was thought desirable to extend the reaction, besides to a few more primary, also to secondary and tertiary alcohols. As will appear soon, propyl alcohol, *isobutyl* alcohol and fermentation amyl alcohol form esters, whereas allyl alcohol, benzyl alcohol, *isopropyl* alcohol and secondary butyl alcohol, also tertiary amyl alcohol, even when dried with the utmost precautions, do not give the esters, but only the trinitromethylnitraminophenol itself, besides the nitrite corresponding with the alcohol, except in the case of benzyl alcohol.

Methyl alcohol acts already at the ordinary temperature on the nitramine. A gas is evolved that can be collected over a strong

<sup>1)</sup> Journ. f. pract. Ch. 81, 177 (1910); 83, 161 (1911); Diss. LIEBL, Genève 1913.

solution of potassium hydroxide and may be readily identified as methyl nitrite. The presence of nitromethane *cannot* be demonstrated amongst the reaction products.

In an experiment made with 1 gram of nitramine and 5 c.c. of methyl alcohol 60.6 c.c. of methyl nitrite (reduced to 0° and 760 mm.) were collected in 4 hours (Theory 67.5 cc).

The methyl ester of trinitromethylnitraminophenol formed in the reaction has been described previously (l.c.).

Interaction of ethyl alcohol likewise gives ethyl nitrite without formation of nitroethane. The ethyl ester of phenol has already been described.

With dry propyl alcohol is formed the propyl ester, melting at 118°, also propyl nitrite boiling at 57°. Nitropropane is not formed.

*Isobutyl* alcohol on heating with the nitramine (in the water-bath) gives the *isobutyl* ester melting at 95° and *isobutyl* nitrite boiling at 65°.

Fermentation amyl alcohol likewise yielded amyl nitrite and an amyl ester melting at 83°. With this alcohol the mass was coloured darker than with the other alcohols. It also appeared that more free trinitromethylnitraminophenol had formed than is found in the case of the other alcohols where it always occurs in small quantities.

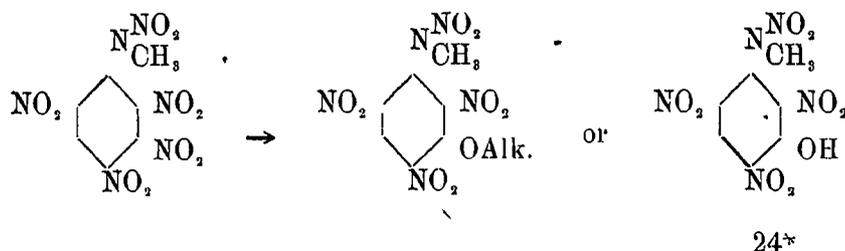
Allyl alcohol, although dried with the greatest care, gave allyl nitrite, but no weighable quantities of ester. Only free phenol was formed:

Benzyl alcohol, which acted violently, gave products containing benzaldehyde but no benzyl ester of the phenol, only the latter itself.

Secondary propyl alcohol and sec. butyl alcohol do not yield esters, but the free trinitromethylnitraminophenol is formed, also the nitrites of those alcohols

Tertiary amyl alcohol (amylene hydrate) reacts in an analogous manner. There is formed in addition to some nitrite also amylene. The main product of the reaction consists of phenol.

In all the above reactions the NO<sub>2</sub>-group of the nitramine is substituted in the position 3, either by the group OAlk, or by the group OH.



*Interaction of ammonia and amines.*

As appears from the often-quoted paper, the interaction of methylamine, which is dependent on the conditions prevailing during the experiment gives rise to different results. Not merely one nitro-group of the nucleus may be substituted, but in addition also the methyl-nitraminogroup. It now seemed not without interest to repeat these reactions not only with ammonia, but also with some other amines, aliphatic as well as aromatic ones. Before stating the results obtained it may be mentioned briefly what is already known as to the interaction of ammonia and amines on the alkylnitramino-group of aromatic nitramines.

Picrylmethylnitramine, according to v. ROMBURGH and MAURENBRECHER<sup>1)</sup> reacts with ammonia, with aliphatic as well as with aromatic amines — such as aniline, paratoluidine etc. — in such a manner that in addition to picramide (substituted picramide respectively) methyl nitramine is formed.

In an analogous manner, using paratoluidine, both methylnitramino-groups in 2.4.6-trinitrometaphenylenedimethylnitramine become substituted.

SOMMER<sup>2)</sup> allowed ammonia and different amines — aliphatic as well as aromatic — to act on 2.3.6-trinitro 4 tolylmethyl nitramine which caused the nitro-group in the position 3 to be substituted. Methylamine also reacted on the nitramino-group. With ammonia, methyl- and dimethylamine it was necessary to work at 100° under pressure as no reaction took place at the ordinary temperature. When we allowed ammonia and different amines to react on the tetranitrophenylmethyl nitramine we obtained reactions analogous to the action of methylamine. Ammonia, however, reacted slower than the amines.

An exception was noticed in the case of diisopropylamine, under the influence of which the nitro-group in the position 3 is replaced by OH. It then yields with the phenol the diisopropylamine salt.

The aromatic amines, aniline and paratoluidine act on the movable nitro-group only, even in heating.

Piperidine also acted abnormally, the piperidine salt of tetranitromethyl nitraminophenol was formed.

Highly peculiar was the interaction of pyridine and chinoline which, although quite dry, gave salts of the trinitromethyl nitraminophenol while simultaneously an evolution of gas took place.

<sup>1)</sup> Proc Roy Akad. Amst. IX, 704 (1907)

<sup>2)</sup> J f Pr. Ch. 67, 513 (1903)

*Interaction of ammonia.* If gaseous ammonia is passed over the nitramine phenomena of incandescence are noticed.

Aqueous ammonia (0.890—0.903) when acting for a short time at a slightly elevated temperature gives 2,4,6-trinitroaminophenylmethylnitramine melting at 181°.5. Hence, only one nitro-group in the nucleus has been substituted.

On prolonged interaction (a few days) of a nearly saturated ammonia solution the well-known 2,4,6-trinitro-m-phenylenediamine is obtained.

*Interaction of ethylamine.* This amine behaves quite analogously to methylamine, with which the reaction has been carried out previously (loc. cit.). A 16% solution of methylamine in water (10 c.c.) gives with the nitramine (2 grams) after half an hour a good yield of 2,4,6-trinitroethylaminophenylmethylnitramine m.p. 131°.5.

Heated for a short time with a 33% amine solution (12 c.c.) and then left at rest for two days, the nitramine (2 grams) gives the 2,4,6-trinitrodiethylaminobenzene previously described by BLANKSMA<sup>1)</sup>.

*Interaction of dimethylamine.* If 3 grams of nitramine are dissolved in 20 c.c. of a 25% dimethylamine solution the 2,4,6-trinitrodimethylaminophenylmethylnitramine m.p. 177° is formed.

If the reaction mixture is heated for 3 hours at 60°—70° and then left at rest for another 18 hours, the nitro-group in the nucleus as well as the methylnitramino-group are replaced by the dimethylamino-group. The resulting 2,4,6-trinitrotetramethyl-m-phenylenediamine melts at 141°.

*Interaction of diisopropylamine.* We did not succeed in replacing the movable nitrogroup by the diisopropylamino-group. A diisopropylamine salt of 2,4,6-trinitro-methylnitraminophenol m.p. 147°.5 was formed.

*Interaction of aniline.* A solution of the nitramine in benzene gives with aniline a dark red substance melting at 114°, which proved to be a compound of aniline with the yellow 2,4,6-trinitro-3-phenylamino-phenylmethylnitramine which melts at 183°. We did not succeed in substituting the methylnitramino-group also.

*Interaction of p-toluidine* causes the formation of the analogous tolyl compound which is coloured red, melts at 141° and formed no compound with p-toluidine.

*Interaction of piperidine.* This secondary amine behaves analogous to diisopropylamine. The movable nitro-group is substituted by OH and we obtain the pyridine salt of the phenol formed as a pale

<sup>1)</sup> Rec. 21, 325 (1902).

yellow substance melting at 172°. It is, however, remarkable that this salt should form even when the piperidine used has been dried for a long time over potassium hydroxyde and when the nitramine is dissolved in toluene, which has been rendered quite anhydrous by means of phosphorus pentoxyde. An evolution of gas could not be observed in the reaction, but an odour resembling that of nitroso-piperidine was noticed.

*Interaction of pyridine.* In this reaction one of us (v. R.) had obtained many years ago a compound melting at 145°, the analysis of which gave results pointing to the formation of a pyridine salt of trinitromethylnitraminophenol. On repeating the reaction under very varying conditions and carefully excluding even traces of moisture the same compound was always obtained (not always especially pure, however). In this case, however, an evolution of gas takes place. If, for instance, to 2 grams of nitramine dissolved in 60 grams of absolutely dry toluene were added drop by drop 5 grams of dry pyridine and the whole heated at 100° 24.1 c.c. of nitrogen and 43.3 c.c. of nitric oxyde (reduced to 0° and 760 mm.) were collected. The course of the reaction has not as yet been elucidated.

*Interaction of chinoline.* This takes place analogous to that of pyridine. The chinoline salt of the phenol formed, exhibited no sharp melting point (173° — 190°). Here also an evolution of gas takes place. The gas evolved is a mixture of nitrogen and nitric oxide.

#### 2.4.6. *Trinitro-methylnitraminophenol.*

As is well known, the nitramine passes on boiling with water into this phenol with formation of nitrous acid. This conversion proceeds very perceptibly even at the ordinary temperature. After 0.286 gram of nitramine had been shaken with 1080 grams of water at 11° for 24 hours, 0.197 gram appeared to have been converted.

This phenol is a powerful acid as has been shown by the measurements carried out by Mr. J. SMIT in the VAN 'T HOFF-Laboratory where the velocity of decomposition of diazoacetic ester<sup>1)</sup> by means of  $N/_{1300}$  nitric acid was compared with that of a  $N/_{1600}$  solution of trinitromethylnitraminophenol.

<sup>1)</sup> BREDIG, Curtius-Festschrift 1907, 1.

B. 40, 4015 (1907).

W. FRAENKEL, Z. f. Ph. Ch. 60, 202 (1907).

MUMM, Z. f. Ph. Ch. 62, 589 (1908).

LACHS, Z. f. Ph. Ch. 73, 291 (1910).

Phenol $\frac{1}{1500}$ N.		Nitric acid $\frac{1}{1300}$ N.
I K	II K	K
0.0261	0.0243	0.0334
0.0257	0.0236	0.0334
0.0266	0.0236	0.0325
0.0264	0.0233	0.0327
0.0265	0.0237	0.0328
0.0257	0.0236	0.0323

The arrangement of the experiment was similar to the method used by WALTON<sup>2)</sup> for measuring the reaction between hydrogen peroxyde and iodine-ions.

From the phenol were also prepared, besides the salts mentioned above: the compound with ammonia m.p. 108°; with ethylamine m.p. 179°; with dimethylamine m.p. 183°.

#### 2.3.4.6-Tetranitrophenylethylnitramine.

For the preparation of this compound could not be applied the direct nitration of diethylaniline because the method of separation with sulphuric acid proved a failure here.

Therefore, 3,4-dinitrodiethylaniline (m.p. 95°) was dissolved, with cooling, in 20 parts of nitric acid (D 1.49). Three parts of sulphuric acid (D 1.84) are then added and after waiting for an hour the whole is heated for a moment to 70°, cooled rapidly and then 12 parts of sulphuric acid are poured in. The mass is poured out into ice-water, the separated yellow, viscid mass is dissolved in nitric acid (D 1.49) with addition of sulphuric acid. After some time almost colourless crystals of the tetranitrophenylethylnitramine m.p. 96° are deposited. The yield is not very favourable. (From 2.8 grams was obtained 1.9 grams and on another occasion 2 grams yielded 1.5 grams).

A better result was attained by treating the 3,4-dinitrodiethylaniline (2 grams) first with 30 c.c. of nitric acid (D. 1.33) and 1 gram of sodium nitrite: the product formed was then dissolved in nitric acid (D 1.49) with addition of sulphuric acid.

The 2.3.4.6-tetranitrophenylethylnitramine dissolves readily in benzene and in toluene; on heating with bases ethylamine is evolved. Alcohols readily react with it, particularly on heating, with formation of nitrous esters. Amines also react with it. For instance, ethyl-

<sup>2)</sup> Z. f. Ph. Ch. 47, 186 (1904).

amine, on heating at 50°—60° in a sealed tube, yielded 2.4.6-trinitro-1.3-di-ethylaminobenzol, m.p. 142°.

On boiling with water is formed the 2.4.6-trinitro-ethylnitraminophenol m.p. 105° described previously by BLANKSMA<sup>1)</sup>. We tried to substitute the alkylnitramino-group in this compound, and in the corresponding methyl derivative, by the ethyl-amino-group with the aid of ethylamine. In this, however, we were till now not successful: the OH-group appears to impede the substitution of the nitramino-group in this case.

All the new compounds obtained and mentioned here have been analysed and will be described more in detail in the Rec. des Trav. Chim. des Pays-Bas.

*Utrecht, Org. Chem. Lab. University.*

**Chemistry.** — “*Contribution to the knowledge of the amides.*” By Prof. FRANCHIMONT.

(Communicated in the meeting of September 27, 1913).

Some years ago Dr. MOLL VAN CHARANTE had already prepared a substance which, on account of its mode of formation and the results of the analysis, he pronounced to be the diamide of sulphonisobutyric acid and which he has lately described under that name<sup>2)</sup>. This substance which endures heating to a temperature over 300° without melting and which decomposes at  $\pm 340^\circ$ , does not react with carbonylchloride, not even at 300° and, as appeared afterwards, not even with oxalylchloride. This strange behaviour, looking at the results obtained by BORNWATER in the action of oxalylchloride on amides, and also the fact that benzenesulphonamide *does* react with oxalylchloride, although with formation of an oxalylderivative, induced me to investigate the behaviour, in this respect, of the amides of isobutyric acid and ethanesulphonic acid which are more closely connected with sulphonisobutyric acid than the benzenesulphonamide.

On adding isobutyramide to oxalylchloride in benzene a strong evolution of heat took place immediately and a stream of hydrogen chloride was evolved while a solid substance was being deposited. After warming for a few hours, the evolution of gas ceased and everything had again dissolved. The following day, after cooling, a

<sup>1)</sup> Rec. 21, 260 (1902).

<sup>2)</sup> Rec. d. tr. ch. d. P. B. T XXXII. p. 90.

very little had crystallized out and a further trifling quantity was recovered by distilling off the benzene. The distillate had a strong odour of *isobutyric nitrile* and evolved much ammonia when boiled with potassiumhydroxide, it did not contain any previously. Boiling with strong hydrochloric acid first and then with potassiumhydroxide also yielded ammonia which likewise points to the presence of the said nitrile. The solid product was but little soluble in cold water or ether; after being extracted with both it was recrystallized a few times from alcohol and then melted at  $160^{\circ}$ . When heated with aqueous potassium hydroxide it gave oxalic acid. On analysis were obtained figures corresponding with those required by *oxalylbisiso-*  
 $\text{CO-NH-CO-C}_3\text{H}_7$ ,

*butyrylamide*  $\text{CO-NH-CO-C}_3\text{H}_7$ . Hence there was obtained, not as was expected from the results obtained by BORNWATER with other amides, a *carbonyl*, but an *oxalyl* derivative, whilst the greater part of the amide had been converted into nitrile. Hence, the oxalylchloride had acted to a large extent as other acid chlorides and anhydrides do sometimes, namely caused formation of water. Perhaps this happens also with other amides and to this might be attributed the frequent bad yield. Why no carbonyl derivative but an oxalyl derivative has formed here remains for the moment obscure.

As *isobutyrylmethylamide*  $\text{C}_3\text{H}_7\text{CO-NH-CH}_3$  was not known, I have prepared this also and I found again confirmed the regularity, to which I have pointed previously<sup>1)</sup>, that methylamides have a lower melting point than the amides. It was prepared from *isobutyryl chloride* and methylamine in ethereal solution at a low temperature and distilled under a diminished pressure. At 17 m.m. it passed over constantly at  $110^{\circ}$  as a colourless liquid. On cooling it crystallized and again melted at fully  $20^{\circ}$ . The analysis showed its purity. In supermelted condition at  $16^{\circ}$  the sp. gr. was 0,9089.

The ethanesulphonamide, obtained by JAMES from the chloride with ammonia in ether, was prepared by me in the same manner; only the melting point I found a little higher ( $60^{\circ}$ ) and not  $58^{\circ}$ . From benzene in which it is little soluble it crystallizes in long delicate needles, from ether, in which it is more soluble, in thick prisms, likewise from acetic ether and acetone in which it is freely soluble. Boiled for seven hours with oxalylchloride in benzene it deposited a solid substance, whilst in the benzene was dissolved but little of a brown syrupy mass, which was left on distillation. It may be recrystallized both from water and alcohol, although it is decom-

<sup>1)</sup> Rec. d. tr. ch. d. P. B. T. XVI. p. 128.

posed on boiling with water. It melts at  $224^{\circ}$ ; its solutions have an acid reaction. The analysis gave figures agreeing with those required

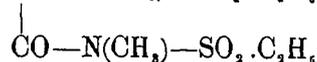


by *oxalylbiethanesulphonamide*  $\text{CO-NH-SO}_2\text{-C}_2\text{H}_5$ . On boiling with water oxalic acid may be already detected therein.

Hence, ethanesulphonamide like benzenesulphonamide yields with oxalylchloride an oxalyl derivative.

I now prepared *ethanesulphonmethylamide*, obtained already in 1886 by me and KLOBBE from the chloride with methylamine in ether, from the chloride by means of an aqueous 33% solution of methylamine; the chloride was diluted with ether. After being dried it was distilled under diminished pressure. On strong undercooling by liquid air it crystallized and even remained solid above  $0^{\circ}$ ; the melting point which was not yet determined accurately, lies presumably between  $3^{\circ}$  and  $7^{\circ}$ . Hence, it melts again lower than the ethylsulphonamide, in harmony with the above-mentioned regularity.

Boiled with oxalylchloride in benzene an evolution of hydrogen chloride only started on warming and had not yet ceased after 10 hours boiling. The benzene was now distilled off when the residue became crystalline. It was washed with water and with ether in which, as in alcohol, it is but little soluble and after careful drying crystallized from boiling benzene, when it forms beautiful thick crystals which melt at  $144^{\circ}$ . In chloroform it is also freely soluble. It is not decomposed on boiling with water but when boiled with aqueous potassium hydroxide it yields oxalic acid. The analysis gave figures required for *oxalylbisethanesulphonmethylamide*



A nitroderivative from ethanesulphonmethylamide had been obtained previously by me and KLOBBE by the action of absolute nitric acid, but neither the ethanesulphonamide nor the *isobutyrylamide* had as yet been treated with nitric acid. I have now supplemented this void and also treated the sulphon-*isobutyricdiamide* of MOLL VAN CHARANTE in the same manner.

The *isobutyrylamide* placed in cooled absolute nitric acid yields, when the solution attains the ordinary temperature, slowly and in theoretical quantity nitrous oxide like all simple amides.

Ethanesulphonamide when placed in absolute nitric acid causes a sudden and rapid (explosive like) evolution of gas; on cooling to  $-18^{\circ}$  the evolution is quiet but yet it ceases within an hour. The gas is nitrous oxide.

Benzenesulphonamide when cooled in ice and salt gives with absolute nitric acid but little gas but this increases on elevation of temperature.

The sulphonisobutyric diamide of MOLL VAN CHARANTE dissolves slowly in absolute nitric acid without evolution of gas even after two days and is reprecipitated unchanged by addition of water particularly on neutralising the acid.

Hence also in regard to absolute nitric acid this substance behaves quite differently than was to be expected from the diamide.

Finally, it may be mentioned here that just as HINSBERG prepared benzenesulphonnitramide from benzenesulphamide by means of nitric and sulphuric acid at low temperatures, ethylsulphonnitramide is to be obtained also from ethanesulphonamide in this manner, though with a poor yield, as a substance crystallizing beautifully from benzene in which it is fairly soluble and melting at  $\pm 70^\circ$ .

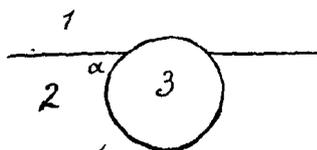
**Chemistry.** — “*The distribution of a colloiddally dissolved substance over two layers*”. By Prof. W. REINDERS. (Communicated by Prof. SCHREINEMAKERS).

(Communicated in the meeting of September 27, 1913).

1. When three non-miscible liquids meet, three things may happen depending on the values of the contact surface tensions  $\sigma_{1,2}$ ,  $\sigma_{2,3}$  and  $\sigma_{3,1}$ , apart from the action of the gravitation; either the three phases meet in one common side or one of them expands between the other two and prevents these from coming into contact.

The first will happen if none of the three contact surface tensions is greater than the sum of the other two; the second if this should be the case. If, for instance  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , 3 will expand between 1 and 2<sup>1)</sup>.

2. If one of the phases (3 for instance) is solid and the other two liquid we can again distinguish the same two cases with this difference, however, that when  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , the expansion of 3 between 1 and 2 is not possible. Phase 3 will then arrive at the contact surface of 1 and 2.



Let us now suppose the phase 3 to be in the form of a small globule. There will then be an equilibrium if  $\sigma_{1,3} = \sigma_{2,3} + \sigma_{1,2} \cos \alpha$ . If  $\sigma_{1,3} > \sigma_{2,3} + \sigma_{1,2} \cos \alpha$ ,  $\cos \alpha$  will be positive and  $\alpha < 90^\circ$ . The greater part

<sup>1)</sup> QUINCKE. Consult the test-books, for instance BOSSCHA-KUENEN II, 658.

of 3 is then enveloped by the liquid 2. If  $\sigma_{1,3} < \sigma_{2,3}$ ,  $\cos \alpha$  will be negative, hence,  $\alpha > 90^\circ$  and the greater part of 3 is drawn into the liquid 1.

3. If now the phase 3 is suspended in the liquid 1 in the form of a fine powder and this suspension shaken with the liquid 2, three things may occur.

a. If  $\sigma_{2,3} > \sigma_{1,2} + \sigma_{1,3}$ , 3 will be completely enveloped by 1 and thus the suspension remains unchanged in 1.

b. If  $\sigma_{1,3} > \sigma_{1,2} + \sigma_{2,3}$ , the stable condition will be such that 3 is completely enveloped by 2. The suspension will then disappear from 2 and pass entirely into the liquid 2.

c. If  $\sigma_{1,2} > \sigma_{2,3} + \sigma_{3,1}$ , or none of the three contact surface tensions greater than the sum of the other two, the powder is deposited entirely on the surface of contact <sup>1)</sup>.

4. Let us now apply these considerations to colloidal solutions, which according to modern views may be looked upon as transition stages between suspensions, or emulsions, and true solutions.

Let us first consider a suspensoid in which solid, floating particles are supposed to be present.

If these particles are fairly large and practically of uniform dimension we may assume that the surface tension in regard to the surrounding medium will be but little dependent on this dimension and therefore, the same for all particles. The same three possibilities which could be distinguished in the case of the coarse suspensions will consequently apply here also. The colloidal substance remains entirely in the first medium, passes entirely into the second or is deposited quantitatively at the surface of contact. In the first case the division coefficient = 0, in the second case it becomes  $\infty$ .

If the size of the particles becomes smaller, the resultant of the molecular attractions which appears as surface tension will be very much dependent on the number of molecules which together form the particle. Hence, the behaviour in regard to a second liquid phase will become dependent on this size. For instance, it will then be possible for particles below a certain size, to pass into the second liquid, for particles of greater dimension to arrive at the contact surface or to remain in the first liquid. According to the degree of

<sup>1)</sup> Instances of these different cases, a principle of separation for a mixture of solid, insoluble substances which is based on the different behaviour in regard to a liquidum couple, and the practical application thereof, are cited in a publication in the *Chemisch Weekblad*. Vol 10, 700 (1913). Also compare J. B. HOFMANN, *Zeitschr. f. physik. Chem.* 83, 385 (1913).

dispersion, colloidal solutions of a same substance will behave in a different manner.

If finally the colloidal particles exist of a few molecules only the idea of surface and surface tension loses its significance. The solution is then an ordinary molecular one and the dissolved substance will distribute itself over both liquids according to the "dividing rule". Other factors than surface tension, then dominate the distribution over the two-phases.

5. Some complications may still occur owing to the fact that the particles deposited at the surface of contact do not keep apart but unite to larger coagulums. This may happen very readily with very instable solutions.

In the case of emulsoids or solutions in which floating droplets of liquid must be assumed, these, if deposited at the contact surface may unite to form a separate liquid layer when  $\sigma_{1,2} < \sigma_{2,3} + \sigma_{3,1}$ . If however the separation has taken place at the contact surface, because none of the three surface tensions was greater than the sum of the other two, the expansion of liquid 3 between 1 and 2 becomes impossible and the isolated droplets of 3 will unite with greater difficulty.

6. In order to prove these considerations experimentally, I have investigated the behaviour of a few different colloidal solutions towards a second liquid. A few provisional results are communicated here.

In the first place, colloidal *gold*.

A red gold solution was obtained by passing CO into a dilute solution of  $\text{AuCl}_3$ . If into this solution was dropped cautiously isobutylalcohol or an aqueous solution of the same, the colloidal solution remained unchanged. Not a trace of coagulation which would show itself by a change of colour to bluish-violet was observed. Hence in homogeneous solution isobutylalcohol has no influence on the stability of the colloidal gold solution.

As soon, however, as the limit of solubility of the isobutylalcohol had been exceeded and this begun to form a separate layer, the gold, on shaking, gradually disappeared from the water and collected at the surface of contact. This then assumes a splendid colour, blue in transmitted, and a golden lustre in incident light<sup>1)</sup>.

<sup>1)</sup> As the alcohol layer does not moisten the glass owing to a thin layer of water collecting between the alcohol and the glass, the whole of the alcohol phase (upper layer) is surrounded at the nether side and the glass walls by a water alcohol demarcation in which the gold is distributed very homogeneously. At first we thus get the impression that the alcoholphase itself was coloured. If,

7 Similar to isobutylalcohol is the behaviour of various other solvents such as amylalcohol, benzene, lightpetroleum, carbon tetrachloride, carbon disulphide and ether<sup>2)</sup>.

8. Goldsolutions prepared in another way (for instance by electric dispersion of gold wire, or by reduction of  $\text{AuCl}_3$  with a solution of phosphorus in ether) and having a red or reddish-violet colour behaved in the same manner; the gold was deposited with a blue colour at the surface of contact. Somewhat different was the behaviour of a brownish coloured solution recently prepared from  $\text{AuCl}_3$  and solution of phosphorus in ether, for this was quite indifferent to ether and no gold was deposited at the contact surface.

9. In order to attain the equilibrium from the other side also, it was endeavoured to prepare a colloidal solution of gold in another dispersion medium. This succeeded in butyl or amylalcohol and in ether, both by electric dispersion of gold wire at a low temperature and by reduction of  $\text{AuCl}_3$  in these solvents by a solution of phosphorus in the same medium. By electric dispersion could also be obtained reddish solutions; those prepared by reduction with phosphorus had a yellowish-brown colour.

On shaking with water the gold in the first solutions passed into the surface of contact. The yellowish-brown amylalcohol solution was quite unaffected by shaking with water; not a trace of gold found its way into the water or collected at the surface of contact. This solution was also very stable in other respects and could be boiled without undergoing any change.

It thus appears that the gold of the yellowish-brown amylalcohol solutions is stable with regard to the aqueous phase. On the other hand, the gold from the red and reddish-violet solutions is stable in the contact layer. When, as is very probable in the case of colloidal silver, the differences in colour must be attributed to a difference in the size of the gold particles present we should have here a case of the possibility suggested in 4.

The yellowish-brown solution of gold in ether is very unstable.

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however, the tube containing the liquids is placed in an inclined position the gold will somewhat lag behind the liquid and it appears that the phase is colourless.

<sup>2)</sup> Carbon disulphide in presence of water forms the bottom layer; this is entirely surrounded by a splendid blue coloured golden skin, which has collected at the place of contact of the carbon disulphide and the water; a very beautiful demonstration of the fact that water penetrates between the glass and the carbon disulphide. When shaking, every drop of carbon disulphide is coloured blue by gold adhering to the surface and thus it looks as if the liquid itself possessed that colour, by removing some with a pipette it will be seen that such is not the case.

At first clear, it after a while becomes opaque and after an hour a portion of the gold is already so strongly coagulated that it is left behind on filtration. When shaken with water immediately after being prepared, the gold passes with a yellowish-red colour into the water; a small portion only deposited at the surface of contact in the form of brown flakes; the ethereal layer, however, was quite decolorised. From the solution which had stood for a while, all the gold disappeared also on shaking with water. The greater part thereof arrived, however, at the layer of contact, whilst the aqueous layer was coloured yellowish-brown and looked turbid with incident light.

An aqueous solution of  $\text{AuCl}_3$ , when shaken with ether to which had been added a few drops of the solution of phosphorus was coloured yellowish-brown whilst the ethereal layer remained colourless.

Hence, in regard to ether, the yellowish-brown modification of gold is stable in the aqueous phase (also see 8) whereas the reddish-violet and blue gold is stable at the surface of contact.

10. Addition of an impeding colloid such as gum arabic to the gold exerts a twofold influence. First of all it may retard, or even entirely prevent, the separation at the surface of contact. Even 0.001 % of the gum caused the separation from a red solution (prepared from  $\text{AuCl}_3$  and CO) to take place with great difficulty and then only imperfectly; with 0.005 % of the gum, a trace of deposit could be observed only after prolonged shaking. The colour of the gold in the contact layer was, however, blue as in the solution free from gum. The separation at the surface of contact with ether was entirely prevented by as little as 0.001 % of gum arabic; all the gold was retained in the aqueous solution with a red colour.

Secondly, without retarding the separation at the contact surface, it may prevent the colour from changing from red to violet and blue. This was observed in the case of  $\text{C}_6\text{H}_6$ ,  $\text{CS}_2$  and  $\text{CCl}_4$ , a very small quantity of gum arabic (0.001—0.005 %) being sufficient.

11. Besides colloidal gold, the colloidal solutions of the following substances were also investigated.

*Silver.* (Collargolum. Fabrik VON HEYDEN). With amylalcohol, isobutylalcohol and carbon tetrachloride a portion passed with a brown colour into the surface of contact, another portion remained unchanged in the water. With benzene and with ether, nothing was deposited at the contact surface and all was retained in the water.

*Ferric hydroxide* ( $1\frac{1}{2}$  years old). This was retained in the water with every liquid used.

*Arsenic trisulphide* ( $1\frac{1}{2}$  year old). With paraffin oil, carbon tetrachloride, benzene and ether the liquid remained unchanged; with amylalcohol and with isobutylalcohol, the sulphide was deposited quantitatively at the surface of contact<sup>1)</sup>.

*Selenium* (prepared from  $H_2SeO_3 + SO_2$ ). With amylalcohol a portion is deposited at the contact surface and another portion in the alcohol layer. With butylalcohol, carbon tetrachloride, benzene and ether all the sulphide collects at the surface of contact.

12. From the above it appears that case *b* — separation at the surface of contact — is a very common one. A few instances, however, could also be found in the other two cases.

In fact, case *b* is so common that it will often be possible to determine the colloidal nature of a solution by exhibiting the separation at the contact surface on shaking with a second liquid.

The above cases relate to non — or only partially — reversible colloids.

With typically reversible colloids such as gelatin, the separation at the contact surface has, however, also been observed and this reaction has even been utilised for demonstrating the presence of these substances in a solution<sup>2)</sup>. In most cases, however, the total quantity that deposits at the contact surface appears to be small. JONKER<sup>3)</sup> found for tannin and alcohol a distribution over the two layers; these solutions so far as the size of the colloidal particles is concerned will have to be classed very closely with the molecular solutions and be considered as homogeneous phases.

The adhesion to the surface of contact of a second liquid is, moreover, quite comparable to the surface adhesion of an added solid substance, a phenomenon that has been observed with different colloidal solutions.

Colloidal gold, for instance, is taken up by carbon powder, barium-sulphate and various fibrous substances; colloidal arsenic trisulphide by carbon and by barium sulphate; carbon by paper; selenium,

<sup>1)</sup> In this case also it was very evident that the separation is due to the action of the surface of contact. An aqueous solution of butylalcohol left the solution entirely unchanged; the instant, however, that an excess of the alcohol was added, thus forming a separate layer, all the  $As_2S_3$  soon deposited at the contact surface.

<sup>2)</sup> K. WINKELBLECH, Zeitschr. f. angew. Chem. **19**, 1953 (1906). The phenomenon is, however, somewhat different as the gelatin arrives at the contact surface as a thin, white lather. Hence, besides the liquid phases the air-phase also cooperates.

<sup>3)</sup> Zeitschr. f. Kolloidchemie **10**, 126.

tellurium, tungsten-blue and many other inorganic colloids by fibrous substances<sup>1)</sup>. These phenomena have been usually described as adsorptions, although the name adhesion would be the more correct one. If, however there exists a continuity between colloidal and molecular solutions, this will then also exist between adhesion and adsorption.

Delft, July 1913.

**Chemistry.** — “*Equilibria in ternary systems*”. IX. By Prof. F. A. H. SCHREINEMAKERS.

We will now consider the four-phase equilibrium  $F + F' + L + G$  in connection with the saturation- and vapour saturation-curves of  $F$  and of  $F'$  under their own vapour pressures.

These saturation-curves under their own vapour pressures may be situated with respect to one another in different ways. 1. they may intersect one another; 2. they may touch one another; 3. the one may be situated outside the other; 4. the one may surround the other.

Let us, in the first instance, consider fig. 2, in which the continuously drawn curves represent the saturation curves, the dotted curves the vapour saturation curves of  $F$  and of  $F'$  under their own vapour pressures.

At the given temperature, therefore, every liquid of the curve  $fxyg$  is saturated with the solid  $F$  and in equilibrium with a vapour of the corresponding curve  $f_1g_1$ ; every liquid of the curve  $f'x'y'g$  is saturated with the solid  $F'$  and in equilibrium with a vapour of the corresponding curve  $f'_1g'_1$ .

Because all these liquids are under their own vapour pressures, the pressure changes will, as we have seen before, move along these curves.

If we now consider  $f$  as a point on the saturation curve of  $F$ , it is under a pressure  $P$ ; if, on the other hand, we consider  $f$  as a point on the saturation curve of  $F'$ , it is under a pressure  $P'$ . The question now arises: Is  $P$  the same as  $P'$  or are they different?

Under the pressure  $P$ , therefore, the system  $F + L_f + G$  exists, and under the pressure  $P'$  the system  $F' + L_{f'} + G$ . At a definite

<sup>1)</sup> R. ZSIGMONDY, Verh. d. Ges. D. Naturf. u. Aerzte, 73 Vers. Hamburg 1901, p. 168. L. VANINO, Ber. d. D. Chem. Ges. **35**, 662 (1902).

W. SPRING, Beobachtungen über die Waschwirkung von Seifen, Zeitschr. f. Kolloidchemie **4**, 161 (1909).

W. BILTZ, Ber. d. D. Chem. Ges. **37**, 1766 (1904).

temperature, however, a definite liquid  $L_f$  cannot be in equilibrium with vapour under two different pressures.

$P$  and  $P'$  must therefore be the same. Further it also follows that the vapours  $G$  and  $G'$  are the same. We call this vapour  $G_{f_1}$ .

The point of intersection of the two saturation curves under their own vapour pressures signifies, therefore, that under a definite pressure the three-phase equilibrium  $F + L_f + G_{f_1}$  can be met with as well as  $F' + L_f + G_{f_1}$ . To every point of intersection  $f$  of the saturation curve belongs, therefore, a definite point of intersection  $f_1$  of the vapour saturation curves under their own vapour pressures. Hence it follows that the point of intersection  $f$  represents the liquid  $L$ , the corresponding point of intersection  $f_1$  the vapour  $G$  of the four-phase equilibrium  $F + F' + L + G$ ; in other words:  $f$  represents the solution saturated with  $F + F'$  under its own vapour pressure;  $f_1$  is the corresponding vapour. The same, of course, applies to the points of intersection  $g$  and  $g_1$ .

The following equilibria, therefore, exist in fig. 2:

1. A series of solutions saturated with  $F$  under their own vapour pressures, with their corresponding vapours; therefore the system  $F + L + G$ .

2. A series of solutions saturated with  $F'$  under their own vapour pressures, with their corresponding vapours; therefore the system  $F' + L + G$ .

3. Two solutions saturated with  $F + F'$  under their own vapour pressures with their corresponding vapours; therefore the system  $F + F' + L + G$ . The one exists under the pressure  $P_f$  with the liquid  $f$  and the vapour  $f_1$ ; the other under the pressure  $P_g$  with the liquid  $g$  and the vapour  $g_1$ . Usually  $P_f$  and  $P_g$  are different; only in exceptional cases can they be equal.

For the sake of abbreviation we shall call in future the point of intersection of two saturation curves under their own vapour pressures "the liquid point of intersection", and the point of intersection of two vapour saturation curves under their own vapour pressures "vapour point of intersection".

If we now assume, that in the figs. 1—3 (VIII) the saturation and vapour saturation curves of  $F$  and of  $F'$  under their own vapour pressures are drawn, then it is evident that the liquid points of intersection fall on the liquid curve  $ac$  and the vapour points of intersection on the vapour curve  $a_1c_1$  of the four-phase equilibrium. In fig. 1, corresponding with fig. 1 (VIII) some of these curves are partly drawn. On the liquid curve  $ac$  [fig. 1—3 (VIII)] we take a point  $N$ , corresponding with the point of maximum temperature  $N$

of fig. 4 (VIII); we imagine the corresponding point  $N_1$  on the

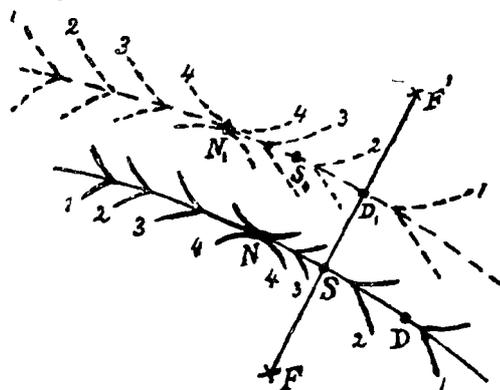


Fig. 1.

consequently also the corresponding points  $N_1$ ,  $S_1$  and  $D_1$ ) must then lie with respect to one another as in fig. 1.

The liquid curve (fig. 1) has, therefore, its maximum temperature at  $N$ , the vapour curve at  $N_1$ . On the liquid curve, therefore, the temperature decreases from  $N$ , on the vapour curve from  $N_1$  in both directions.

Let us now take a temperature  $T_1$ , lower than the maximum temperature of sublimation  $T_D$ ; the saturation- and vapour saturation curves under their own vapour pressures (which are only partly drawn in the figure) corresponding to this temperature  $T_1$ , are indicated by "1". In fig. 2 we find the complete diagram. From figs. 1 and 1—3 (VIII) it follows, (as is also drawn in fig. 2), that at temperatures lower than the maximum point of sublimation, the two liquid points and also the two vapour points of intersection are situated in opposition with respect to  $FF'$ .

We now take a temperature  $T_2$  between the maximum point of sublimation  $T_D$  and the minimum meltingpoint  $T_S$ . The saturation and vapour saturation curve under their own vapour pressures, corresponding with this temperature  $T_2$  and only partly drawn in the figure, are indicated by "2". One of the liquid points of intersection is situated between  $S$  and  $D$ , the corresponding vapour point of intersection between  $S_1$  and  $D_1$ . We find the complete diagram in fig. 3. The points  $f'$  and  $g$  are situated in opposition,  $f'_1$  and  $g_1$  in conjunction with respect to the line  $FF'$ . The figs. 2 and 3 differ from one another only as regards the position of the point  $g_1$  with respect to the line  $FF'$ . When fig. 2 passes into fig. 3 the point  $g_1$  falls on the line  $FF'$ ; this is the case at the maximum temperature of sublimation  $T_D$ ; the points  $g$  and  $g_1$  of this transition figure agree then with the points  $D$  and  $D_1$  of figure 1.

We now take in fig. 1 a temperature  $T_s$  between the melting point  $T_S$  and the point of maximum temperature  $T_N$ . The saturation and vapour saturation curve under their own vapour pressures, corresponding to this temperature, are partly drawn and indicated by 4. One of the liquid points of intersection is situated between  $S$  and  $N$ , the corresponding vapour point of intersection between  $S_1$  and  $N_1$ . Fig. 4 indicates the complete diagram. The points  $f$  and  $g$  as well as the points  $f_1$  and  $g_1$  are situated in conjunction as regards the line  $FF'$ . When fig. 3 passes into fig. 4, the point  $g$  falls on the line  $FF'$ ; this is the case at the minimum melting point  $T_S$ . The points  $g$  and  $g_1$  of this transition figure agree with the points  $S$  and  $S_1$  of fig. 1.

At the maximum temperature  $T_N$  the two saturation curves touch one another in the point  $N$ , the two vapour saturation curves in  $N_1$ . We find the complete diagram in fig. 5. At this temperature, therefore, only one single solution  $N$  exists, saturated under its own vapour pressure with  $F + F'$ ; the corresponding vapour is represented by  $N_1$ . If we raise the temperature still more, the two saturation- as well as the two vapour saturation-curves fall outside each other, and finally disappear. The manner in which this takes place has already been described in communication I.

In deducing diagrams 2—5 we have based our arguments principally on fig. 1, in which the points  $F$ ,  $F'$ ,  $S$  and  $D_1$  are situated as in type 1. As we have seen before, however, that 12 types can be distinguished, we shall now consider from another point of view the appearance of two saturation- and two vapour saturation curves under their own vapour pressures. We shall namely distinguish 7 chief groups with respect to the temperature. We assume again in the first instance that the volume of  $F + F'$  increases on melting (congruent and incongruent). The points  $N$ ,  $S$ , and  $D$  are situated

with respect to one another as in fig. 4 (VIII) and 1.

I. The temperature is lower than the maximum point of sublimation  $T_D$ . It is easy to see that not only the two liquid points of intersection but also the two vapour-points of intersection are situated in opposition as regards the line  $FF'$ .

One of the many diagrams, satisfying these conditions, is drawn in

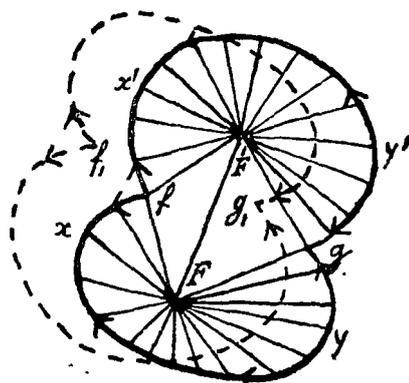


Fig. 2.

fig. 2. The points  $F$ ,  $F'$ ,  $f$  and  $g$  are situated in this figure in such a way that they form the angular points of a quadrilateral, they may, however, also form a triangle, surrounding the point  $F'$  or  $F''$ . The same applies to the points  $F$ ,  $F'$ ,  $g_1$  and  $f_1$ .

In addition to the above mentioned instances, the different diagrams may yet still differ from one another with respect to the reactions which may take place in either of the two four-phase systems  $F + F' + L + G$ . For the system  $F + F' + \text{liquid } g + \text{vapour } g_1$ , we distinguish the following cases:

*a.* The point  $g_1$  is situated within the triangle  $FF'g$ .

Reaction:  $F + F' + L \rightleftharpoons G$ .

*b.* The points form a quadrilateral; the line  $Fg_1$  intersects  $F'g$ .

Reaction:  $F' + L \rightleftharpoons F + G$ .

*c.* The points form a quadrilateral; the line  $Fg$  intersects  $F'g_1$ .

Reaction:  $F + L \rightleftharpoons F' + G$ .

*d.* The point  $g$  is situated within the triangle  $FF'g_1$ .

Reaction:  $L \rightleftharpoons F + F' + G$ .

For the system  $F + F' + \text{liquid } f + \text{vapour } f_1$ , we may of course distinguish the same cases.

If we consider the above-mentioned reactions in the direction from left to right, vapour is formed, and, therefore, the volume increases. The three-phase equilibria, which are formed, when the reactions take place from left to right, exist therefore at lower temperatures, and those which are formed when the reactions take place from right to left exist, therefore, at higher pressures than the four-phase equilibrium. Hence the following is easily deduced: out of the point of intersection of the two saturation curves under their own vapour pressures, the pressure

1. decreases along both curves, when reaction *a*
2. increases along the one curve and decreases along the other, when reaction *b* or *c*
3. increases along both curves, when reaction *d* takes place in the four-phase equilibrium.

The same of course applies to both the vapour saturation curves under their own vapour pressures. As follows from the position of the points of intersection in fig. 2, the reaction "*a*" is there assumed for the equilibrium  $F + F' + \text{liquid } g + \text{vapour } g_1$ , the reaction "*d*" for the equilibrium  $F + F' + \text{liquid } f + \text{vapour } f_1$ . The pressure changes along the curves in the vicinity of the points of intersection of this figure are in accordance with the previous considerations.

It is evident that yet many other cases are possible, which can be obtained by combining the reactions *a*—*d*, two at a time. It

should however be kept in mind that in the immediate vicinity of the maximum point of sublimation only the reactions  $\alpha$ ,  $b$  and  $c$  can take place (compare the reaction series  $A_1$ ,  $B_1$  and  $C_1$ ). Reaction  $d$  can take place at a greater distance from this point only.

We may also consider the different cases from yet another point of view. For this purpose we take two saturation curves and their corresponding vapour saturation curves. We let these intersect one another in such a way, that the two liquid points of intersection as well as the two vapour points of intersection are situated in opposition with respect to the line  $FF'$ .

If we consider stable conditions only, merely a part of each curve will remain. We may now distinguish several cases, according as the points of maximum and minimum pressure are situated on the stable or metastable parts of these curves, and these will be in agreement with what has been said above. It is evident that for each stable or metastable point of maximum or minimum pressure on a saturation curve there exists a stable or metastable point on the corresponding vapour saturation curve.

In fig. 2 the points of maximum pressure are indicated by  $x$  and  $x'$ , the points of minimum pressure on the saturation curves by  $y$  and  $y'$ . The two curves intersect each other in fig. 2 in such a way that these four points are stable, consequently the corresponding four points (not drawn in the figure) on the vapour saturation curves are also stable.

II. The temperature is equal to the maximum point of sublimation  $T_D$ .

The two liquid points of intersection are situated in opposition with respect to the line  $FF'$ ; one of the vapour points of intersection is situated on the line  $FF'$ . We imagine in fig. 2 or 3 the point  $g_1$  on the line  $FF'$ . When a congruent sublimation takes place,  $g_1$  is situated between the other two points, with an incongruent sublimation  $F$  or  $F'$  is situated there.

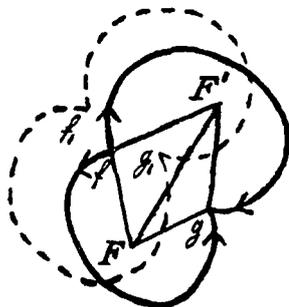


Fig. 3.

III. The temperature is higher than the maximum point of sublimation  $T_D$ , but lower than the minimum melting point  $T_S$ .

The two liquid points of intersection are situated in opposition with respect to the line  $FF'$ ; the two vapour points of intersection are situated in conjunction with respect to that line. One of the many diagrams satisfying these conditions is drawn in fig. 3. In the equilibrium  $F + F' + \text{liquid } g$

+ vapour  $g_1$ , one of the reactions  $a-d$  no longer takes place; instead one of the reactions

e)  $F+F' \rightleftharpoons L+G$ ; f)  $F \rightleftharpoons F'+L+G$ ; g)  $F' \rightleftharpoons F+L+G$  takes place.

As follows from the position of the points  $g$  and  $g_1$  in fig. 3, the reaction  $e$  takes place. Hence it follows that the pressure decreases from  $g$  along the two curves.

IV. The temperature is equal to the minimum meltingpoint,  $T_S$ .

The two vapour points are situated in conjunction with respect to the line  $FF'$ ; one of the liquid points of intersection is situated on the line  $FF'$ . We shall call this figure "fig. 3a". When a congruent melting takes place,  $g$  is situated between the other two points; when an incongruent melting takes place,  $F$  or  $F'$  is situated there.

We have seen before that the minimum melting point  $T_S$  of the complex  $F + F'$  can be lower than that of one of the two components  $F$  or  $F'$  taken separately. Imagining in fig. 3a the saturation curve of  $F$  to be expanded, then  $T_S$  is lower than the minimum melting point of  $F$ ; when both the saturation curves in fig. 3a are expanded, then  $T_S$  is lower than the minimum melting point of either of the two compounds  $F$  and  $F'$ . As the expanded saturation curves are generally not very far removed from  $F$  and  $F'$ , this last mentioned case can only occur when the points  $F$  and  $F'$  are situated close to each other, that is if they differ only a little in composition.

V. The temperature is higher than the minimum melting point,  $T_S$ , but lower than the point of maximum temperature  $T_N$ .

The four points of intersection are all situated on the same side

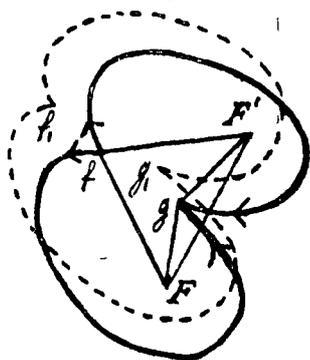


Fig. 4.

of the line  $FF'$ . In fig. 4 one of the many possible diagrams is drawn. As long as the point  $g$  is still situated in the vicinity of the line  $FF'$ , reaction  $a$  cannot take place in the four-phase equilibrium  $F+F'+$  liquid  $g$  + vapour  $g_1$ , but instead one of the reactions  $b-d$  takes place. As follows from the position of the points  $g$  and  $g_1$  in fig. 4, the reaction that takes place is  $d$ , therefore:  $L \rightleftharpoons F + F' + G$ .

Vapour is formed as the reaction proceeds from left to right. Although in such a case the volume generally increases, in this particular instance the volume, however, decreases. We have namely seen before that this formation of vapour in points between  $N$  and  $S$  takes place with decrease of volume.

As the three-phase equilibria  $F + L + G$  and  $F' + L + G$  are formed here, when the reaction proceeds from left to right, both these equilibria exist under pressures lower than those of the four-phase equilibrium. On both saturation curves under their own vapour pressures, the pressure decreases therefore from the point  $g$  outwards.

In the system  $F + F' + L + G$  the volume increases, of course, with the formation of vapour.

VI. The temperature is equal to the point of maximum temperature  $T_N$ .

The two saturation curves under their own vapour pressures touch one another; the same applies to the two vapour saturation curves. The two points of contact are situated on the same side of the line  $FF'$ . In fig. 5 one of the many possible cases has been drawn. As the point  $N$  is generally situated in the vicinity of the line  $FF'$ , consequently in the four-phase equilibrium reaction  $a$  does usually not take place, but instead one of the reactions  $b-d$  takes place.

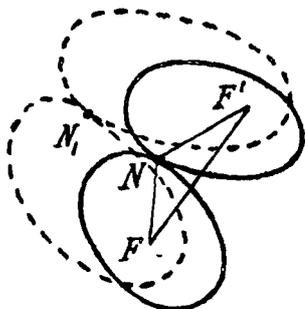


Fig. 5.

In fig. 5 the curves touch one another externally. It is evident that they may also touch one another internally, or that one or more of the four curves may be expaxed.

From our previous considerations it follows that, during a reaction between the four phases of the system  $F + F' +$  liquid  $N +$  vapour  $N_1$ , the volume remains constant.

While the point of contact between two saturation curves under a constant pressure is situated on the line  $FF'$  (the only exceptions being metastable points of contact, which may be situated on the spinodal line, when the liquids separate into two layers), the point of contact of two saturation curves under their own vapour pressures is always situated outside the line  $FF'$ .

VII. The temperature is higher than the point of maximum temperature  $T_N$ .

The two saturation curves under their own vapour pressures neither intersect nor touch each other; the one is situated either outside or completely round about the other. The same, of course applies to the two vapour saturation curves under their own vapour pressures.

For this purpose we have deduced from fig. 1, that, at the maximum temperature  $T_N$  the two saturation curves as well as the two vapour saturation curves under their own vapour pressures touch

each other, and also that the two points of contact are not situated on the line joining  $F$  and  $F'$  of the solid phases. This also follows from the equations of these curves.

The saturation curve under its own vapour pressure is, as we have seen before [8 and 9] (II) fixed by

$$[(x-\alpha)r + (y-\beta)s] dx + [(x-\alpha)s + (y-\beta)t] dy = A \cdot dP \quad (1)$$

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = C \cdot dP \quad (2)$$

We may write for this, after eliminating  $dP$

$$\{(x-\alpha)C - (x_1-x)A\}(r dx + s dy) + \{(y-\beta)C - (y_1-y)A\}(s dx + t dy) = 0 \quad (3)$$

For the saturation curve of  $F'$  under its own vapour pressure we have:

$$\{(x-\alpha')C - (x_1-x)A'\}(r dx + s dy) + \{(y-\beta')C - (y_1-y)A'\}(s dx + t dy) = 0 \quad (4)$$

If the two saturation curves under their own vapour pressures touch one another, then, for this point of contact,  $\frac{dy}{dx}$  from (3) and (4) must necessarily have the same value. This is the case when:

$$\frac{(x-\alpha)C - (x_1-x)A}{(x-\alpha')C - (x_1-x)A'} = \frac{(y-\beta)C - (y_1-y)A}{(y-\beta')C - (y_1-y)A'} \quad (5)$$

If we substitute herein the values of  $A, A'$  and  $C$  we find after reduction:

$$n v + n' v' + m V + m_1 V_1 = 0 \quad (6)$$

where  $n, n', m$  and  $m_1$  have the same values as in (6) (VIII).

(6) is not satisfied by a point on the line  $FF'$ ; in this case, namely  $m_1$  becomes  $= 0$ , and consequently, we should have to satisfy, at the same time:

$$n v + n' v' + m V = 0 \quad (7)$$

As the value of the first part of (7) is, however, dependent on the volumes of the three phases  $F, F'$  and  $L$ , consequently (7) is usually not satisfied. This also follows from the meaning of the first part of (7); this, namely, represents the change of volume which takes place in the minimum melting point of the complex  $F + F'$ , and this is, of course, only in highly exceptional cases equivalent to zero.

The first part of (6) represents, as we have seen before, the change of volume which takes place in a reaction in the four-phase system  $F + F' + L + G$ . In agreement with previous considerations consequently, we see that two saturation curves under their own vapour pressures touch, if the four-phase reaction takes place without change of volume.

If the condition is calculated that two vapour saturation curves may touch, then a form is obtained, which is deduced from (6) by

substituting therein  $x_1$ ,  $y_1$ , and  $V_1$  for  $x$ ,  $y$  and  $V$ , and vice versa. In this way condition (6) is again obtained. From this follows: if two saturation curves under their own vapour pressures touch each other, then their corresponding vapour saturation curves must also touch, and vice versa. This is the case when the four phase reaction takes place without change of volume.

When considering figs. 2—5 we have supposed that in the four-phase systems always a four-phase reaction takes place. As a transition instance a three phase reaction may, however, also take place.

If we limit ourselves to such reactions taking place between liquid, vapour and one of the solid bodies, then we have:  $h) F + L \rightleftharpoons G$   $i) L \rightleftharpoons F + G$   $j) F \rightleftharpoons L + G$   $k) F' + L \rightleftharpoons G$   $l) L \rightleftharpoons F' + G$   $m) F' \rightleftharpoons L + G$ .

In the four-phase equilibrium  $F + F' + \text{liquid } g + \text{vapour } g_1$  (figs 2, 3 and 4) reaction  $h$ ,  $i$  or  $j$  takes place, if the points  $F$ ,  $g$  and  $g_1$  are situated in a straight line. Reaction  $h$  takes place if the point  $g_1$ , reaction  $i$  if the point  $g$ , and reaction  $j$  if the point  $F$  is situated between the other two points.

If, however, the three points  $F$ ,  $g$  and  $g_1$  are in a straight line, then the pressure for the system  $F + \text{liquid } g + \text{vapour } g_1$  will be a maximum or minimum, as we have seen before. The point  $g$  will then be the point of maximum or minimum pressure for the saturation curve of  $F$ , the point  $g_1$  such a one for the vapour saturation curve under its own vapour pressure. Consequently in fig. 2 the point  $g$  coincides with the point  $y$  or the point  $f$  with the point  $x$ .

The previous considerations may also be expressed thus: when in the equilibrium  $F + F' + L + G$  one of the three-phase reactions  $h$ — $m$  takes place, a point of maximum or minimum pressure of a saturation curve is situated on the liquid curve of this equilibrium, and a similar point of the vapour saturation curve under its own vapour pressure on the vapour curve of this equilibrium.

In connection with the previously deduced properties (communication VIII) we find, consequently, that if in a four phase equilibrium  $F + F' + L + G$  a three-phase reaction takes place between liquid, gas and one of the solid bodies then:

1. the four-phase curve, the limit curve of this compound and the solution path of this compound belonging to this point will touch one another in the  $P, T$ -diagram.

2. in the concentration diagram on the liquid curve of the four phase equilibrium a point of maximum or minimum pressure of the saturation curve of the compound will be situated, and on the

vapour curve of this equilibrium a similar point of the vapour saturation curve under its own vapour pressure.

If one of the properties mentioned under 1. or 2. appears, then, reasoning backwards, the three-phase reaction, mentioned above, will also take place in the four-phase equilibrium.

Above we have considered only the case that the volume increases at the congruent or incongruent melting of the complex  $F + F'$ ; corresponding properties make their appearance when the volume decreases. These the reader can easily deduce for himself.

In the same way in which we deduced above the properties of two saturation- and vapour saturation curves under their own vapour pressures, the reader can consider the appearance of two boilingpoint curves and their corresponding vapour curves.

**Astronomy.** — “*On the constancy of the velocity of light*”. By  
Prof. W. DE SITTER.

In my communication to the meeting of February of this year (see these Proceedings, Vol 15, page 1297) I pointed out that the existence of spectroscopic doubles whose motion obeys the laws of KEPLER, is incompatible with the theory of RITZ, while in agreement with that of LORENTZ.

Since then Messrs. P. GUTHNICK<sup>1)</sup> and E. FREUNDLICH<sup>2)</sup> have brought forward the hypothesis that the velocity of light might depend on the velocity of the source in a manner differing from the simple addition postulated by the theory of RITZ. The most simple hypothesis would be

$$v = c + \alpha u,$$

where  $v$  is the velocity of light emitted by a source having the velocity  $u$ . The problem then is no longer to decide whether  $\alpha = 0$  or  $\alpha = 1$ , intermediate values being excluded, but to assign an upper limit to  $\alpha$ .

We have then, using the notations of my former paper

$$\alpha = \alpha \frac{\Delta}{c^2}.$$

If the true orbit is a circle, then the equation (1) becomes:

$$u = u_0 \cos \frac{2\pi}{T} (t - t_0) \dots \dots \dots (1)$$

If  $\alpha$  is very small we find for the equation (2) the following approximate expression

<sup>1)</sup> Astronomische Kriterien für die Unabhängigkeit der Fortpflanzungsgeschwindigkeit des Lichtes von der Bewegung der Lichtquelle, Astr. Nachr. 4670 (195, 265).

<sup>2)</sup> Zur Frage der Konstanz der Lichtgeschwindigkeit, Physik. Zeitsch. 14, 835.

$$u = u_0 \cos \left[ \frac{2\pi}{T} (\tau - \tau_0) + \kappa \frac{2\pi}{T} \frac{u_0 \Delta}{c^3} \cos \frac{2\pi}{T} (\tau - \tau_0) \right], \quad (2)$$

where naturally  $u, u_0, c, \Delta, \tau$  and  $T$  must all be expressed in the same units (km. and sec.) The observed velocities will thus show a spurious excentricity, of the amount

$$e = \kappa \frac{\pi}{T} \frac{u_0 \Delta}{c^2}.$$

This unites with the true excentricity and cannot be separated from it by observations.

Now it is easy to derive an upper limit for  $\kappa$ . Take a well known star like  $\beta$  Aurigae. The observations give

$$p = 0''.014 \quad e = 0.005 \quad u_0 = 110 \quad T = 3.96 \text{ days.}$$

As the largest values which are still compatible with the observations we can take

$$p < 0''.05, \quad \text{or} \quad \Delta > 65 \text{ lightyears,}$$

$$e < 0.015.$$

$$\text{We find then} \quad \kappa < 0.002.$$

Quite possibly other stars will give still smaller values of  $\kappa$ . The smallest values, of course, are found from the stars having the smallest parallaxes. Unfortunately the parallax of most spectroscopic doubles is still unknown, and it is thus impossible to give numerical values. We can however assume as certain that for the majority of these stars a value would be found which is still smaller than that given above.

*Postscript.* During the discussions at the meeting the remark was made (by Prof. KORTWEG) that the star  $\beta$  Aurigae might have a true excentricity of such amount as exactly to cancel the spurious excentricity produced by the motion. This is, of course, entirely correct. If this true excentricity<sup>1)</sup> were  $e = 0.90$  we should find  $\kappa = 0.12$ , [taking again  $p = 0''.05$  and using the same approximate formula as above, though this is not correct for such large excentricities]. Thus if we knew only this one star, we should have to adopt as upper limit for  $\kappa$  this value 0.12. There are however a considerable number of stars with large values of  $u_0$ , whose observed excentricity is very small or zero. Several of these certainly have very small parallaxes. It would evidently be absurd to assume that all of these possessed exactly that true excentricity and position of the periastron which would cancel the apparent excentricity for an observer on our earth.

<sup>1)</sup> For  $\beta$  Aurigae a large excentricity is particularly improbable on account of the presumably large dimensions of both components as compared with their mutual distance.

**Microbiology.** — "*Oxidation of manganocarbonate by microbes*".

By Prof. Dr. M. W. BEIJERINCK.

In experiments on nitrification, manganocarbonate being used as indicator of oxidation, it was found that the nitrifying microbes themselves could not attack this substance, but that other organisms possess this power in a high degree.

When two pieces of filter paper, with a little manganocarbonate between them and moistened with a dilute solution of ammoniumchloride and kaliumfosfate, are infected with garden soil and kept at about 25° C., dark brown or black spots of a manganicompound will appear upon them after some days.

The reactions characteristic of the thus produced manganicompound, are the sudden decomposition of hydrogenperoxide and the oxidation of hydroiodic acid under secretion of iodium, which reactions are not caused by the manganocarbonate itself.

In the microscopic field the newly formed manganicompound is sometimes precipitated as a detritus, in other cases in the shape of black sferites, no doubt chiefly consisting of  $Mn_2O_3$  or  $MnO_2$ .

When examining the related microbes, bacteria and various species of mould were recognised as cause of this oxidation.

The best way to obtain these organisms in a form fit for further experiments, proved to be the sowing of the material, developed on the filter paper, on plates obtained by dissolving agar in water to which, likewise as to the filter paper, had been added, besides c.a. 1% manganocarbonate, 0,05% kaliumfosfate and 0.05% ammoniumchloride or as much nitrate. With an equable distribution of the carbonate such plates are as white as paper. When cultivating thereon the oxidising microbes, the bacteria form a deep brown granulous deposit, partly at the glass wall, whilst the mould species produce large black spots, whereby in the agar black sferites are formed, which will sometimes grow out to  $\frac{3}{10}$  millimeter diameter and are then visible to the naked eye.

As to the bacteria, the manganicompound mostly remains dif-fusedly precipitated in the extensive colonies, without producing distinct sferites.

It is true that in these brown spots, which after some weeks attain one or two cm. in diameter, small grains are found, but these prove to consist of clumps of bacteria, enclosed in a brown or black envelope or film of manganioxides. The capsulated bacteria have the shape of very thin, short rodlets; the loose ones, occurring in the same spots, that of micrococci.

With much trouble I obtained pure cultures of these bacteria on agarplates containing 0.05% to 0.1% manganolactate, whereon appear extremely small, capsulated colonies, which, after being crushed, prove to consist of very delicate, quickly moving rodlets, whilst the brown wall of the capsula again gives the usual manganireactions.

Agar alone proved to be the best food for these bacteria. The said rate of manganolactate could be assimilated, but on media, richer in organic food no development was observed. If, however, organic substances are quite absent the bacteria cannot oxidise the manganolactate. Although to my opinion, they are closely related to the nitrate ferment, they are not able to convert nitrites into nitrates, nor can they oxidise ammonium salts to nitrites.

By their motility they are distinguished from the genus *Siderocapsa*<sup>1)</sup> described by MOLISCH.

The mould species which oxidise manganocarbonate to manganioxides, and which can likewise be easily grown on filterpaper plates from garden soil, grow, like the manganese bacteria, also very well on agarplates containing nothing but manganocarbonate and some mineral salts. On pure agar, without manganocarbonate, they also develop, but less quickly, so that the carbonate evidently serves as food, and not only as a catalyser.

On plates of broth or malt extraction they likewise grow very well, but more slowly than ordinary moulds, and they quite lose thereupon their characteristic properties.

They can, however, also be cultivated on various other media where they produce much mycelium and sometimes fructify, but only oxidise the added manganocarbonate in the presence of a very slight concentration of the dissolved organic nutrient substances.

These moulds belong to very different groups of the Fungi, but all seem to be real inhabitants of the soil. So I have found species of the genera *Botrytis*, *Sporocybe*, *Trichocladium*, and in particular of *Mycogone*, which I knew already as common moulds of fertile garden soil. As might be expected, new forms also appeared, among which a new species of *Mycogone* with tetrahedrally arranged brown spores, common in the garden of the Laboratory for Microbiology.

Somewhat more minutely I examined a *Papulospora*, which I will call *P. manganica*, and a *Sporocybe* to which, for its common occurrence on the filterpaper, the name of *S. chartoikoon* is given.

<sup>1)</sup> Die Eisenbakterien, S 10, Jena 1910.

Our *Papulospora* is very much like *P. sepedonioides* PREUSS,<sup>1)</sup> but differs in some respects from the description given of it by SACCARDO.<sup>2)</sup> The very fine mycelium remains in the substrate and produces only extremely short hyphae bearing small spore-heads, which do not grow out of the surface of the medium and under the microscope easily divide into the oblong spores. When these spores are cultivated in dilute broth they form a fine, branched, multi-cellular mycelium, which produces isolated spores on shorter or longer hyphae, and this is quite in accordance with the description in the literature of the genus *Monosporium*.

When sown on agarmanganocarbonate plates, at 25 to 30° C. the spores produce, after few days already a very delicate, strongly branched mycelium, soon followed by brown-colouring of the surroundings. Shortly after spherites appear in the brown field, first brown, but later jetblack. If cultivating on agar with about  $\frac{1}{10}$  ‰ manganolactate, the spherites come later and are at first colourless, but finally they also grow black. Besides as spherites, the manganic compound is also deposited as a brownish black precipitate at the mycelial threads. The fact that the spherites may be colourless, proves that they must contain something else than manganioxides only, and cautious dissolving in hydrochloric acid of the black substance always leaves a spherical substrate wherein the manganese is precipitated.

Hence, the spherites remind very strongly of the calcosferites of shells and egg-shells, described by HARTING<sup>3)</sup> in 1872, and also of the spherites of calcium-carbonate, artificially precipitated in gelatin or albumin, all consisting of an organic substance, in which calcium-carbonate or calciumfosfate, or both, are deposited. HARTING thinks that this substance, in case the spherites form in gelatin, chemically differs from the gelatin itself and calls it "calcoglobuline". Evidently a similar conception may be applied to the manganese spherites of *Papulospora* found in agar. The formation of spherites in the agar can continue for months successively, so that evidently the mould does not produce noxious substances. It is then observed that the

<sup>1)</sup> ENGLER's Pflanzenfamilien, Bd. 1, Abt. 1 S. 428, Fig. 221 D.

<sup>2)</sup> SACCARDO, Sylloge fungorum, Bd. 4, Pag. 59, 1885.

<sup>3)</sup> Recherches de morphologie synthétique (Acad. Royale des sciences Néerland.), Amsterdam, v. D. Post 1872. Very beautiful spherites of ironfosfate may be obtained by allowing ferroammoniumsulfate to diffuse against sodiumfosfate. They likewise consist of a spherical substrate in which the ferrisalt is deposited. The late Prof. VAN 'T HOFF, who long ago examined these spherites for me, came to the conclusion that the ironfosfate occurs in it as ultramicroscopic crystal needles or trichites, belonging to the monoclinic system, radiating from the centre and arranged in layers.

deposition is periodical. At first I thought that in this periodicity light is concerned, but the formation of rings also occurs in the dark, so that they seem to be of the same nature as the rings of LIESEGANG, which, for example, are formed when silvernitrate diffuses in plates of chromate gelatin, wherein the silverchromate precipitates in rings, separated by rings without silverchromate.

As to the way in which the manganocompound originates from the manganocarbonate, it appears that this may take place as well within as without the mycelium. That this can indeed occur in the cells or at least in the cell-walls, is shown by the great accumulation in the wall, and this is quite in accordance with the character of nutrient substance of the carbonate, referred to above. The increase of the sferites, however, takes place in a way suggesting the idea that also to a fairly great distance from the mycelium an oxidising-agent is spread, able to transmit the oxygen of the air to the carbonate. I infer this from the fact that the formation of sferites often occurs in the midst of manganocarbonate plates, which remain snow-white in the vicinity, and I suppose that if the blackish brown oxide originated from the rather far distant mycelium, the way between should be coloured brown by a solution of that oxide. It must, however, be noted that such a brown-colouring of the white culture medium is observed in other cases, as with *Sporocybe chartoikoon*, and furthermore that I have not been able to oxidise manganocarbonate by means of oxidase and peroxidase of different origin, of which we should first of all think as causing the said distance-reaction. That peroxidase could not be concerned was to be expected, as for its action hydrogenperoxide must be present, which directly reduces the manganocompound. But that this oxidation could neither be enacted by oxidase was not to be foreseen.

In this relation I wish moreover to remark that the manganocarbonate is kept by me as a diluted pap in stoppered bottles under water, in order always to have it ready for experiments. It then remains white for years without any precaution, whilst likewise my manganocarbonate agarplates continue unchanged for months, nay, even for more than a year, at free accession of air. Hence the statement met with in some manuals for chemistry, that this substance oxidises already at the air, requires a nearer explanation of the circumstances accompanying this change, for example strong drying over a BUNSEN flame, or presence of alkaline vapours.

To the organic substances that can oxidise manganocarbonate, chinon belongs. Formation of sferites I have not observed, and there is not the least reason to accept that the described moulds

and bacteria would produce this compound, easily recognisable by its colour. So, if later it should be proved that the manganese moulds really produce a substance causing oxidation out of the cells, it may now already be asserted that it can neither be oxidase nor chinon.

From the preceding we see that with the oxidation of manganocarbonate by microbes, many questions are related, worth a nearer examination, especially with regard to the conversions which these very common microbes cause in the soil.

**Physics.** — “*On the law of partition of energy.*” IV. By Prof. J. D. VAN DER WAALS JR. (Communicated by Prof. J. D. VAN DER WAALS.)

§ 12. In my previous communications on this subject I started from the earlier formula of PLANCK, in which no zero-point energy was assumed. In fact the assumption of zero-point energy involves great difficulties. In my opinion the supposition that a vibrator vibrating with slighter energy than  $\nu h$  would not emit energy<sup>1)</sup> is not so much responsible for these difficulties — something similar would already be found in a charge, which moved in a perfectly conducting inclosure — but rather the assumption that radiation coming from the outside yet acts on the electron in a normal way, and sets it vibrating.<sup>2)</sup>

In spite of these difficulties PLANCK's later formula for the energy of a vibrator has of late been preferred by different physicists. The quantitative grounds adduced for this, seem to be still pretty un-

<sup>1)</sup> Strictly speaking it might be said that PLANCK's vibrators in a certain sense do radiate, also when they contain less energy than a quantum. For they absorb energy, and absorption is a kind of emission. If e.g. we imagine a source of light and a black screen and investigate the light behind the screen by means of electro-magnetic potentials, we find darkness there, only because the contributions to those potentials, yielded by the electrons of the screen, just cancel the contributions furnished by the electrons of the source of light. If the electrons of the screen did not emit potentials and forces derived from them, we should have to observe the direct light of the source behind the screen. So PLANCK's supposition does not really come to this that vibrators when they do not possess exactly a whole number of quanta, do not radiate, but that they radiate in a particular way unilaterally.

<sup>2)</sup> It is remarkable that it is assumed here that the elementary process of absorption is not reversible, whereas by the cooperation of many suchlike processes reversible observable phenomena do originate.

certain as yet. Thus EHRENFEST<sup>1)</sup> could account for the course of the specific heat of hydrogen without assuming zero-point energy, whereas EINSTEIN and STERN<sup>2)</sup> derived from this course a proof for the existence of zero-point energy.

I will now draw attention to a phenomenon, which, so far as I know, has never been considered in the light of a possible existence of a zero-point energy<sup>3)</sup>, and for which it seems very difficult to account even qualitatively without the assumption of zero-point energy. This phenomenon is the radio-activity. A radio-active atom, namely, which has continued to exist unchanged for a long time, suddenly explodes. So something must have been modified, either in the atom itself, or in its surroundings. If no zero-point energy is assumed, no movement would be present in the atom which follows from the value of the specific heat. Accordingly nothing would change there. With thermal equilibrium, however, the changes in the surroundings are determined by the thermal motion; they seem, therefore, unable to explain the appearance of radio-active phenomena, as they are independent of the temperature. Thus no circumstance governed by chance is found on which the setting in of a radio-active explosion of an atom could depend.

Matters are different if it is assumed that several particles vibrating with a high frequency are present in the atom. On account of the high frequency they will possess no thermal energy, but only their zero-point energy. So this energy can manifest itself neither by radiation, nor by a contribution to the specific heat. If it is now assumed that the different particles have different frequencies, and that they exhibit different amplitudes (varying from 0 to  $\nu h$ ) and phases in different atoms of the same kind, a circumstance is given in their motion, which renders the setting in by chance of a definite unstable configuration of the particles of the atom possible, and thus leads to a radio-active explosion. Then the energy of the radio-active rays and of the generation of heat might be found from the zero-point energy. A change in potential energy might also contribute to this, but so far as we know this might be as well positive as negative, and the supposition would naturally suggest itself that the

<sup>1)</sup> P. EHRENFEST, Verh. d. D. phys. Ges. 1913, S. 451.

<sup>2)</sup> EINSTEIN and STERN. Ann. d. Physik IV, 40, 551, 1913.

<sup>3)</sup> Note added in the English translation, when I was correcting the proofs. As Dr. KEESOM was so kind as to point out to me, I was mistaken when I thought that this interpretation of the radio-active phenomena had not been given before. It was already given by PLANCK himself. Vorlesungen über Wärmestrahlung, 2<sup>nd</sup> ed. p. 140.

potential energy of the formed products is greater than that of the atoms before the decomposition, so that this increase of potential energy too would have to be accounted for by the zero-point energy.

Such a supposition of particles moving with great velocity in the radio-active atom has been made already before. But considered without connection with the zero-point energy it seemed too arbitrary, and HAHN and MEITNER's and VON BAYER's experiments, which showed that the  $\beta$ -rays of a certain radio-active atom are homogeneous, seemed to point to a definite loss of potential energy of the emitted particles, which was found back in the form of kinetic energy<sup>1)</sup>. This homogeneity of the rays, however, might now be explained in a different way, viz. by assuming that a particle that vibrates with a period  $\nu$  in the atom, is also emitted with an energy  $\nu h$ . Then there would be a close correspondence between radio-activity and the light-electric effect. The difference between the two phenomena would only consist in this, that for the latter light falling on the atom from the outside, for the former cooperation of the different intra-atomic motions gave rise to the emission.

According to this supposition the frequency of the internal vibrations for  $\beta$ -rays emitted with a velocity  $v = 0,92 c$ . would have to be estimated at  $\nu = 8,25 \times 10^{19}$ .

SOMMERFELD<sup>2)</sup> calculates  $\lambda = 6 \times 10^{-11}$  for the  $\gamma$ -rays with this velocity of the  $\beta$ -rays, which corresponds to  $\nu = 5 \times 10^{20}$ . Hence the period of the internal vibrations according to this supposition would have to be somewhat greater than corresponds with the wavelength of the corresponding  $\gamma$ -rays. At any rate the value which we find in this way for the frequency is so great that even at the highest temperatures attainable we are very far from the point at which, according to PLANCK's formula, we could expect any perceptible change in the energy of the motions, so that the otherwise so unaccountable fact that not the slightest influence of the temperature is found on the radio-active phenomena is very satisfactorily interpreted.

Perhaps little weight should be attached to such not quantitatively testable considerations. I myself also doubt whether they supply a sufficient ground to justify us in adopting a zero-point energy in spite of the difficulties which attend it. Yet I have thought I ought to point out the advantages which it offers.

<sup>1)</sup> It is perhaps also possible to retain this view, and only add to it the assumption that, in order to be able to be emitted, a particle must beforehand have been brought by the zero-point motion in such a position of maximum potential energy that it is shot out from there with that definite energy.

<sup>2)</sup> SOMMERFELD. *Congres Solvay, 1911*, p. 342.

Physics. — “On the system *hexane-water*.” By Dr. F. E. C. SCHEFFER.  
(Communicated by Prof. J. D. VAN DER WAALS).

1. In the 17<sup>th</sup> contribution<sup>1)</sup> to the theory of binary mixtures Prof. VAN DER WAALS has demonstrated that the phenomena which occur when the concentration of the vapour phase with three-phase pressure lies between that of the two coexisting liquid phases, may be derived from the course of the plaitpoint curve already drawn in fig. 43 of the 14<sup>th</sup> contribution<sup>2)</sup>. In this  $T-x$  projection the plaitpoint line exhibits two minima and one maximum; the minimum  $P_{ab}$  and the maximum  $P_{cd}$  are heterogeneous double plaitpoints, hence they lie in the covered region, and correspond to cusps in the  $P-T$  projection. The other minimum indicated in fig. 43 by  $Q_2$ , is a homogeneous double plaitpoint, and may occur both in the stable and in the covered region. Further two points are found on the plaitpoint curve which indicate the highest, resp. the lowest temperature at which three-phase equilibrium can occur. These two points, the critical endpoints, which indicate stable states, must lie on the branches  $AP_{cd}$ , resp.  $BP_{ab}$  in fig. 43.

Whereas the different situation of the lower critical endpoint on the branch  $BP_{ab}$  does not bring about an essential modification in the phenomena, three possibilities present themselves with regard to the situation of the higher critical endpoint, which give rise to the distinction of three different cases; the endpoint of the three-phase pressure can namely either lie on the leftside (Type 1), or on the rightside (Type 3) of the minimum on the plaitpoint line, or it can just coincide with it (Type 2). The last case, to which fig. 43 corresponds, may be considered as the transition between the two preceding ones.

We have an example of type 3 in the system ether-water.

For the peculiarities which present themselves for this system I may refer to my publication in these Proceedings<sup>3)</sup> and to Prof. VAN DER WAALS' 21<sup>th</sup> contribution<sup>4)</sup>.

The chance of the occurrence of type 2 seems naturally very slight; yet it is very well possible that further investigation will make us acquainted with a system for which the distance between the minimum of the plaitpoint line and the endpoint of the three-

1) These Proc. Vol. XIV p. 655.

2) These Proc. Vol. XI p. 816.

3) These Proc. Vol. XV p. 380.

4) These Proc. Vol. XV p. 602.

phase line is so small that it is smaller than the errors of observation. Then we shall be compelled to class such a system with type 2. And that the chance to such a situation may not be so slight as might be supposed at first sight, appears from my investigation of the system ether-water, where two such transitions are found. In this system the distance between the points  $Q_2$  and  $A$  (see fig. 43 of Prof. VAN DER WAALS' 14<sup>th</sup> contribution) is so small that I could not possibly decide whether the minimum of the plaitpoint curve occurs in the figure, lies on the axis, or would be found just outside the figure. Besides, it appeared that in the critical endpoint the slopes in the  $P$ - $T$  projection of the three-phase line and the plaitpoint curve differed so little that practically we have to do with a transition case here too.

Of type 1 no example was known as yet. In the 17<sup>th</sup> contribution Prof. VAN DER WAALS has only shortly alluded to this case, and in fig. 51 he has given a  $P$ - $T$  projection which corresponds with this case; but omitted a full discussion, particularly also because this case is attended with great complications. I have, however, now succeeded in finding an example of this type in the system hexane-water, the particularities of which I wish to describe in the following pages.

2. Without further purification the vapour pressure line was determined with KAHLBAUM's synthetically prepared hexane, and the three-phase line with a great quantity of water (47 mol. %  $H_2O$ ). For the filling of the test-tube, just as for the following investigation, the apparatus was used which I described in my paper on the system ether-water<sup>1)</sup>. The following values were found for the hexane  $t_k = 235,3$ ,  $P_k = 30,1$  atm., for the critical endpoint  $t_k = 222,3$ ,  $P_k = 51,95$ . It appeared from these data that the three-phase pressure lies higher than the vapour tension of the two components (at the same temperature), and that therefore most probably the concentration of the vapour lies between that of the coexisting liquid phases. Whether, however, we had to do here with type 1 or 3, could not be decided from these observations.

Before proceeding to an accurate investigation I purified the hexane in the following way. A fractionation of the hexane yielded a fairly large middle fraction of the boiling point  $68,9^\circ$  (range 0.1);  $t_k = 234,55$ ;  $P_k = 30,1$ . Accordingly only the critical temperature had been appreciably changed by this fractionation.

Then the hexane was heated with reflux by the side of sodium

<sup>1)</sup> These Proc. Vol. XV p. 382, 383 and fig. 1.

for 30 hours, then shaken with a sulphuric acid-nitric acid mixture, washed three times with a solution of potassium hydroxide, four times with water, dried on potassium hydroxide, and then fractionated. Repeated fractionation, the last time on phosphorus pentoxide yielded a large fraction, which distilled over within a range of  $0^{\circ}05$ . Boiling point  $69.0^{\circ}$ . For the hexane purified in this way we found:

$$t_k = \underline{234.6} \quad ; \quad P_k = \underline{30.15}.$$

The range of pressure for isothermal condensation, determined about 10 degrees below the critical temperature, amounted to from 0.1 to 0.2 atmosphere.

By means of this hexane the critical endpoint was determined with a pretty considerable quantity of water. (47 mol. %  $H_2O$ ). This experiment yielded:

$$t_k = \underline{222.05} \quad ; \quad P_k = \underline{52.05}.$$

These values differ but little from those which were obtained with the impure hexane. So the stable part of the plaitpoint curve on the hexane side extends over a range of  $21.9$  atm. and  $12^{\circ}55$ .

3. In order to investigate the mixtures with a great quantity of hexane, I have, starting from pure hexane, prepared mixtures with increasing quantity of water, till I reached the critical endpoint. Of these mixtures I have determined the initial and the final condensations of the hexane layer. I have had to relinquish the thought of a determination of the disappearance or appearance of the waterlayer here as in my investigation of the system ether-water, as a slight quantity of water again becomes invisible here. Besides, we could dispense with these determinations as well now as on the former occasion, as their knowledge is not required for an insight into the phenomena. For if there is no layer rich in water by the side of the vapour and the liquid rich in hexane the pressure deviates from the three-phase pressure; if there is one, the pressure gets on the three-phase line which is equal for all the mixtures, and reversely from the fact that the found pressure deviates or does not deviate from the three-phase line, determined with excess of water, we may conclude whether we have to do with a two-phase or with a three-phase equilibrium. Besides, in the observation of one or more points of the three-phase curve, which was possible for almost all the mixtures if only the temperature be low enough, I had a criterion of the purity of the mixtures. The observations of these three-phase pressures have been given in the subjoined table I, and deviate

nowhere appreciably from the three-phase pressure of the mixture with great quantity of water.

In fig. 1 the  $P$ - $T$  projection is given of the vapour pressure lines of the components, that of the hexane by  $AB$ , that of the water by  $CD$ . The critical point  $B$  of the hexane here happens to lie in the immediate neighbourhood of the waterline, so that the volatility of the two components at the critical point of hexane is equally great. The vapour tension line  $CD$  of the water must be thought prolonged towards higher temperature as far as the critical point of water, which according to the latest determinations from the Deutsche Reichsanstalt lies at  $374^\circ$  and  $217.5$  atm.<sup>1)</sup> The three-phase line is indicated by  $EF$ ; hence it lies appreciably higher than the vapour tension lines of both components.

On the plaitpoint line  $BF$  the critical points are given of eight mixtures; in each of these plaitpoints the liquid and the vapour branch of the sections for constant concentration meet. As a rule only a small number of points of the vapour branch have been determined, because at low temperature the volume would have to be more considerably increased than the test-tube allowed. The further continuation of the vapour branches towards lower temperature might be realized by a slighter filling of the test tube, but this would at the same time increase the error in the concentration of the mixtures. The examined mixtures all contain a great excess of hexane; the water-content varies between 0 and 27 mol. percentages, but if one considers that the molecular weight of hexane is almost five times as great as that of water, and that hence the greatest quantity of water only amounted to a little more than seven percentages by weight, and not even so many percentages of volume, because the specific weight of hexane is smaller than water, it appears that if the error in the concentration is to be small, a great filling is required. In this investigation just as in my investigation concerning the system ether-water, a Cailletet tube with widened upper end has rendered excellent services. The mixture that contained the smallest quantity of water (2.3 mol. percent.), contained 3.4 mgr. of water to about 700 mgr. of hexane; when a Cailletet tube of the common shape had been used, the total filling could at most have been a fifth part.

For the mixtures from 5 to 8 (8 inclusive) the phenomenon of the isothermal retrograde condensation could be clearly realized, as in fact will also be clear from fig. 1. In the neighbourhood of the

<sup>1)</sup> LANDOLT BÖRNSTEIN-ROTH, Tables p 447.

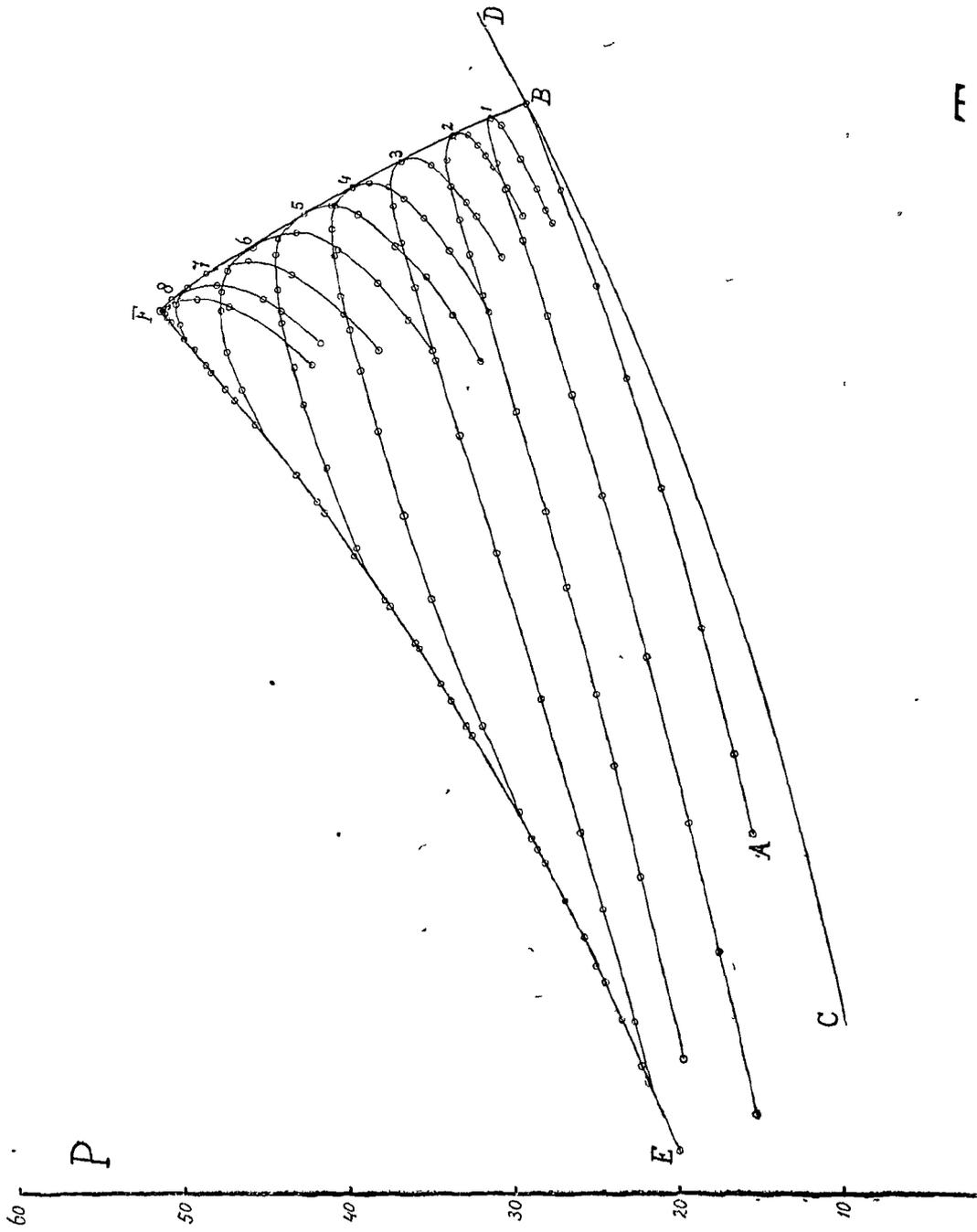


Fig. 1.

critical endpoint the vapour branch of a ninth mixture is found in the  $P$ - $T$ -figure, the water-content of which was somewhat greater than corresponds to the critical endpoint, and the critical point of which accordingly coincides with  $F$ , and no longer lies on the stable vapour branch.

The distance between this concentration and that of the critical endpoint, however, is so small that the vapour branch still terminates on the three-phase line in the immediate neighbourhood of the critical endpoint. With still greater water-content the point of intersection of vapour branch and three-phase line moves to lower temperature, and then the vertical tangent will disappear from the stable part of the vapour branch, and this will put an end to the retrograde phenomenon; I have, however, not continued the investigation of this, as it was perfectly needless for the insight into the phenomena.

I have realized the intersection between the liquid branch and the three-phase line for the mixtures from 3 to 8 inclusive; below these points of intersection these mixtures yield the three-phase pressures which are equal for all concentrations, and hence the criterion of purity which I mentioned in the beginning of this paragraph. I have not prolonged the liquid branches of the mixtures 1 and 2 so far that the above-mentioned intersection takes place, as this intersection takes place outside the temperature range investigated by me.

The investigations which have served for the construction of figure 1, are collected in table 1. The vapour tension line of the hexane, the three-phase line determined by means of a mixture with about 47 mol. percent. of water, besides the observations obtained with the nine above-mentioned mixtures, are found there. In the table the critical data are given in bold type, above them the values of the liquid branch, below them those of the vapour branch are given.

4. I have constructed the  $T$ - $x$  projection of the critical line in fig. 2 by the aid of these data, this projection appears to deviate only very little from a straight line. In the same figure are also given the points of intersection of the liquid branches of the sections for constant concentration of the above-mentioned mixtures with the three-phase line. These points of intersection indicate the states where liquid rich in hexane exists by the side of a very small quantity of vapour and of liquid rich in water, and so the locus of these points of intersection yields a liquid branch of the three-phase region. In the critical endpoint this branch passes with a horizontal tangent

into the vapour branch which extends towards higher water concentrations and is not drawn in the figure. In an analogous way the  $P-x$  projection of the plaitpoint curve and of the liquid branch of

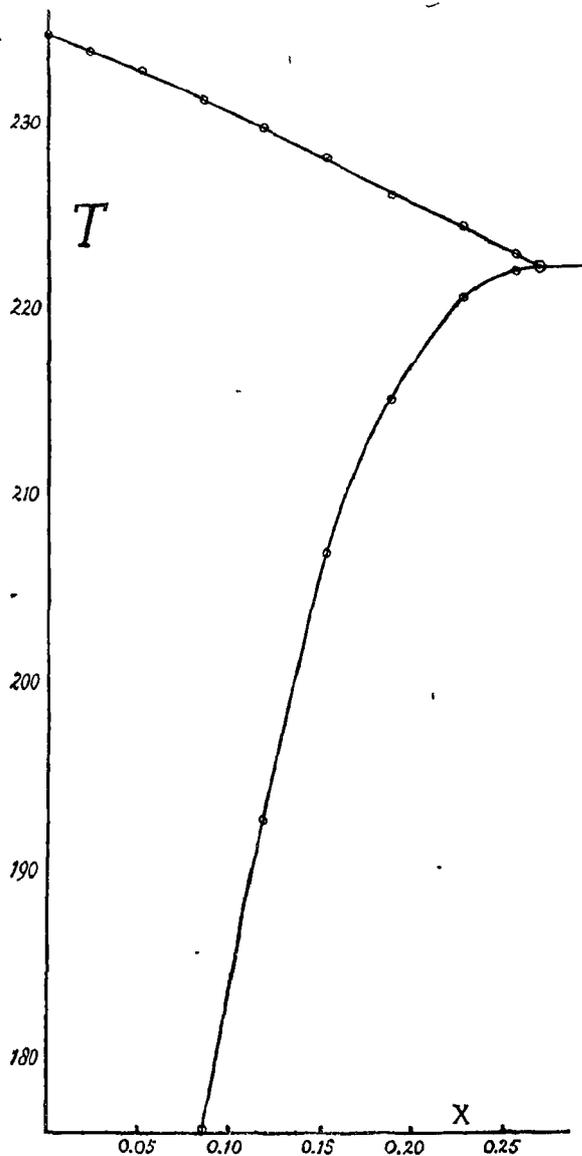


Fig. 2.

the three-phase region is indicated in fig. 3. It appears again that both lines have a perfectly regular course; the projection of the plaitpoint line has a feeble curvature; it is concave seen from below; here too the liquid branch of the three phase equilibria is connected with the not drawn vapour branch by means of a horizontal tangent.

TABLE 1.

Hexane		Three-phase line		(1) $x=0.023$		(2) $x=0.052$		(3) $x=0.086$		(4) $x=0.118$		(5) $x=0.153$		(6) $x=0.189$		(7) $x=0.228$		(8) $x=0.257$		(9) $x=0.277$	
$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$	$t$	$p$
191.2	15.7	177.4	22.3	174.6	15.4	177.8	19.8	172.4	20.0	180.2	23.55	190.85	29.2	182.4	24.6	189.4	28.3	202.4	36.35	187.2	27.1
195.9	16.9	183.3	25.15	184.25	17.7	188.6	22.5	180.0	22.8	185.0	25.9	196.95	32.8	200.0	34.75	216.8	47.4	220.4	50.55	222.2	52.1
203.4	19.0	190.2	28.8	191.8	19.6	195.2	24.2	186.7	24.8	192.45	29.9	202.1	36.0	207.6	40.1	218.85	49.2	221.4	51.35	222.4	51.6
211.75	21.5	199.05	34.2	201.65	22.3	199.4	25.35	191.2	26.2	197.5	32.2	208.1	39.95	210.8	42.4	219.8	49.8	221.65	51.55	222.8	49.7
218.2	23.75	204.6	37.9	211.25	25.2	205.8	27.2	199.1	28.65	205.05	35.4	212.8	41.9	212.4	43.7	221.2	50.8	221.95	51.7	222.35	47.8
223.7	25.65	205.0	38.2	217.2	27.05	210.3	28.55	207.8	31.45	210.0	37.1	216.6	43.3	217.45	47.0	222.45	51.0	222.75	51.3	218.9	42.9
229.4	27.9	210.15	42.0	221.9	28.6	216.2	30.4	214.8	33.8	215.0	38.75	218.75	43.9	219.6	47.9	223.45	50.4	223.6	48.5		
234.6	30.15	215.4	46.2	226.4	30.15	223.1	32.5	219.25	35.3	218.6	39.85	221.35	44.7	222.1	48.3	224.25	49.3	222.8	45.8		
		222.05	52.05	229.4	31.2	225.5	33.3	223.5	36.6	221.0	40.55	223.35	44.95	223.2	48.3	225.1	46.7	222.1	44.7		
				231.0	31.8	227.6	33.95	226.2	37.45	223.05	41.1	225.45	45.1	224.5	47.95	224.35	44.15	220.2	42.3		
				233.65	32.2	229.6	34.45	228.4	37.95	225.4	41.5	226.4	44.95	225.9	46.4	222.0	40.9				
				233.25	31.55	231.15	34.8	231.05	37.5	227.0	41.7	226.95	44.6	226.8	43.9	219.8	38.75				
				231.2	30.4	232.65	34.35	230.85	35.7	228.4	41.5	227.9	43.4	225.8	41.35						
				229.4	29.3	232.6	33.45	228.6	33.55	229.5	40.45	228.4	41.75	223.8	38.95						
				228.2	28.8	232.05	32.9	227.8	32.95	229.8	39.5	227.85	40.1	221.6	37.0						
				227.4	28.35	231.4	32.4	225.4	31.4	229.55	38.3	226.4	37.8	219.8	35.5						
						230.8	31.9			228.8	37.35	224.2	35.95								
						229.5	31.1			227.65	36.05	221.95	34.2								
						227.85	30.15			225.75	34.5	219.2	32.6								
								222.15	32.1												

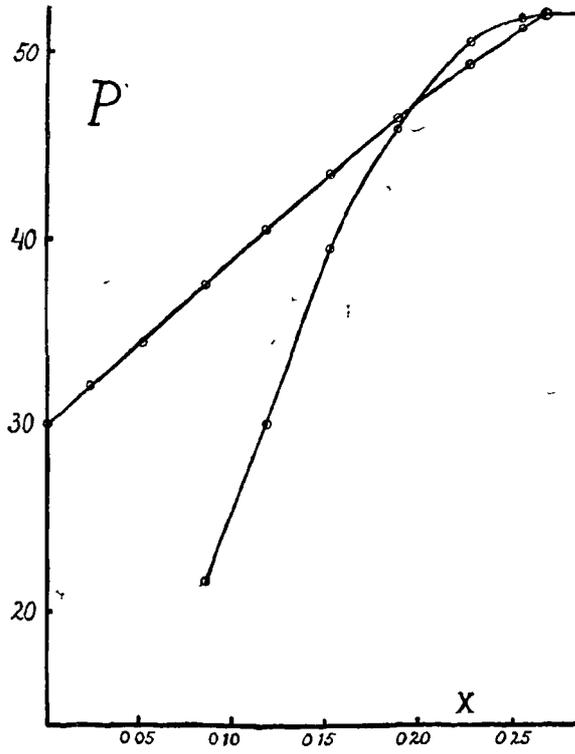


Fig. 3.

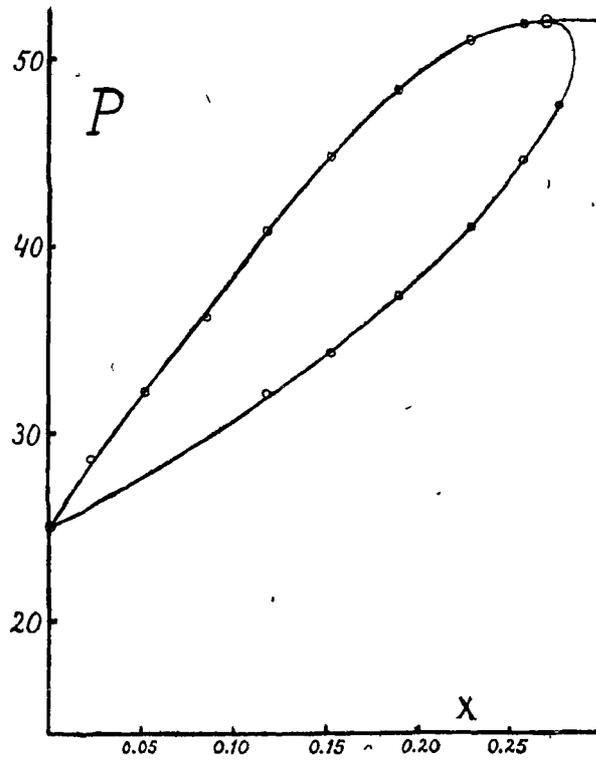


Fig. 4.

The second intersection of these lines occurring in this figure is of course quite incidental, i.e. the point of intersection has no special physical signification.

Finally I have given in fig. 4 the  $P$ - $x$  section for the temperature of the critical endpoint. In this section the initial and the final condensations of the hexane layer are found, the liquid branch is again in connection with the vapour branch in the critical endpoint; the retrograde portion of the vapour branch is only narrow. The above-mentioned ninth mixture has served to determine the point of the vapour branch which lies at higher water concentration than the critical endpoint.

5. When we now review the results yielded by this investigation, it appears that this system really belongs to the type which we denoted by 1 in § 1; in the  $T$ - $x$  projection the critical line, namely, descends, proceeding from the hexane side towards greater water concentration. a minimum temperature is, however, not reached, as the endpoint of the three-phase line appears before that time. Hence the minimum that was to be expected lies in the covered region. It is, however, remarkable that the  $T$ - $x$ -projection does not betray the tendency towards this minimum; if there is question of a curvature, it would sooner have the opposite sign. And an analogous particularity also presents itself in the  $P$ - $T$  projection; the curvature of this projection would theoretically have to be expected so, that the tendency to the reaching of a vertical tangent is expressed; the curvature lies here, however, certainly to the other side. So in connection with the theoretical considerations we should have to conclude here to the existence of a point of inflection in the plaitpoint line in the covered region.

6. When comparing the pressures of the threephase equilibrium with the vapour tensions of the two components, we come to the remarkable conclusion *that the three-phase pressure is higher than the sum of the vapour tensions of the components at the same temperature.* This conclusion appears from table 2, in which the difference between the three-phase pressure and the sum of the vapour pressures for some temperatures are given.

The difference of pressure appears to increase with the temperature, so that it has reached its greatest value of a little more than three atmospheres at the critical endpoint.

These facts seem astonishing at first sight, because one is naturally inclined to consider the vapours of the two components and

T A B L E 2.

Temperature	Three-phase pressure	Hexane-pressure	Water pressure	Difference
195	31.6	16.7	13.8	1.1
200	34.8	18.0	15.3	1.5
210	41.8	20.9	18.8	2.1
220	50.2	24.3	22.9	3.0
222.05	52.05	25.0	23.8	3.25

the three-phase vapour as rarefied gases. If this is the case, it may be derived from the laws of the rarefied gases by a thermodynamic way that the three-phase pressure is necessarily smaller than the sum of the vapour tensions of the two components. For the proof we refer to the second part of the *Thermodynamik* of VAN DER WAALS-KOHNSTAMM (p. 476). The conclusions stated there: "Dem Partialdruck einer Komponente in einer absolut stabilen Phase kann niemals grosser sein als der Sättigungsdruck der reinen Komponente" and "Für alle absolut stabilen Phasen ist also der Partialdruck kleiner als der Sättigungsdruck; auch wenn der Dreiphasendruck höher liegt als die beiden Sättigungsdrucke, wird er also dennoch immer kleiner sein als die Summe dieser beiden Tensionen" refer therefore only to equilibria of real gasphases, i. e. gases, which do not possess an appreciable surface tension. If, however, the gas phases depart from the rarefied gas laws, so if the phases have surface layers, the quantities  $a_1$ ,  $a_2$  and  $a_{12}$  resp.  $b_1$ ,  $b_2$ , and possibly also  $b_{12}$  play a part, and the above-mentioned proof is no longer valid.

7. It appears from the determinations of § 3 that the water-content of the liquids rich in hexane increases pretty considerably on approach to the critical endpoint. Though it was not indispensable for the purpose of this investigation to know the concentration of the liquids rich in water of the three-phase equilibrium, I have yet carried out some experiments with a view of getting to know these concentrations. It then appeared that the quantity of hexane occurring in the liquids rich in water, is particularly small. With a mixture of 0.06 mol. perc. of hexane it was still possible for me to follow the three-phase line throughout the investigated temperature range. The hexane content of the water-layer is therefore decidedly smaller than 0.06 mol. perc.

So in this water layer we meet with a solution in which the hexane occurs in "gas concentration". If we now question what osmotic pressure would occur when we bring this hexane-water layer (in three-phase equilibrium) into contact with pure water by means of a membrane only permeable to water, we can therefore easily calculate this pressure by the aid of VAN 'T HOFF'S laws on the osmotic pressure. In the three-phase layer rich in water less than 0.06 gram-molecule of hexane is found to 100 gram-molecules of water. A hundred gram-molecules of pure water have a volume of  $1,8 \times 1,195$  liters under their own vapour pressure at  $220^\circ$ , as the specific volume of water at this temperature amounts to 1,195. Now the pressure on this water layer at  $220^\circ$  is not the saturated vapour pressure of water (22,9 atm.), but the three-phase pressure (50,2 atm.). So we should have to take the compressibility of water into account at the said temperature. As, however, the water is here still very far from the critical temperature, the compressibility is probably slight here, and roughly we may estimate the volume at  $1,8 \times 1,195$  liters = 2.15 liters. A gram-molecule of hexane, therefore, is found in more than  $\frac{2.15}{0.06}$  liters = 36 liters.

At  $0^\circ$  C. and one atmosphere one gram-molecule of gas occupies a volume of 22,41 liters, so at  $220^\circ$  C. one of  $\frac{273 + 220}{273} 22.41$  l. = 40.5 l. Hence the osmotic pressure of the hexane is smaller than  $\frac{40,5}{36}$  or about 1.1 atmospheres.

So the three-phase mixture with a pressure of 50.2 atm. would be osmotically in equilibrium with water of  $50.2 - 1.1 = 49.1$  atm.

If, therefore, the pressure of the pure water is lower than 49.1 atm., water from the three-phase mixture will pass through the membrane, and so when we bring the three-phase mixture into contact with water under its saturated vapour pressure (22.9 atm.), water passes through the membrane. Hence we should get here unmixing, so splitting up of the hexane-water mixture in the components.

One might surmise a contradiction here to the second law of thermodynamics. For if one considers that hexane and water both under their own vapour pressure, spontaneously mix under formation of the three-phase mixture, and that the three-phase mixture on the other hand cedes water to water under its own vapour pressure through a semi-permeable membrane, one might conclude to a conflict with the second law. But of course this is only seemingly so.

In case of osmotic equilibrium the thermodynamic potential of the water is equal on both sides of the wall. If water under vapour pressure is brought into contact with the three-phase mixture, unmixing will take place as appears from the above calculation; so the thermodynamic potential of the water in the three-phase mixture is greater than the thermodynamic potential of the water under vapour-pressure.

Reversely if in a vessel water by the side of vapour is made to mix with hexane by the side of vapour, we shall have to conclude to a rise of the thermodynamic potential of the water.

In order to examine whether the same thing is also the case for hexane, we must be able to calculate the osmotic pressure of the three-phase mixture with respect to a wall permeable to hexane. This, however, is impossible, as the fluid phase contains about 27 mol. percent. of water at the critical endpoint, and can, therefore, no longer be considered as dilute solution. It is, however, possible to find out something about the value of the osmotic pressure of the binary equilibria in which dilute solutions of water take part. When, for instance, the  $P-x$  section for the critical endpoint (fig. 4) is considered, it appears that a liquid with 2 mol. percent. of water possesses an external pressure of 28 atm., if it coexists with vapour. This solution contains one gram-molecule of water to 49 gram-molecules of hexane. The specific volume of hexane at  $222^\circ$  amounts to 2,69 according to YOUNG. Now at this temperature the hexane is not far from the critical temperature, and we must, accordingly, expect a pretty great compressibility. If the compressibility were zero, the volume of one gram-molecule of water would amount to  $49 \times 86 \times 2,69$  c. c. or about 11,3 l. As now one gram-molecule of gas occupies a volume of 40,6 l. at this temperature under the pressure of one atmosphere, the osmotic pressure of the mixture with respect to a membrane permeable to hexane would amount to about 3,6 atmospheres. The difference in external pressure between the mixture and the pure hexane under the vapour pressure is, however, three atmospheres. So we conclude that in the experiment in which the two-phase mixture (2 mol. % of water in the liquid) is brought into contact with hexane under the vapour-pressure by means of a membrane only permeable to hexane, hexane will pass to the two-phase mixture. The compressibility does not affect this conclusion, as the osmotic pressure is still increased in consequence of the compressibility, and the qualitative result can, therefore, not be modified by it.

If this behaviour continues to exist for greater concentrations, the

three-phase mixture separated by a membrane from pure hexane would absorb hexane, but separated from the pure water it would expel water. So the thermodynamic potential of the water in the three-phase mixture is greater than that of pure water; that of hexane would be smaller than that of pure hexane on the said assumption. If hexane and water is brought together each under its own vapour-pressure, three-phase equilibrium sets naturally in. In this a rise occurs in the thermodynamic potential of the water.

The thermodynamic potential of one component in a binary mixture is indicated by:

$$M_1\mu_1 = Z - x \left( \frac{dZ}{dx} \right)_{pT}$$

If in a pure substance *A* a little of a second substance *B* is dissolved, the thermodynamic potential of *A* is changed by an amount:

$$dM_1\mu_1 = \left( \frac{dZ}{dp} \right)_{xT} dp - x \left( \frac{d^2Z}{dx^2} \right)_{pT} dx - x \left( \frac{d^2Z}{dx dp} \right)_T dp$$

or

$$dM_1\mu_1 = \left( v - x \left( \frac{dv}{dx} \right)_{pT} \right) dp - x \left( \frac{d^2Z}{dx^2} \right)_{pT} dx.$$

For a dilute solution this value becomes:

$$dM_1\mu_1 = v dp - MRT dx.$$

This value is zero for osmotic equilibrium and the osmotic pressure is indicated by:

$$dp_0 = \frac{MRT}{v} dx \dots \dots \dots (1)$$

If now the change of the external pressure is considered when a little of *B* is dissolved in *A* under the vapour-pressure in such a way that the obtained solution is again under its own vapour pressure, then:

$$v_{21} dp = (x_2 - x_1) \left( \frac{d^2Z}{dx_1^2} \right)_{pT} dx_1.$$

Hence the change in external pressure amounts to:

$$dp = \frac{x_2 - x_1}{v_{21}} \left( \frac{d^2Z}{dx_1^2} \right)_{pT} dx_1.$$

For dilute solutions the gas volume  $v_1$  may be substituted for  $v_{21}$ , if the temperature does not lie in the neighbourhood of the critical temperature; hence:

$$dp = \frac{x_2 - x_1}{v_2 x_1} MRT dx_1 \dots \dots \dots (2)$$

If then the expressions (1) and (2), are compared, it appears that the value of  $dp$  can be greater or smaller than  $dp_0$ . For the same solution  $dx$  is namely  $= dx_1$ . Hence if  $\frac{x_2 - x_1}{x_1} > \frac{v_2}{v}$  the change in external pressure will be greater than the osmotic pressure; if  $\frac{x_2 - x_1}{x_1} < \frac{v_2}{v}$  the osmotic pressure will increase more rapidly than the pressure along the liquid binodal. In the first case the thermodynamic potential  $A$  will be greater in the mixture than in the pure state; in the second case it will be smaller. The former is the case for the dilute solutions of hexane in water; the latter for dilute solutions of water in hexane.

The case, therefore, which presents itself on the waterside will evidently in general be found when the liquid branch in the  $P$ - $x$  section rises very rapidly in pressure with increase of  $x$ , i.e. much more rapidly than the corresponding gas binodal. Then the value of  $\frac{x_2 - x_1}{x_1}$  can be greater than the quotient of vapour- and liquid volume. The discussed phenomenon will, accordingly, be met with in several cases. Solutions of gases sparingly soluble in water, e.g. hydrogen, will certainly present the same phenomenon.

*Anorg. Chem. Laboratory of the University of Amsterdam.*

**Physiology.** — “*Variations of state in gelatin-solutions.*” By  
L. ARISZ. (Communicated by Prof. H. ZWAARDEMAKER)

In a previous communication<sup>1)</sup> a number of experiments were discussed from which it appeared that a gelatin-solution undergoes a change by a variation of temperature, in consequence of which the intensity of the TYNDALL-phenomenon assumes another value under for the rest equal conditions. The following formula has been given by Lord RAYLEIGH for the intensity of the TYNDALL-phenomenon:

$$I = f\left(\frac{v^2}{\lambda^4 r^2}\right)$$

$v$  = size of the particles

$r$  = distance of the particles

$\lambda$  = wavelength

As particles to which the dispersion must be attributed the gelatin

<sup>1)</sup> These Proc. XVI p. 331.

particles are chiefly to be considered. It may be derived from the formula that when the size of the particles increases  $n^3$  times (and as the concentration remains equal the distance increases  $n \times$ ) the intensity becomes  $n^4 \times$  greater. I believe that there is, therefore, every reason to assume that a modification in the size of the gelatin-particles is responsible for the investigated phenomenon.<sup>1)</sup>

A number of other variations in the gelatin solutions always take place perfectly continuously, nor is a sudden change of intensity ever observed in the TYNDALL phenomenon at a definite temperature. So there cannot exist a temperature at which the size of the gelatin particles suddenly changes; it must much sooner be assumed that large and small particles always occur side by side, and when in a solution a change of the intensity takes place, this points to a modification in the mutual relation. It is probable that there exists a great number of possible combinations; for simplicity's sake it will be assumed in what follows that the gelatin only occurs in two forms, large ( $L$ ) and small ( $S$ ) particles, so that we may say

$$\frac{L}{L+S} = f(T).$$

I have supplemented my earlier determinations by ascertaining the relation between the temperature and the equilibrium intensity at that temperature for several concentrations. Again a solution containing glycerin was used for this. I did not consider every state which remained constant at a certain temperature, as a true equilibrium. This was only done when it appeared to be the limit which was reached in course of time, both when the initial intensity was greater and when it was smaller. The results are given in fig. 1. For each of the examined concentrations the intensity at 70° has been assumed as unity; so it is only possible to draw conclusions with regard to the way in which the equilibrium intensity varies with the temperature: the figure is not adapted for a comparison of the absolute values for the different concentrations. For so far as the character of the equilibrium line is established, the line is drawn; when this is not the case, it is dotted; the dotted part is left out of consideration here.

If the variation of the intensity only depended on the temperature, the curves for the different concentrations would have to coincide. This is, however, by no means the case: for the  $1/4\%$  solution the line ascends only slowly from right to left throughout the inves-

<sup>1)</sup> See also VON MENZ *Zs. f. Physik. Chem.* **66**. 129. 1908. BACHMANN *Zs Anorg. Chem.* **73**. 1911.

tigated temperature region. For the 1% solution a more rapid rise sets in at  $\pm 30^\circ$ , and the 5% solution exhibits a similar gradual

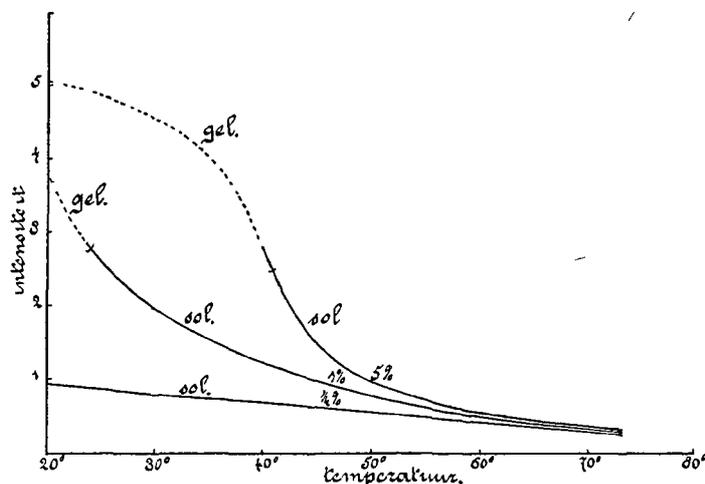


Fig. 1. Variation of the intensity of the TYNDALL-phenomenon with the temperature in a  $\frac{1}{4}\%$ , 1%, and 5% gelatin glycerin solution.

change of direction already at  $\pm 55^\circ$ . It is clear that the change of intensity does not only depend on the temperature, but also on the concentration ( $c$ ) of the solution. And the number of large particles being estimated from the intensity, the formula may be extended to:

$$\frac{L}{L+S} = f(T, c.)$$

It is also indicated in fig. 1 at what temperature the transition from sol into gel will take place. When the decision whether the solution is sol or gel is never given before the system is in equilibrium, it can be accurately determined whether a liquid or a solid state belongs to a temperature. The  $\frac{1}{4}\%$  solution is always a sol in the examined temperature region; the 1% solution is a gel below  $19^\circ$ , the 5% solution below  $40^\circ$ . For every concentration therefore, a limiting value of the number of large particles can be assumed; the solution is a gel if this number is greater than that limiting value, and a sol in the opposite case. This limiting value evidently does not lie where the more pronounced curvature (in fig. 1) begins, but only at a somewhat lower temperature.

The variations of the number of large particles may be estimated, besides by means of the TYNDALL-intensity, also by means of the viscosity. A modification of the latter is namely always attended

with one of the light intensity. It is therefore possible to consider an increase of the viscosity as a proof that large particles are formed, whereas disappearance of large particles will always manifest itself by a decrease of the viscosity.

Hitherto experiments have been discussed, in which the concentration was kept constant. I will now proceed to examine the relation

$$\frac{L}{L+S} = f(T, c.) \text{ for constant temperature.}$$

In contrast with the preceding ones these experiments have all been made with a solution of gelatin in water without any addition. Beforehand the gelatin used was freed from all salts etc. in water, and dried over  $H_2SO_4$  in vacuo.

The simplest case that we meet with is the dilution of a gelatin solution which is a *sol*. We started from a  $\frac{1}{2}\%$  solution, which was made at  $70^\circ$ , and was then kept at  $20^\circ$  for five days. During this time a considerable increase of the viscosity was found, from which it might be inferred that the number of large particles increased. This solution was diluted at the same temperature with an equal amount of water to  $\frac{1}{4}\%$ , and then the change of its viscosity was determined from time to time. It appeared that a decrease took place. This may be represented in the following way. In fig. 2 the viscosity is indicated on the ordinate, and the concentration on the abscissa.  $N-N$  is the equilibrium line, which has been drawn so

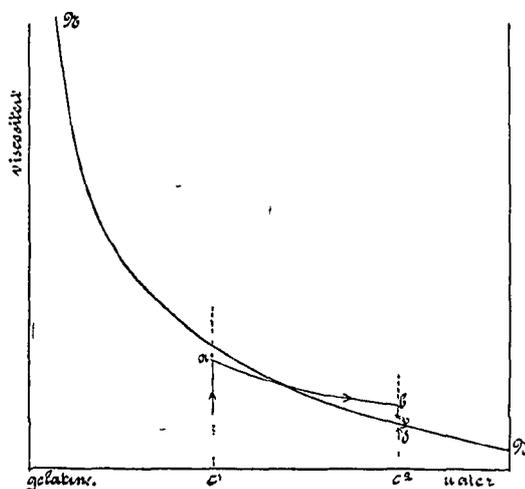


Fig. 2. Influence of the dilution of a gelatin solution on the viscosity.

$N-N$  is the equilibrium line.

the arrows indicate in which direction a change takes place.

that the viscosity increases with increasing gelatin-content. As the variations of the viscosity as a consequence of the heating in the  $\frac{1}{2}\%$  solution had not yet ceased at the moment of the dilution, we must assume that the equilibrium between large and small particles had not yet set in. The state for the conc.  $c_1$  ( $\frac{1}{2}\%$ ) must therefore be represented by a point below the equilibrium line, e.g. *a*. At the moment of the dilution from  $c_1$  to  $c_2$  the number of large particles undergoes only a slight variation, so that for  $c_2$  the state may be represented by *b*. This point lies above the equilibrium line; a gradual diminution of the viscosity is the consequence of this, which does not cease until the state of equilibrium *p* is reached.

That actually an approach to the equilibrium at the given temperature and concentration takes place, may be proved by heating part of the diluted ( $\frac{1}{4}\%$ ) solution at  $70^\circ$  for some minutes, and then reducing it again to  $20^\circ$ . At this high temperature the equilibrium ratio is quickly reached for the  $\frac{1}{4}\%$  solution, so that after the cooling there are fewer large particles than at the equilibrium (represented by *d* in fig. 2); now an increase of the viscosity must be found. It appears from table I that a tendency really exists in both cases to approach the same final value.

TABLE I.  
Variation of the viscosity with the time at  $20^\circ$  in a  $\frac{1}{4}\%$  solution, prepared by dilution of a  $\frac{1}{2}\%$  solution (the viscosity of water at  $20^\circ$  taken as unity).

time	viscosity
0	4.62
after 20 hours	4.21
" 36 "	3.91
" 60 "	3.52

Variation of the viscosity with the time at  $20^\circ$  in the same solution after a heating at  $70^\circ$ .

time	viscosity
0	1.49
after 20 hours	1.81
" 36 "	1.89
" 60 "	1.98

The same thing has also still proved possible when the number of large particles has about the limiting value. At 12° gelatification begins to set in, for the  $\frac{1}{2}\%$  solution after 5 days. After the dilution to  $\frac{1}{4}\%$  the state of mixing was imperfect for a time, which follows from the irregular values of the viscosity determination. The following days these irregularities appeared to vanish, and a marked diminution of the viscosity could be demonstrated. To facilitate a comparison in the subjoined table also the variations have been given which the  $\frac{1}{4}\%$  solution exhibits after a previous heating at 12°.

TABLE II.  
Variation of the viscosity with the time at 12° in a  $\frac{1}{4}\%$  solution, prepared by dilution of a gelatinized  $\frac{1}{2}\%$  solution.

time	viscosity
0	$\pm 12.8$
after 20 hours	$\pm 12.6$
" 36 "	10.8
" 60 "	9.95

Variation of the viscosity with the time at 12° in the same solution after heating at 70°.

time	viscosity
0	1.82
after 20 hours	2.28
" 36 "	2.35
" 60 "	2.42

*It is evident that in these two cases the state of equilibrium is not reached until all the gelatin is uniformly distributed throughout the water and the ratio between large and small particles corresponding to this degree of solution has been established.*

When water is added to a gelatin solution with so many large particles that it is in the *gel*-condition, the changes are more intricate. I will examine them at different temperatures.

If a sheet of (practically) anhydrous gelatin is put in much water of 30°, and this temperature retained, it quickly absorbs water,

remaining at first in the solid state. (*Imbibition*). The rate at which the water is absorbed may be determined by weighing. The first stages of this process have been expressed in fig. 3. The line exhibits a curvature, which points to a decrease of the velocity with which water is absorbed with increasing water-content. When, however, the water-content of the gel has attained a certain limit, a segregation of the solid mass sets in; it separates into flakes which become smaller and smaller till at last a state is reached in which the gelatin is uniformly distributed throughout the water (*Solution*). This whole series of changes must be considered as a penetration of the water between the gelatin particles, which are at first in close contact with each other, which connection, however, is gradually lost. *So by the words imbibition and solution two parts of the same process are indicated.*

When dry gelatin and water are brought together at temperatures above 30°, the same process takes place. At 30°, however, it is more than 24 hours before the final state is reached; at higher temperature the process is much quicker.

Below 30° the velocity with which the water enters the gelatin, is still much smaller. Here too it decreases with increasing water content, but a consequence of this is that a uniform distribution of

TABLE III.

Influence of the temperature on the velocity with which  
100 mg. of gelatin dissolves in water.

Temp.	Duration of the solution
30°	> 24 hours
35°	2½ "
40°	13 minutes
50°	± 2 "
70°	± 2 "

gelatin and water is no longer reached. The lower the temperature, the slighter the velocity with which water is absorbed, and the smaller the water content at which the velocity becomes infinitely small. The permanent state then reached is indicated as *maximum of imbibition*.

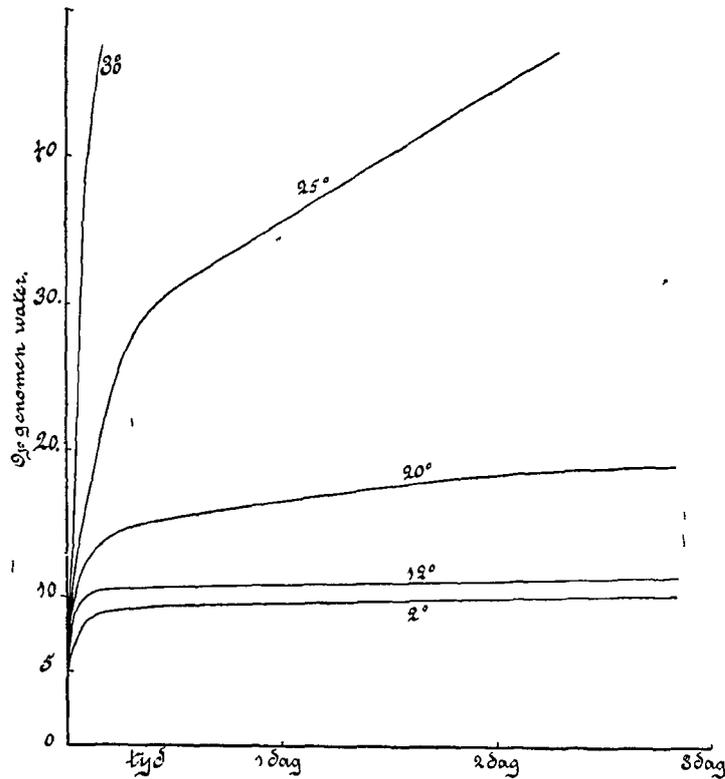


Fig. 3.

Imbibition of dried gelatin in water. The ordinate marks how many grams of water 1 gram of gelatin has absorbed. On the abscissa the time.

TABLE IV.

Influence of the temperature on the velocity with which gelatin imbibes water. Quantity of water which 1 gr. of gelatin has absorbed.

	30°	25°	20°	12°	2°
after 2 hours	36.60 gr.	16.00 gr.	12.13 gr.	9.98 gr.	8.44 gr.
" 7 "	82.90 "	28.60 "	14.81 "	10.51 "	— "
" 20 "	— "	33.73 "	15.70 "	10.65 "	9.69 "
" 44 "	— "	42.80 "	18.22 "	11.01 "	10.00 "
" 68 "	— "	47.52 "	19.64 "	10.98 "	10.09 "

At temperatures below 30° a constant state is reached as well as for temperatures above 30°; there is, however, a great difference between these cases; above 30° the final state is a uniform distri-

bution of gelatin and water, hence a true equilibrium; below 30° this uniform distribution has not yet been reached in the final state: *the maximum of imbibition is an apparent equilibrium.*

Besides, by the above considerations the validity of this thesis is proved by the fact that the maximum of imbibition entirely lacks the characteristics of a true equilibrium. When a sheet of gelatin that has imbibed water, is heated with the water to such a temperature that a uniform distribution of water and gelatin takes place, and then cooled down again to the original temperature, there is no question of a separation into two phases, water and "gelatin of maximum imbibition." To be sure a true equilibrium is not established in the solution then either, but the uniform distribution is retained. Besides it is, however, possible to show that at every temperature by the side of water not only a single "maximum of imbibition" can exist, but an infinite number. Which of them is reached in each special case depends on the state in which the gelatin is brought together with the excess of water.

It has appeared in table 4 that anhydrous gelatin at 12° reaches the final state in water, when a ten-fold weight of water has been absorbed. When a 10% gelatin-gel, prepared by dissolving anhydrous gelatin at 70°, and then cooling it, is brought into an excess of water, the weight remains by no means unchanged. An important quantity of water is absorbed, and with the exception of the first hours, at a rate which exceeds the imbibition of dried gelatin. The determinations have not been carried on till a permanent state set in, but the gradual diminution of the velocity suggests that it must really exist, and then not a 10%, but a 5% gel remains unchanged by the side of water.

It is found in the same way that also a 5% and a 2% gel increases in weight in excess of water.

TABLE V.

Influence of the concentration of the gel on the rate at which it imbibes at 12°. Quantity of water which 1 gr. of gelatin has absorbed.

	anhydrous gel	10% gel	5% gel	2% gel
after 5 hours	— gr.	12.68 gr.	23.85 gr.	66.90 gr.
„ 20 „	10.65 „	16.59 „	28.23 „	94.70 „
„ 44 „	11.01 „	17.95 „	31.62 „	96.00 „
„ 68 „	10.98 „	18.47 „	32.80 „	97.10 „
„ 92 „	— „	18.70 „	33.80 „	— „

The lefthand ends of these curves indicate the quantity of water present in the gelatin gel at the moment that it was brought into contact with an excess of water. It is seen from their course that

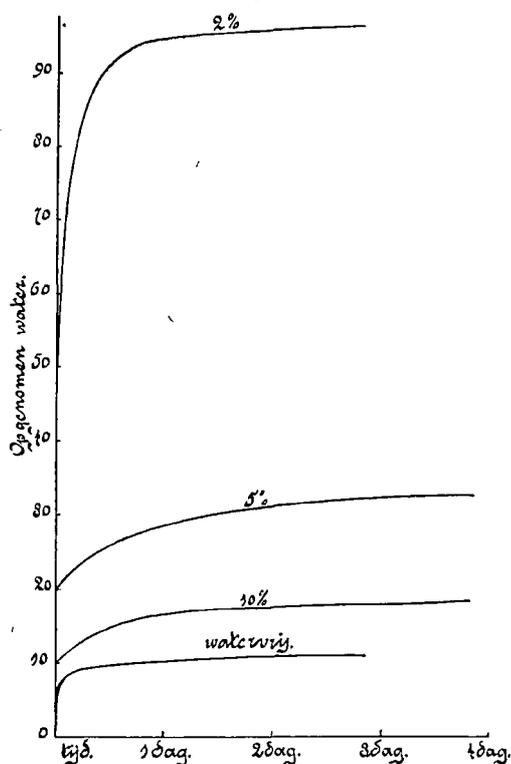


Fig. 4.

Imbibition of gelatin gels of different concentrations. The leftside ends of the curves indicate with how many grams of water 1 gram of gelatin was combined to a gel. On the abscissa the time.

the more water is absorbed and that the rate at which this takes place, increases, as the water-content is already greater at the outset. The different water-content can, however, not be the essential factor, for the same concentration is found at the end of one and at the beginning of another line. The cause must lie in the gelatin.

Diagram fig. 5 enables us to form an idea of all these changes.

The gelatin solution must be considered as a pseudo-ternary system with water, large particles, and small ones as components.

The line  $N-N$  is the equilibrium line. It has been drawn so that in anhydrous state the number of large particles has the greatest value, and in great dilution the smallest value, in this it is assumed that these two kinds of particles are always present side by side.

Whether an approach to the value of equilibrium occurs for constant concentration will depend on the place which the point representing the state, occupies. The part of the figure left of the equilibrium

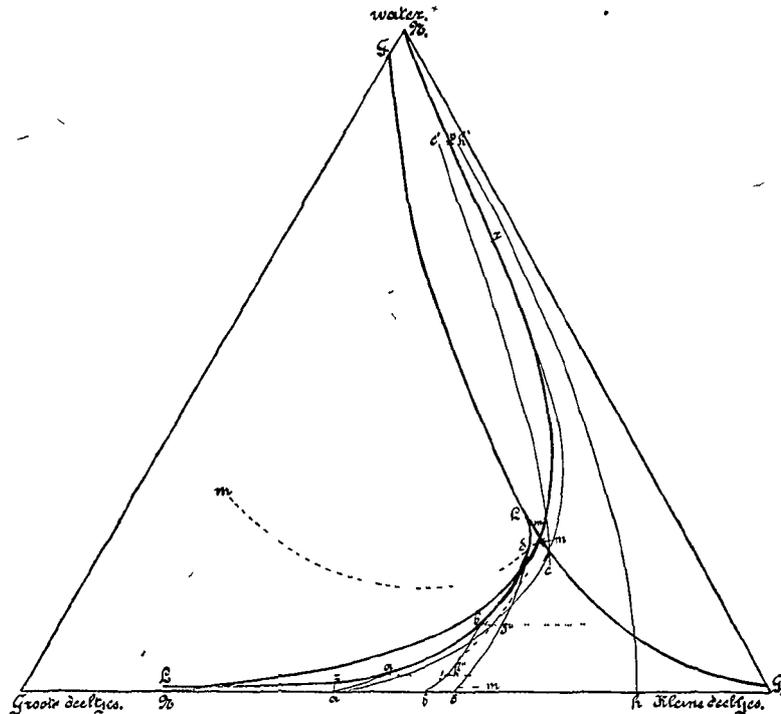


Fig. 5.  $NN$  is the equilibrium line.  
 $GG$  is the sol-gel boundary.  
 $LL$  is the line of the imbibition-maxima.  
 $MM$   $M'M'$  are the boundaries of the region, in which the approach to the equilibrium takes place infinitely slowly.  
 $aa'$ ,  $bb'$  etc. represent the changes which the system undergoes.

line is split up into two parts by  $M-M$ , and likewise a line  $M'-M'$  is given on the right side of the line of equilibrium. If the state lies above  $M-M$  or under  $M'-M'$ , an approach to the equilibrium takes actually place; in the portion of the figure between  $M-M$  and  $M'-M'$  the velocity of the approach is, however, infinitely small, so that every state remains practically constant here. A change of the number of particles in this region can only be the consequence of a change of the concentration. The representation of these two lines rests on the supposition that a change in the number of large particles will be the more difficult as there are already more large particles present, and as the water-content is smaller.

In the second place a line  $G-G$  (sol-gel limit) is indicated. It intersects the equilibrium line in a point where the number of large particles has the above mentioned limiting-values.

It has further been assumed that a solution which consists exclusively of small particles is already a sol with very slight water-content, and one in which exclusively large particles occur, is only a sol in very great dilution. Hence a state denoted by a point on the left side of this line is a gel, and on its right a sol.

Finally there is still a line  $L-L$ , on which the different maxima of imbibition lie. The occurrence of maxima of imbibition though there exists a tendency to a uniform distributed of all the gelatin and water present in the system, leads to the supposition that the gelatin particles exert a force on each other, which opposes the segregation of the parts when water is imbibed. As the maxima of imbibition lie the higher as the imbibing gel contains less gelatin, and a small number of large particles goes together with slight concentration of gelatin, this line has been traced so that only little water is absorbed for a great number of large particles, whereas with decreasing number of large particles the water-content augments. The maximum of imbibition becoming identical to a state of uniform distribution at the limiting value, the line  $L-L$  must gradually approach to the sol-gel limit  $G-G$ , and finally coincide with it. If, the equilibrium being denoted by  $p$ , the state is represented by a point of the line  $L-L$ , e.g.  $a'$ , this means that so much water has been absorbed by the gelatin as the place of  $a'$  indicates, the rest of the water being present in free condition.

If by means of drying, water is extracted from a gelatin solution, whose state is represented by  $p$ , the concentration increases slowly and the number of large particles augments. The change can take place along the line  $p-a$ , which lies wholly on the right of the equilibrium line, so that in anhydrous state a number of large particles exist as indicated by  $a$ .

If this dried gelatin is suddenly brought into contact with so much water that the equilibrium in the system is again represented by  $p$ , there exists in the first place a tendency to absorption of water, and moreover a tendency to a diminution of the number of large particles. As a result of both the change of  $a$  will take place in the direction  $a-a'$ ; it will be a long time before the distance  $a-a'$  is covered; every quantity of absorbed water causes large particles to disappear, and this renders the absorption of more water possible; this goes on till the line of the maxima of imbibition is reached. A further absorption of water would have to take place along the line  $L-L$ ,

when a diminution of the number of large particles to the equilibrium value could take place. As  $a$ , however, lies in the area between  $M-M$  and  $M'-M'$ , this change does not take place, and the reached condition continues to exist.

The same thing takes place when the relation between small and large particles is another than  $a$ , e.g.  $b$  or  $d$ . In these cases the change must take place resp. along  $b-b'$  and  $d-d'$ ; and when consulting the figure, it is easy to see that the more water will be absorbed by the gel as there are fewer large particles present at the beginning. These smaller values are found in aqueous gels. Point  $b''$  can be reached, as was stated in table V and fig. 4, by heating a gelatin solution with the concentration  $a'$ , and allow it to gelatinize again; transformation of small particles into large ones taking place later, at the moment that the condition is represented by  $b''$  the change of concentration can take place, which then proceeds along  $b''-b'$ , till the permanent state  $b'$  has been reached.

As the gelatin solution was already more dilute before the addition of the water, it has a smaller number of large particles immediately after the gelatification. This implies the fact established above that a gel imbibes the more water as it contained the more water beforehand.

If on cooling the limit between sol and gel is about reached, the condition along the line  $e-e'$  changes on addition of water, so that though a uniform distribution is attained, the condition still differs from the equilibrium by a too great number of large particles. This case is the same as was mentioned in table II: in the part of fig. 5 on the right side of the  $G-G$  limit the changes are as described above for dilution of a concentrated sol.

It has already been pointed out that dry gelatin does not "dissolve" in water, but "imbibes", because there are many large particles in this condition. Through a special treatment of a gelatin solution, however, the gelatin may be made anhydrous in such a condition that it consists almost entirely of small particles. This condition may be represented by  $h$  in fig. 5. If so much water is added to gelatin in this condition that the equilibrium of the system is brought to  $p$ , the change must be represented by  $h-h'$ , and a perfectly homogeneous state of uniform distribution of gelatin and water must also occur at  $12^\circ$ .

The separation between gelatin and water must not be effected in this case by drying, but by freezing. When a dilute gelatin solution ( $1/4\%$ ) of  $\pm 70^\circ$  is suddenly reduced to a temperature below the freezing-point, the gelatin very quickly gets into the temperature

region where a change practically no longer takes place. During the ice-formation all the water is extracted from it without a possibility of large particles being formed. By subsequently raising the temperature above the freezing-point this anhydrous gelatin is brought in contact with excess of water, on which immediately a condition of perfect homogeneity sets in; not only is the solution perfectly transparent, but there is not a single, local irregularity to be seen, and it flows so regularly through a viscosimeter as can only be expected from perfectly homogeneous liquids.

If during the freezing many large particles are formed, the possibility of a perfectly regular distribution after the thawing is excluded. The absorption of water by the gelatin follows the type of imbibition. We then have as it were an infinite number of small gel-particles, which retain their individuality. A more or less turbid, opaque mass is obtained, which does not get clear again without heating.

In conclusion a remark on the signification of the quantity of water, with which the gelatin is brought together. For the imbibition it is practically immaterial whether so much water is added that the condition of equilibrium becomes  $p$  or  $r$ . If, however, the quantity of water is very slight, things are different. If for the anhydrous gelatin the condition  $a$  (fig. 5) is assumed, so great a tendency to diminution of the number of large particles will not exist in this case that the change is represented by  $a - a'$ , but a line will be followed along which the number of large particles changes but slightly:  $a - z$ . The change may of course go so far until the line of the maxima of imbibition  $L - L$  is reached, and no further; and as appears from the figure it is reached here at a slighter water-content than when the change was represented by  $a - a'$ . Absorption of only a very small quantity of water takes place when the dry gelatin is brought in contact with water-vapour. Imbibition in water-vapour and in water cannot lead to the same result.

*Here the paradoxal phenomenon described by VON SCHROEDER will be recognized that gelatin which has had a maximum imbibition in vapour, absorbs a great deal of water more when it is subsequently immersed into liquid water, which he thought in conflict with the second law of thermodynamics. Led by the given considerations it is possible to form a conception of the influences that come into play here.*

**Physics.** — “*Magnetic researches. IX. The deviations from CURIE’S law in connection with the zero-point energy*”. By É. OOSTERHUIS. Supplement N<sup>o</sup>. 31 to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 28, 1913).

§ 1. CURIE <sup>1)</sup> found that for a number of paramagnetic substances the susceptibility is inversely proportional to the absolute temperature. Later measurements have shown, however, that with many substances considerable deviations from CURIE’S law occur. They were first disclosed about simultaneously by an investigation of HONDA <sup>2)</sup> (afterwards continued by OWEN <sup>3)</sup>) who showed that the majority of paramagnetic elements does not obey CURIE’S law and by an investigation of liquid and solid oxygen by KAMERLINGH ONNES and PERRIER <sup>4)</sup>, which proved that a substance which follows the law at higher temperatures, may begin to deviate from it at lower temperatures. Liquid oxygen showed an increasing deviation with falling temperature approximately in accordance with the relation  $\chi = CT^{-\frac{1}{2}}$  ( $\chi$ : susceptibility per gramme,  $T$ : absolute temperature); with solid oxygen at hydrogen temperatures the susceptibility deviated even more and seemed to approach a constant value. The investigation at low temperatures which promised to give an insight into the nature of paramagnetism <sup>5)</sup> was continued by KAMERLINGH ONNES and PERRIER <sup>6)</sup> with several other substances. By the results obtained they were led to the conception that for all paramagnetic substances or at least for one class of them the deviations from CURIE’S law are governed by a law of corresponding states, the corresponding temperature for each substance to be taken proportional to a certain temperature characteristic of that substance. The data obtained later on by KAMERLINGH ONNES and the author <sup>7)</sup> may serve to confirm this view, as will be shown in § 7.

The majority of the substances investigated in the cryogenic laboratory at Leiden may be reduced to the following three types :

<sup>1)</sup> P. CURIE. Ann. chim. phys. (7). 5, p. 289; 1895.

<sup>2)</sup> K. HONDA. Ann. d. Phys. 32. p. 1027. 1910.

<sup>3)</sup> M. OWEN. Ann. d. Phys. 37. p. 657. 1912.

<sup>4)</sup> H. KAMERLINGH ONNES and A. PERRIER. Comm. N<sup>o</sup>. 116 (April 1910).

<sup>5)</sup> Comp. H. KAMERLINGH ONNES, Comm. Suppl. N<sup>o</sup>. 21b.

<sup>6)</sup> H. KAMERLINGH ONNES and A. PERRIER. Comm. Nos 123a, 124a.

<sup>7)</sup> H. KAMERLINGH ONNES and E. OOSTERHUIS. Comm. Nos. 129b, 132e, 134d.

a. For some substances (crystallized ferrous-sulphate, crystallized manganese sulphate etc.) the relation  $\chi T = \text{constant}$  was found to hold as far down as the temperature of liquid nitrogen, but at hydrogen temperatures  $\chi T$  was always found smaller than would follow from CURIE's law.

b. With other substances (e g. anhydrous manganese sulphate) the product  $\chi T$  began to diminish at once when the temperature was lowered below room-temperature; in that case the relation  $\chi(T + \Delta) = \text{constant}$  appeared to hold for the range between ordinary temperature and nitrogen-temperatures; in liquid hydrogen, however, further deviations became apparent.

c. With platinum the susceptibility was found to change very little with temperature and in the range between liquid nitrogen and liquid hydrogen to be almost independent of the temperature, entirely in accordance with the results of HONDA and OWEN who found the product  $\chi T$  for platinum (and for many other elements) to diminish continually with falling temperature.

§ 2. LANGEVIN<sup>1)</sup> in his kinetic theory of paramagnetism has given a theoretical deduction of CURIE's law. He finds, that the susceptibility is inversely proportional to the kinetic energy of rotation of the molecules. When this energy is taken proportional to the absolute temperature, this gives  $\chi$  proportional to  $\frac{1}{T}$  or  $\chi T = \text{constant}$ , i. e. CURIE's law.

§ 3. It seems natural to try an explanation of the deviations from CURIE's law by dropping the assumption that the rotational energy  $U$  of the molecules is proportional to the absolute temperature and adopting a different temperature relation for  $U$ <sup>2)</sup>.

In a different connection EINSTEIN and STERN<sup>3)</sup> were led to the assumption that the rotational energy of a molecule with two degrees of freedom is equal to

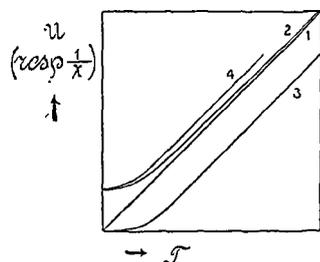
$$\frac{h\nu}{e^{kT} - 1} + \frac{1}{2} h\nu \dots \dots \dots (1)$$

<sup>1)</sup> P. LANGEVIN, Ann. chim. phys. (8) 5, p. 70; 1905.

<sup>2)</sup> KAMERLINGH ONNES and PERRIER ascribed the deviations from the law to the electrons freezing to the atoms, in consequence of PLANCK's vibrators coming to rest. In that case, if the rotational velocities remain proportional to  $\sqrt{T}$ , the susceptibility approaches a constant value. In this paper a theory is developed in which the elementary magnets themselves remain unchanged.

<sup>3)</sup> A. EINSTEIN and O. STERN, Ann. d. Phys. 40, p. 551; 1913.

( $\nu$  = frequency of the rotational movement,  $h$  and  $k$  the constants in PLANCK'S radiation-formula). The connection between  $U$  and



assuming  $\nu$  independent of the temperature, is then approximately as indicated by curve 2 in the figure. The straight line 1 gives the relation according to original assumption:  $U = kT$ .

The form (1) gives for  $T = 0$  a value of  $U$  differing from 0, viz.  $= \frac{1}{2} h\nu$

the zero-point energy is left out, the term  $\frac{1}{2} h\nu$  in (1) disappears and the dependence of  $U$  on  $T$  is represented by curve 3.

If we may assume that the proportionality of the susceptibility  $\frac{1}{U}$  holds (§ 2) and, therefore, that  $\frac{1}{\chi}$  is proportional to  $U$ <sup>1)</sup>,  $\frac{1}{\chi}$  show the same law of dependence on temperature as  $U$ , and it will be possible by measurements of the susceptibility of paramagnetic substances at different temperatures to obtain an insight into changes of the rotational energy of the molecules for these substances.

§ 4. Starting from this assumption it can be concluded also from the measurements of the susceptibility, that a curve as given by 3 is unable to represent the changes in  $\frac{1}{\chi}$  or  $U$ . In fact all observations at low temperatures which give deviations from CURIE'S law always show that the product  $\chi T$  has smaller values at low temperatures than at higher, whereas according to curve 3 the product  $\chi T$  would continually increase towards lower temperature. The assumption of a zero-point energy (curve 2 and also 4, see below) on the other hand leads to deviations from CURIE'S law in the same sense as found experimentally. According to a remark in the paper by EINSTEIN and STERN quoted above WEISS had arrived at a similar view and had inferred the existence of a zero-point energy from CURIE'S measurements of the susceptibility of gaseous oxygen. According to curves 2 and 4  $\frac{1}{\chi}$  and  $\chi$  ought to approach a constant finite value at low temperatures; this is actually the case

<sup>1)</sup> In this case also  $U$  is the rotational energy for two degrees of freedom, is, therefore, given by the expression (1), because the dependence of the susceptibility on the temperature is determined solely by the rotation about axes at right angles to the magnetic axis of the molecule; for the sake of simplicity the moment of inertia — and therefore  $\nu$  — is taken equal for those axes.

platinum, and the other substances which have been investigated in liquid hydrogen show a similar tendency. There is therefore every reason for the assumption of the temperature-function (1) with the inclusion of a zero-point energy.

§ 5. It was further tried for a number of substances, whether the dependence of the susceptibility on the temperature is in quantitative agreement with the above hypothesis. In the calculations the frequency  $\nu$  which occurs in the formula for  $U$  was not taken independent of the temperature ( $\nu$  independent of  $T$  gives the curve 2 but following EINSTEIN and STERN it was assumed that

$$\nu^2 = 2\nu_0 \frac{U}{h} \dots \dots \dots (2)$$

The change of  $U$  (or  $\frac{1}{\chi}$ ) with  $T$  according to the relations (1) and (2) is represented by curve 4;  $\nu_0$  is the value which  $\nu$  assumes at very low temperatures: it is related to the moment of inertia  $I$  of the molecule by the formula

$$\nu_0 = \frac{h}{4\pi^2 I} \dots \dots \dots (3)^1$$

In the first place it may now be observed that for temperatures, which are not too low, the relation between  $U$  and  $T$  expressed by (1) and (2) leads to the empirical relation  $\chi(T + \Delta) = \text{const.}$ , which was deduced from the observations (comp. § 1). This is seen by developing (1) in a series and neglecting the terms beyond the third which is certainly allowed for high values of  $T$ ; this gives

$$U = h\nu \left( \frac{1}{h\nu} - \frac{1}{2} + \frac{1}{12} \frac{h\nu}{kT} \right) + \frac{1}{2} h\nu$$

$$U = kT + \frac{1}{12} \frac{h^2 \nu^2}{kT}$$

When we substitute:  $\nu^2 = 2\nu_0 \frac{U}{h}$  in this, we find

$$U = kT + \frac{1}{6} \frac{h\nu_0}{kT} U$$

<sup>1)</sup> The relations (2) and (3) are at once arrived at when it is remembered that  $U = \frac{1}{2} I(2\pi\nu)^2$ . For  $T=0$  this gives:  $\frac{1}{2} h\nu_0 = \frac{1}{2} I(2\pi\nu_0)^2$  or  $\nu_0 = \frac{h}{4\pi^2 I}$ .

When this is introduced into  $U = \frac{1}{2} I(2\pi\nu)^2$  the result is (2).

$$U = \frac{kT}{1 - \frac{1}{6} \frac{h\nu_0}{kT}} = kT \left( 1 + \frac{1}{6} \frac{h\nu_0}{kT} \right) = k \left( T + \frac{1}{6} \frac{h\nu_0}{k} \right) = k(T + \Delta).$$

As further by hypothesis  $\frac{1}{\chi}$  is proportional to  $U$ , the following relation is obtained

$\frac{1}{\chi} = C(T + \Delta)$  or  $\chi(T + \Delta) = C$ , which is the relation found empirically e.g. for anhydrous manganese sulphate above nitrogen temperatures. That for other substances, like crystallized manganese sulphate above nitrogen temperatures, CURIE'S law was found approximately fulfilled, is obviously due to a small value of  $\Delta$ , or of  $\frac{h\nu_0}{k}$ .

By means of formulae (1) and (2) the value of  $\frac{U}{kT}$  was calculated for a series of values of  $\frac{kT}{h\nu_0}$ ; if the underlying suppositions are correct,  $\frac{1}{\chi T}$  must have the same relationship to  $T$  for a paramagnetic substance as  $\frac{U}{kT}$  to  $\frac{kT}{h\nu_0}$ . The comparison of the two functions is made by means of logarithmic diagrams<sup>1)</sup>; in the one diagram the abscissae were  $\log \frac{kT}{h\nu_0}$  and the ordinates  $\log \frac{U}{kT}$ , in the other  $\log T$  and  $\log \frac{1}{\chi T}$  respectively. For nearly all the substances examined the curves could be made to coincide with sufficient approximation. The shift along the axis of abscissae required to produce coincidence gives the value of  $\frac{h\nu_0}{k}$  for the substance under consideration.

Subjoined in the two tables are the results obtained for two of the substances. At the head of the table is found the value of  $\frac{h\nu_0}{k}$  which has to be assumed for the particular substance to bring about the closest coincidence of the two curves. The first column gives the absolute temperature  $T$ , the second the observed values of  $\chi$ . Starting from any one of the observed values, the values for the other temperatures may be calculated by means of (1) and (2). The fourth

<sup>1)</sup> Comp. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm Suppl N<sup>o</sup>. 23, § 33.

column gives the calculated values of  $\chi$ , the fifth the percentual differences between the values observed and calculated. Finally in the third column are given the values of the product  $\chi T$  in order to show the magnitude of the deviations from CURIE'S law.<sup>1)</sup>

T A B L E I.				
Crystallised manganese sulphate. <sup>1)</sup>				
Mn SO <sub>4</sub> · 4 H <sub>2</sub> O				
$\frac{h\nu_0}{k} = 6.6$				
$T$	$\chi_{\text{obs.}} \cdot 10^6$	$\chi_{\text{obs.}} \cdot T \cdot 10^6$	$\chi_{\text{calc.}} \cdot 10^6$	$100 \frac{\chi_{\text{obs.}} - \chi_{\text{calc.}}}{\chi_{\text{obs.}}}$
288.7 K.	66.3	19140	66.3	—
169.6	111.5	18910	112.6	— 0.9
77.4	247	19120	245	+ 0.8
70.5	270	19030	268	+ 0.7
64.9	292	18950	291	+ 0.4
20.1	914	18370	904	+ 1.1
17.8	1021	18170	1015	+ 0.6
14.4	1233	17760	1231	+ 0.2

T A B L E II.				
Anhydrous manganese sulphate. <sup>2)</sup>				
Mn SO <sub>4</sub>				
$\frac{h\nu_0}{k} = 83$				
$T$	$\chi_{\text{obs.}} \cdot 10^6$	$\chi_{\text{obs.}} \cdot T \cdot 10^6$	$\chi_{\text{calc.}} \cdot 10^6$	$100 \frac{\chi_{\text{obs.}} - \chi_{\text{calc.}}}{\chi_{\text{obs.}}}$
293.9 K.	87.8	25800	86.3	+ 1.7
169.6	144.2	24460	145.4	— 0.8
77.4	274.8	21270	284.0	— 3.3
64.9	314.5	20410	325.7	— 3.5
20.1	603	12120	603	—
17.8	627	11160	619	+ 1.3
14.4	636	9158	628	+ 1.3

<sup>1)</sup> Comm. No. 132e.

<sup>2)</sup> Comm. No. 132e.

Crystallized manganese sulphate does not show distinct deviations from CURIE'S law till hydrogen temperatures are reached and therefore belongs to class *a* of § 1, the anhydrous salt on the other hand shows deviations over the whole range (class *b*). For both substances the agreement between observed and calculated values appears satisfactory, although the differences seem somewhat larger than the experimental errors. In the same manner we found:

$$\text{for crystallized ferrous sulphate: } \frac{h\nu_0}{k} = 10$$

$$\text{for crystallized manganese chloride: } \frac{h\nu_0}{k} = 13.$$

For a substance like platinum the deviations from CURIE'S law are enormous and the value of  $\frac{h\nu_0}{k}$  must be correspondingly large. The measurements with platinum made at Leiden (Comm. N<sup>o</sup>. 132e) give  $\frac{h\nu_0}{k}$  about equal to 1500, those by HONDA (above normal temperature) give a still higher value.

§ 6. The above shows that substances which deviate strongly from CURIE'S law give large values of  $\frac{h\nu_0}{k}$ . This result is in itself evident, considering that substances with a high value of  $\frac{h\nu_0}{k}$  must also have a large zero-point energy ( $\frac{1}{2}h\nu_0$ ), so that  $U$  (or  $\frac{1}{\chi}$ ) will be far from proportional to  $T$  at low temperatures.

According to (3)  $\nu_0$  is inversely proportional to the moment of inertia of the molecule. It may therefore be expected that substances with large moment of inertia (i.e. small  $\nu_0$ ) will show small deviations from CURIE'S law and vice-versâ. This is in general well confirmed by the results. A substance like gadolinium-sulphate  $\text{Gd}_2(\text{SO}_4)_3 \cdot 8 \text{H}_2\text{O}$  (comp. Comm. N<sup>o</sup>. 122a) with very heavy molecules, each moreover loaded with 8 molecules of water of crystallization, shows hardly any deviation from CURIE'S law even in liquid hydrogen. Anhydrous manganese sulphate deviates strongly even at the ordinary temperature; with the crystallized salt, each molecule of which carries 4 water molecules and must therefore have a large moment of inertia, distinct deviations from the law only appear at hydrogen temperatures. Platinum which deviates very strongly would have molecules with very small moment of inertia.

The possibility of the water of crystallization acting through the increase of the moment of inertia which it produces was previously expressed by KAMERLINGH ONNES and PERRIER. They worked on the view that the deviations were due to the PLANCK-vibrators coming to rest and that their frequency would be smaller for the molecule of crystallized gadolinium-sulphate than for the unloaded molecule.

By comparing anhydrous and crystallized manganese sulphate an estimate may be formed of the distance between the centre of the water-molecules and of the sulphate molecule. The moments of inertia of  $\text{MnSO}_4$  and of  $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$  are found equal to  $8.7 \times 10^{-41}$ , and  $109.7 \times 10^{-41}$ . On the supposition that two of the water-molecules are placed along a line at right angles to the axis of rotation and the other two on the axis, the difference of the two above numbers gives for the distance in question the value  $4.4 \times 10^{-9}$ . This distance is of the order of the molecular dimensions, but smaller than the adopted value for the radius of a hydrogen molecule ( $1 \times 10^{-8}$ ): our result would thus seem to indicate that the water-molecules partly penetrate into the molecule to which they are attached.

§ 7. At the suggestion of Dr. KEESOM — to whom I am indebted for several useful hints — I have also compared the observations with a different formula which takes into account the possibility of more than one frequency of rotation, whereas EINSTEIN and STERN assumed that at a definite temperature all the molecules rotate with the same velocity. On Dr. KEESOM's theory the molecular rotational motions in the body under consideration are analysed into a number of stationary waves, which may be supposed to be governed by similar partial differential equations as, say, sound waves in a gas with corresponding conditions at the boundary (crests may take the place of nodes). Along these lines he was led to the hypothesis, that equation (4) of Suppl. N<sup>o</sup>. 30a (May 1913) with the additional assumption  $\nu_m = U\frac{1}{2}$  (as in equations (5) and (7) l. c.) might also hold for the rotational motions. I have found that the correspondence between observation and calculation by the new formula is not appreciably better than by the method followed above and I have therefore in this paper confined myself to the calculation according to the EINSTEIN-STERN view i. e. assuming one value of  $\nu$  at each temperature.

§ 8. *Summary.* The existence of a zero-point energy has recently been made probable by various investigations.

1. The change of the specific heat of hydrogen at low temperatures

has been explained by EINSTEIN and STERN in a satisfactory manner by the assumption of a zero-point energy.

2. The assumption of a zero-point energy for the translational motion of gas-molecules appears to be also required <sup>1)</sup>.

3. KEESOM <sup>2)</sup> has shown that the quanta-theory with the additional assumption of a zero-point energy is of great importance in the theory of free electrons in metals and removes a number of difficulties inherent in the equipartition-theory.

4. In conclusion it is shown in this paper, that the assumption of a zero-point energy for the rotations finds a strong support in the observations on the susceptibility of paramagnetic substances; it appears that by means of it the majority of the deviations from CURIE'S law observed at low temperatures <sup>3)</sup>, which seem to be reducible to three seemingly largely different types may be correlated <sup>4)</sup> and quantitatively explained in a satisfactory manner.

**Physics.** — "*The vapour pressures of hydrogen from the boiling point down to near the triple-point.*" By Prof. H. KAMERLINGH ONNES and Dr. W. H. KEESOM. Communication N<sup>o</sup>. 137*d* (*On the measurement of very low temperatures. XXIII*) from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of June 28, 1913).

§ 1. The vapour pressures of hydrogen between the boiling point and the triple-point have been determined by DEWAR <sup>5)</sup> and by TRAVERS and JAQUEROD <sup>6)</sup>. The value, which was obtained at

<sup>1)</sup> Communication to the Wolfskehl-Congress at Göttingen by H. KAMERLINGH ONNES and W. H. KEESOM. Comp. also W. H. KEESOM. Comm. Suppl. N<sup>o</sup>. 30*a*.

<sup>2)</sup> W. H. KEESOM. Comm. Suppl. N<sup>o</sup>. 30*b*.

<sup>3)</sup> The abnormal behaviour of anhydrous ferrous sulphate which has a maximum in its susceptibility is here left out of account.

<sup>4)</sup> The theory given in this paper confirms the supposition by KAMERLINGH ONNES and PERRIER mentioned in § 1, that as regards paramagnetism corresponding temperatures exist, which must be taken proportional to a definite temperature, characteristic of each substance; on the above theory the temperature of maximum-susceptibility chosen by the authors for the purpose is to be replaced by the "internal" temperature  $\frac{1}{2} \frac{h\nu_0}{k}$ , which may be calculated from the zero-point energy.

<sup>5)</sup> J. DEWAR. Proc. Roy. Soc. London, A. 76 (1905), p. 336.

<sup>6)</sup> M. W. TRAVERS and A. JAQUEROD. Phil. Trans. (A) 200 (1902), p. 155.

Leiden for the heat of vaporization of hydrogen at the boiling point<sup>1)</sup>, differed, however, appreciably from the values which follow with the aid of the CLAPEYRON-CLAUSIUS formula from the measurements of the vapour pressures mentioned above, taking into account the compressibility of hydrogen vapour according to the measurements of KAMERLINGH ONNES and W. J. DE HAAS<sup>2)</sup>. A deviation between the AVOGADRO scale of temperatures fixed by the aid of the gas thermometer, and the KELVIN scale of temperatures<sup>3)</sup> of such an amount as would be indicated by the difference between these results may be considered improbable<sup>4)</sup>. It seemed therefore of interest to undertake a new determination of the vapour pressures of hydrogen in the region mentioned.

§ 2. The measurements were made with the aid of a vapour pressure apparatus as described by KAMERLINGH ONNES and BRAAK in Comm. No 107*a* (May 1908) Pl. I apparatus A.

The temperatures were measured<sup>5)</sup> with the aid of the platinum resistance thermometer<sup>6)</sup>  $P_{t_f}$ . We could avail ourselves of a more recent comparison (May 1913) of  $P_{t_f}$  with the hydrogen thermometer performed at 6 points, regularly distributed over the range from the boiling point to near the triple-point, by KAMERLINGH ONNES and HOLST in their research concerning the comparison of the scales of the hydrogen and the helium thermometers. The corrections<sup>7)</sup> to

1) For a preliminary report see: W. H. KEESOM, *Handelingen 13de Nat. en Geneesk. Congr.* 1911, p. 181. According to a later calibration of the ampère- and voltmeter, which were used, with the aid of a water calorimeter the values given there are to be diminished by an amount of 2<sup>0</sup>/<sub>100</sub>. Hence the value found with the smallest velocity of vaporization for the heat of vaporization of hydrogen at the boiling point (more accurately at an average pressure of 751,5 mm) becomes 110,2 cal<sub>15</sub>. The vapour pressures according to DEWAR lead to the value 106, whereas those according to TRAVERS and JAQUEROD give a still smaller value.

2) H. KAMERLINGH ONNES and W. J. DE HAAS. *Comm.* N<sup>o</sup>. 127*c* (May 1912).

3) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. *Math. Enz.* V 10, Leiden. *Comm. Suppl.* N<sup>o</sup>. 23, § 82*a*.

4) This view is supported by the fact, that KEESOM, *Suppl.* N<sup>o</sup>. 30*a* § 4, has found that the application of the quantum-theory with the introduction of the zero-point energy to the molecular translatory motion for a gas at such a density that the dimensions and the mutual attraction of the molecules need not to be considered, leads to an appreciable divergence from the equation  $p = RT/v$  at extremely low temperatures only.

5) We gladly record our cordial thanks to Mr. G. HOLST for the aid afforded to us by performing these temperature measurements.

6) The bath was kept constant within 1/300 of a degree.

7) The corrections given here differ somewhat from those given in the Dutch edition of this paper, in accordance with the results of the research of KAMERLINGH ONNES and HOLST mentioned in the text.

the KELVIN scale for this hydrogen thermometer ( $p_{000} = 120$  c.m.) (+ 0.14 down to  $-253^\circ$ , + 0.15 for  $-254^\circ$  and  $-255^\circ$ , + 0.16 for  $-256^\circ$ , + 0.17 for  $-257^\circ$ , + 0.18 for  $-258^\circ$ , + 0.20 for  $-259^\circ$ ) were deduced down to  $-257^\circ$  from the corrections of the scale of the international hydrogen thermometer found for this region by KAMERLINGH ONNES and W. J. DE HAAS, Comm. No. 127c (June 1912), those for the lower temperatures were calculated according to the research of KAMERLINGH ONNES and HOLST mentioned above.

75.95 cm. of mercury was adopted as the international atmosphere<sup>1)</sup> at Leiden.

§ 3. The results are given in the following table.<sup>2)</sup>

Vapour pressures of hydrogen.						
$\theta$ KELVIN degrees	$p$ internat. cm. of mercury	$p_{\text{calc.}}$	$p_{\text{obs.}} - p_{\text{calc.}}$	$\theta_{\text{obs.}} - \theta_{\text{calc.}}$	pressure of the bath	
-252.63	78.91	79.01 <sup>5</sup>	- 0.10 <sup>5</sup>	0.00	78.34	much liquid
[252.66	77.97	78.33	- 36	- 2]	78.15	" "
253.76	56.07	56.02	+ 5	0	55.62	" "
255.12	35.17	35.10	+ 7	+ 0 <sup>5</sup>	35.26*	" "
255.17	34.53 <sup>5</sup>	34.46	+ 7 <sup>5</sup>	+ 0 <sup>5</sup>	34.18	" "
256.08	24.16	24.20	- 4	0	24.00*	" "
256.08	24.19	24.20	- 1	0	24.47 <sup>5</sup> *	little "
256.09	23.99	24.11	- 12	- 1	23.77	much "
257.19	14.97	14.95	+ 2	0		" "
258.31	8.60	8.60	0	0	8.53	" "

The difference 0.03 cm. between the values of the pressure found at  $-256^\circ.08$  with much and with little liquid corresponds to a difference in temperature of 0.003 of a degree and lies within the limits of accuracy; moreover it is in a direction opposite to that

<sup>1)</sup> Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. No. 23 Einheiten  $\alpha$ .

<sup>2)</sup> The numbers given in this table, and those derived from it further on in this paper differ slightly from those given in the Dutch edition in accordance with the slightly altered values of the corrections to the KELVIN scale (cf. 441 p. note 7) and an improved calculation of the temperatures.

which would follow from the supposition of an increase of pressure at condensation; hence there is no evidence of an influence of admixtures.

The pressure in the cryostat has also been given in the table (column 6). The manometer, on which this pressure was read, was connected to a side tube of the cover of the cryostat; this cover had at this place the same width as the cryostat glass. At the pressures marked with an \* the tube, which formed the connection with the manometer, was continued within the cryostat by a glass tube which reached down into the liquid<sup>1)</sup>. By this means we obtained the result that the vapour pressure was measured at a liquid surface where no continued vaporization (and hence cooling of the upper layers) takes place. The influence of this can be clearly seen: in the observations without \* for all but one<sup>2)</sup> the pressure of the bath was found smaller than that in the vapour pressure apparatus, for the observations with \* just the reverse is the case. On the average in these latter observations the difference is moreover smaller. The temperature difference which corresponds to the largest pressure differences is 0.03 degrees. If for the measurement of the temperature in liquid hydrogen one is satisfied with this degree of accuracy, it is sufficient for the purpose to measure the pressure in the cryostat in the way indicated.

As the triple-point could not be properly observed in the vapour pressure apparatus, for determining the triple-point temperature the temperature of the bath was read when the first crystals became visible in the latter. The indication of  $P_{t_f}$  then became constant; 1.415  $\Omega$  was read. Extrapolation (over 0.8 degree) of the calibration curve of  $P_{t_f}$  gives for the triple-point temperature — 259° 14 C. in KELVIN degrees = 13° 95 K. The pressure of the bath was 5.07 cm. at this point.

§ 4. The curve which represents  $\log p$  as a function of  $\frac{1}{T}$  is slightly concave upwards.<sup>3)</sup> In the 3<sup>rd</sup> column the values are given of  $p$

<sup>1)</sup> In order to have a better guarantee that the pressure which is read belongs to the temperature of a definite place in the liquid, this tube might be surrounded by a heat conducting tube reaching above the liquid surface, as in the vapour pressure apparatus (cf. N<sup>o</sup>. 107a, Pl. I).

<sup>2)</sup> For this one, placed between [ ], the experimental data indicate that in the vapour pressure apparatus temperature equilibrium probably was not yet arrived at. [Added in the translation].

<sup>3)</sup> The measurements of TRAVERS and JAQUEROD give a  $\log p$ ,  $T^{-1}$ -curve which is slightly *convex* upwards. The following table gives some numbers which

calculated from a WREDE-RANKINE-KEESOM formula<sup>1) 2)</sup>:

$$\log p = 4.6063 - \frac{58.40}{T} + \frac{61}{T^2} \quad (1)$$

The 4<sup>th</sup> column gives the differences of the observed values and the values calculated from (1), the 5<sup>th</sup> column the corresponding differences in temperature.

From (1) follows for the boiling point: 20.33°K. = -252.76°C.<sup>3)</sup>

Extrapolation by (1) would give 5.41 cm. for the pressure corresponding to the triple-point temperature found in § 3 (with extrapolation of the calibration curve of  $P_{t_j}$ ). The double extrapolation makes this value somewhat uncertain; it can in the mean time be regarded as a confirmation of the value found by KAMERLINGH ONNES and BRAAK<sup>4)</sup>.

§ 5. The heat of vaporization of hydrogen at a pressure of 75,15 cm. calculated according to CLAPEYRON-CLAUSIUS from (1), if for calculating  $v_{vap}$  the value  $B_{A(71)}$  is taken from KAMERLINGH ONNES and W. J. DE HAAS, Comm. N<sup>o</sup>. 127c, with  $v_{liq}$  after KAMERLINGH ONNES and CROMMELIN, Comm. N<sup>o</sup>. 137a, becomes:

$$\lambda = 105.5 \text{ cal}_{16}.$$

enable a comparison with the data given by TRAVERS and JAQUEROD.

$p$ internat. cm. of mercury	$T$ KELVIN-scale (K.O. and K)	$T^*$ KELVIN-scale (T. and J.)
76	20.33	20.33
35	17.96	17.90
10	15.07	15.07

\*) Temperatures measured with a hydrogen thermometer, corrected by us to the KELVIN scale with corrections derived from the numbers given in § 2. [Added in the translation].

1) Cf. H. KAMERLINGH ONNES and W. H. KEESOM. Math. Enz. V 10, Leiden Comm. Suppl. N<sup>o</sup>. 23, § 83 g.

2) Cf. 442 p. note 2.

3) This number coincides with that derived from the measurements of TRAVERS and JAQUEROD, cf. note 1. [Added in the translation].

4) H. KAMERLINGH ONNES and C. BRAAK. Comm. N<sup>o</sup>. 95e (Oct. 1906). According to (1) to the pressure 5,38 cm. found there a temperature of 13° 94 K. corresponds.

This 'value<sup>1)</sup> is smaller than that found by direct measurement at the smallest velocity of vaporization<sup>2)</sup>: 110.2. It is possible that this result indicates that the precautions taken to prevent condensation of the vaporized hydrogen within the calorimeter have not been sufficient. In fact at a velocity of vaporization twice as great as that at which the value mentioned above was found smaller values were obtained, *viz.* 108.5 and 109.3 at 76.1 and 77.75 cm. pressure respectively.

**Physics.** — "*Vapour pressures at very low reduced temperatures.*

II. *The vapour pressure of carbon dioxide in the range from — 140° C. to about 160° C.*" By SOPHUS WEBER. Communication No. 137c from the Physical Laboratory at Leiden. (Communicated by Prof. KAMERLINGH ONNES).

(Communicated in the meeting of September 27, 1913).

§ 1. In these measurements the heated-wire manometer described before was used<sup>3)</sup>; it was calibrated by the aid of a set of pipettes as shown in fig. 1. The manometer is sealed to the vessel  $P_2$  at  $J$  and is placed, together with  $P_1$  and  $P_2$  in a waterbath, in which a temperature of about 20° C. is maintained by means of a thermostat. This temperature is read on a mercury thermometer. The electric connections are the same as in fig. 4 of the first paper. In order to keep back mercury vapour or other vapours which might originate in  $P_2$  the tube  $I$  the volume of which is only 1% of the whole volume was placed in alcohol cooled to about — 100° C. by the aid of liquid air. In a high vacuum the vapours given off by the grease of the stopcocks will be condensed in  $I$ . I have tried to prevent this flow of vapour to  $I$  while retaining the taps by interposing at

<sup>1)</sup> It may be noticed that this value nearly coincides with that calculated from the vapour pressure measurements of DEWAR (cf p. 441 note 1). The difference which shows the value derived from the vapour pressure measurements of TRAVERS and JAQUEROD (cf. p. 441 note 1) is due to the diverging course of their vapour pressure curve, cf. p. 444 note 1. [Added in the translation]

<sup>2)</sup> Cf. p. 441 note 1.

<sup>3)</sup> H. KAMERLINGH ONNES and SOPHUS WEBER, Comm. N<sup>o</sup>. 137b (June 1913).

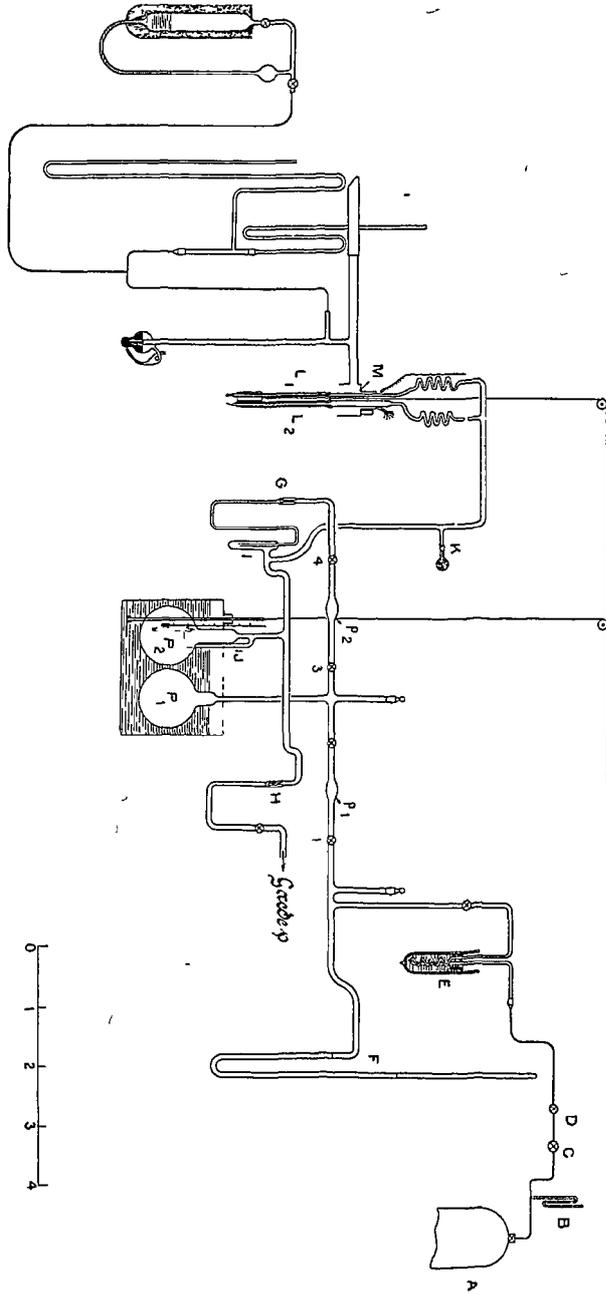


Fig. 1.

*G* and *H* glass valves as introduced by KAROVODINE in TÖPLER-HAGEN's mercury pump.

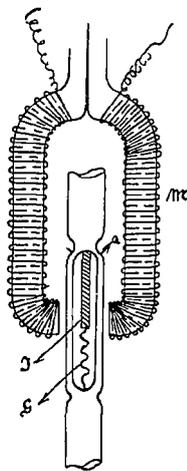


Fig. 2.

Fig. 2 shows one of these valves, *a* is a ground surface. Inside the glass tube a small piece of iron is fastened: without a current through the electromagnet *M* the communication is open to the gas; when the current is closed the vapours can only diffuse through the narrow interstices left open at *a*. The measurements seem to confirm that by the use of these valves a better vacuum may be obtained.

The calibration was performed in the following manner. By means of the high-pressure taps *D* and *C* some carbon dioxide was taken from the cylinder *A* containing carbon dioxide which had been thoroughly dried and distilled several times. This gas was solidified in *E* by means of liquid air and subsequently strongly exhausted with a GAEBDE-pump. It was then distilled into pipette *p*<sub>1</sub> and the pressure read with the manometer *F*. The pipettes *P*<sub>1</sub>, *p*<sub>2</sub> and *P*<sub>2</sub>, which communicated with the heated-wire manometer were evacuated and the vacuum was measured with the aid of this manometer, which had been previously compared with an absolute manometer. The gas in *p*<sub>1</sub> was then distributed over *p*<sub>1</sub>, *P*<sub>1</sub>, and *p*<sub>2</sub>. If stop-cock 3 is now closed and 4 opened, the gas in *p*<sub>2</sub> is distributed over *p*<sub>2</sub> and *P*<sub>2</sub>, by which the pressure in *P*<sub>2</sub> increases by a known amount. By connecting *p*<sub>2</sub> with *P*<sub>1</sub> and with *P*<sub>2</sub> successively the pressure in *P*<sub>2</sub> again increases by an amount which is known, at least if the dimensions of the apparatus are known. They were:

$$p_1 = 13.997 \text{ cm}^3$$

$$P_1 = 2108.15 \text{ ,,}$$

$$p_2 = 13.464 \text{ ,,}$$

$$P_2 = 2555.7 \text{ ,,}$$

Each time when the pressure had been raised by a known amount the loss of heat of the WOLLASTON-wire under definite conditions was measured. The following table may serve as an instance of the calibration: *q* is proportional to the loss of heat per second and *p* is the pressure in baryes computed by means of the system of pipettes. The initial pressure is taken as zero in the table; in reality it amounted to 0.029 baryes.

TABLE I	
$p$	$q$
0.000	0.6731
5.059	0.8019
10.099	0.9292
15.120	1.0551
20.122	1.1804
25.106	1.3044
30.070	1.4279
35.016	1.5305
39.943	1.6724
44.851	1.7932
49.740	1.9132
54.611	2.0332
59.464	2.1522

§ 2 After the calibration was completed the manometer was put into connection with a vapour pressure tube. This tube was of the form described in the previous communication. The measurements were conducted in the following manner. The apparatus was first exhausted as far as possible and was allowed to stand for some days, until the walls did not give off any more air. The vapour pressure tube which was placed in a cryostat together with a thermometer and a stirrer was then successively surrounded by ethylene, methane and oxygen, and the vacuum was measured at temperatures between  $-130^{\circ}$  C. and  $-180^{\circ}$  C. Carbon dioxide was then distilled into the apparatus and the vapour pressure measured at a series of temperatures. The difference between the two readings at each temperature after correcting for the thermal molecular pressure gives the vapour pressure of carbon dioxide.

In order to be able to obtain the corrections for the thermal molecular pressure it is necessary to work with different tubes suitably chosen. In this investigation two tubes were used, tube I with a diameter of 1.75 cm. and tube II of 0.563 cm.

The results of the measurements are contained in table II

TABLE II					
Pressure					
Temp. <i>T</i> -273.09	Measured tube I	Measured tube II	I corr.	II corr.	Calculated according to NERNST
-134.67	1430.6	1430.6	1430.6	1430.4	1429.9
136.78	1001.2	1002.8	1001.2	1002.5	1002.0
138.69	720.0	720.6	719.9	720.2	719.3
140.63	509.2	510.8	509.1	510.2	508.7
143.07	324.7	323.9	324.6	323.1	324.2
145.44	207.0	204.2	206.8	203.1	206.70
148.27	117.72	119.7	117.42	118.0	117.30
151.46	48.42	50.30	47.90	47.86	47.84
155.00	28.33	30.65	27.70	28.21	27.56
158.55	12.92	14.09	12.34'	12.12	12.00
159.72	9.82	10 72	8.66	8.94	9.015
161 39	6.74	7.50	5.85	6.00	5.942
163.19	4.43	4.99	3 75	3.77	3.737
164.03	3.63	4.07	3 03	2.98	2.993
168.83	1.222	1.288	0.806	0.797	0.790

The first column contains the temperature as determined by means of a calibrated Pt.-thermometer. The second and third give the results of the measurements with the two tubes expressed in baryes, the fourth and fifth the same numbers after correcting for the thermal molecular pressure. For the measurements between  $-150^{\circ}$  and  $-162^{\circ}$  these corrections are somewhat uncertain, as they have been determined experimentally for hydrogen and oxygen only. Moreover the tubes had not been chosen as favourable as possible, as will be clear from the following.

The corrections are calculated by means of KNUDSEN's formulae <sup>1)</sup>. In the previous communication it was shown that with the degree of accuracy of our measurements these formulae may be considered as correct, if the region where approximately  $1 < \frac{\lambda}{2R} < 10$  is excluded. If BREITENBACH's observations on the viscosity of carbon dioxide are extrapolated by means of SUTHERLAND's formula <sup>2)</sup> it may be concluded that the corrections cannot be computed in the range between 25 and 3 baryes for the wide tube and between 75 and 8 baryes for the narrow tube. Supposing that the mean free path is known with sufficient accuracy it will be seen that between 25 and 8 baryes there is a range for which the correction cannot be calculated. An additional tube of say 1 mm. diameter ought to have been used.

It appears further that below 3 baryes there is a range of pressures, where the correction can be found for both tubes. With the formula which holds for this range the mean free path may be determined by eliminating the unknown vapour pressure. The result of this calculation is found to agree within the limits of accuracy of the observations with the mean free path as calculated with SUTHERLAND's formula. In table II this shows by the close agreement between the vapour pressures under I corr. and II corr.

The conclusion seems therefore justified that the mean free path of carbon dioxide is known with sufficient accuracy at these temperatures, and that the corrections may be deduced by means of KNUDSEN's formulae with the exception of the range between 25 and 8 baryes.

Leaving this range out of account in the mean time we will now discuss the formulae for those ranges where in our opinion they are still applicable.

$$(1). \frac{2R}{\lambda} > 10.$$

In this range we use the following formula theoretically deduced by KNUDSEN.

<sup>1)</sup> MARTIN KNUDSEN. Ann. der Phys. 31 (1910), p. 205, 633; 33 (1910), p. 1435.

<sup>2)</sup> The extrapolation by means of SUTHERLAND's formula is probably allowable in this case, as the range of reduced temperature is comparatively small. Over larger ranges of reduced temperature SUTHERLAND's formula does not appear to be applicable (H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER. Comm. N<sup>o</sup>. 134a, March 1913).

$$\frac{dp}{dT} = \frac{0.00139 \frac{1 + \frac{c}{273}}{1 + \frac{c}{T}} \eta_0 k_1}{R + 32.07 \frac{\left(1 + \frac{c}{T}\right) \sqrt{Q_0}}{\left(1 + \frac{c}{273}\right) \eta} R^2 \frac{p}{T} k_2} \dots \dots (I)$$

The meaning of the symbols is the same as in KNUDSEN's paper. According to the theory the constants  $k_1$  and  $k_2$  are independent of the nature of the gas. Experimentally this formula has been confirmed for hydrogen and oxygen, and  $k_1$  and  $k_2$  appear actually to be independent of the nature of the gas. The equation which may be integrated in a fairly simple manner loses its validity for small values of  $\frac{2R}{\lambda}$ . For carbon dioxide the formula was used with the values of  $k_1$  and  $k_2$  which were found from the measurements with hydrogen and oxygen. As shown by Table II the numbers under I corr. and II corr. agree well with each other which may be looked upon as a partial confirmation of the underlying suppositions. Fig. 3 gives a graphic representation of  $\frac{dp}{dT}$  according to the different formulae. The abscissae give the pressures in baryes, the ordinates  $\frac{dp}{dT}$  for the tube with  $2R = 0.563$  cm. Curve 1 represents the relation according to formula I. For the corrections the formula has not been used, when  $\frac{2R}{\lambda} < 10$ ; it depends, however, on the degree of accuracy required, where the limit has to be taken.

$$(2). \frac{2R}{\lambda} < 1.$$

In this case the following formula was used for  $\frac{dp}{dT}$ :

$$\frac{dp}{dT} = \frac{1}{2} \frac{1}{1 + \frac{2R}{\lambda} \frac{p}{T}}$$

where  $p$  and  $\lambda$  are connected by the relation  $p \cdot \lambda = \text{const.}$ ; this constant is determined by the viscosity corresponding to the temperature  $T$ .

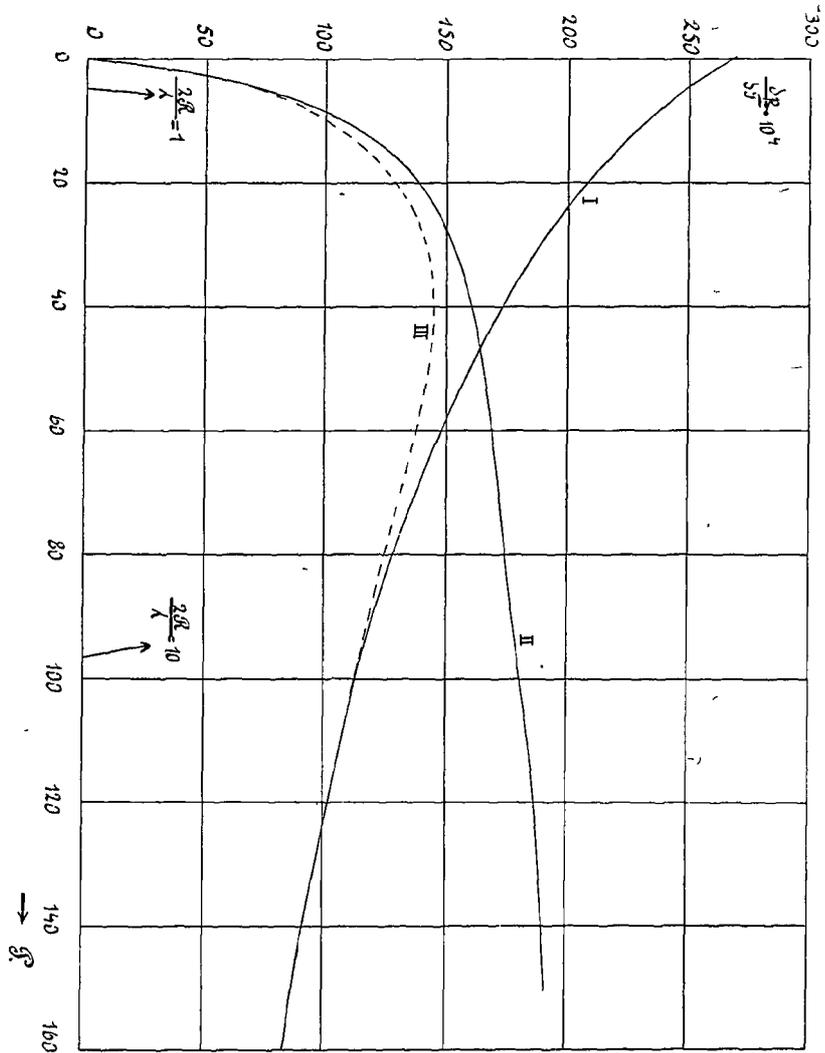


Fig. 3.

For sufficiently small values of  $\frac{2R}{\lambda}$  the formula reduces to

$$\frac{dp}{dT} = \frac{1}{2} \cdot \frac{p}{T} \text{ or after integration } \frac{p_1}{p_2} = \sqrt{\frac{T_1}{T_2}}$$

The limit for the application of formula II has been taken at  $\frac{2R}{\lambda} = 1$ , which gives about the same accuracy as in the former case.

The relation between  $p$  and  $\frac{dp}{dT}$  according to formula II is also given in fig. 3.

$$(3). \quad 1 < \frac{2R}{\lambda} < 10.$$

In this region the formulae can probably only be used as rough approximations. Curve *III* in fig. 3 has been obtained by reducing the observations for hydrogen and oxygen to carbon dioxide by means of the law of corresponding states. The values given by *III* have been used in this range for calculating the corrections. The results under I corr. and II corr. agree fairly well with each other. The observations are, however, not sufficient to draw conclusions with regard to the value of thermal molecular pressure in this intermediate region.

This region has, therefore, not been sufficiently studied as yet and new measurements in this range would be of the greatest interest.

In table II column 5 under "calc. according to NERNST" the pressures are given calculated by the aid of NERNST's formula. In the former paper use was made of the formula with the values of the constants found by FALCK<sup>1)</sup>, viz.

$$\log p = - \frac{6000}{4.571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0.00913}{4.571} T + 3.1700 \quad (I)$$

In order to obtain a satisfactory agreement at higher pressures the constants had to be slightly modified as follows

$$\log p = - \frac{6007.9}{4.571} \cdot \frac{1}{T} + 1.75 \log T - \frac{0.009008}{4.571} T + 3.1700 \quad (II).$$

$p$  is here expressed in atmospheres.

The coefficient of  $\log T$  and the chemical constant are unchanged, and the other two constants have been only slightly altered. This alteration can have no influence on FALCK's theoretical deductions. The very low vapour pressures which we measured before with the absolute manometer are also unchanged, as the term proportional to  $T$  has but little influence in that region. In that case NERNST's formula reduces to the vapour pressure formula according to KIRCHHOFF-RANKINE-DUPRÉ<sup>2)</sup>.

It can hardly be expected that formula *II* should give good agreement at temperatures much higher than those given in table II. At higher temperatures FALCK finds greater deviations which, however, he considers to be due to errors of observation. I have

<sup>1)</sup> F. FALCK: Phys. Z. S. 1908, p. 433.

<sup>2)</sup> H. KAMERLINGH ONNES und W. H. KEESOM: Die Zustandsgleichung Leiden Comm. Suppl. N<sup>o</sup>. 23, pag. 300.

made only one measurement at temperatures higher than those given in table 2.

Temperatures	$p$	Calc. by
$T - 273.09$	cm. Hg	form II.
$- 129.29$	0.3943	0.2536
$- 129.28$	0.3948	0.2539

Although this measurement is the only one it may be considered sufficient together with the observations by ZELENY and SMITH<sup>1)</sup> to infer a considerable deviation from the formula at this temperature.

In conclusion I am glad to record my gratitude to Prof. H. KAMERLINGH ONNES for his kind assistance and his ever ready interest in my work.

**Physics.** — “*On the magnetization of ferromagnetic substances considered in connection with the assumption of a zero-point energy*”. By Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 32a to the Communications from the Physical Laboratory at Leiden. (Communicated by Prof. H. KAMERLINGH ONNES).

(Communicated in the meeting of September 27, 1913).

### I. *On the spontaneous magnetization.*

§ 1. *Introduction.* NERNST<sup>2)</sup> was the first who suggested that the quantum-theory has to be applied also to the rotations of gas molecules. Since that time the measurements by EUCKEN<sup>3)</sup> and those by SCHEEL and HEUSE<sup>4)</sup> have confirmed the anticipation expressed by KAMERLINGH ONNES<sup>5)</sup>, that the decrease which according to that application is to be expected in the specific heat at constant volume of hydrogen in the gas state, would already occur at realisable temperatures. By this result they have demonstrated very clearly the necessity of that application. At the same time they have given

<sup>1)</sup> ZELENY u. SMITH. Phys. Z. S. pag. 667, 1906.

<sup>2)</sup> W. NERNST. ZS. f. Elektrochem. 17 (1911), p. 270 W. NERNST and F. A. LINDEMANN, ibid. p. 825. Cf. also A. EINSTEIN, Rapports conseil SOLVAY 1911, p. 432.

<sup>3)</sup> A. EUCKEN. Berlin Sitz.-Ber. 1912, p. 141.

<sup>4)</sup> K. SCHEEL and W. HEUSE. Berlin Sitz.-Ber. 1913, p. 44. Ann. d. Phys. (4) 40 (1913), p. 473.

<sup>5)</sup> Rapports conseil SOLVAY 1911, p. 301. ZS. f. Elektrochem. 17 (1911), p. 826. Cf. also H. KAMERLINGH ONNES and W. H. KEESOM. Math. Erz. V 10, Leiden Comm. Suppl. N<sup>o</sup>. 23, § 57 f.

valuable data for a more detailed treatment of the question <sup>1)</sup> as to the way in which the quantum-theory has to be applied to the molecular rotations.

As far as the general character is concerned, EINSTEIN and STERN <sup>2)</sup> obtain a good agreement with EUCKEN's measurements by the supposition, that the mean energy of rotation of a molecule at the temperature  $T$  is determined by the formula which PLANCK recently <sup>3)</sup> has given for the mean energy at the temperature  $T$  of an oscillator with definite frequency. In this formula the hypothesis of a kinetic energy at the absolute zero is included. As frequency they accept for the rotating molecule the number of revolutions per unit of time. Hence the frequency is immediately connected with the energy by a second relation.

Although generally speaking the agreement is very satisfactory, still at ordinary and at not very low temperatures differences exist, which justify a closer investigation as to the way in which the quantum-theory has to be applied to the molecular rotations. EINSTEIN and STERN themselves already indicated that their calculations are not complete in so far as they suppose only one frequency of rotation to be present in the gas at a given temperature. SACKUR <sup>4)</sup>, who independently of EINSTEIN and STERN also applied the quantum-theory, but in a somewhat different manner, to the rotatory motion of the molecules, had gone farther in this matter in including different possible velocities of rotation in his considerations. The same was done by EHRENFEST <sup>5)</sup>, who applied the rules of statistical mechanics in a way which more closely corresponds to the considerations by PLANCK. In both modes of treatment the principle of finite energy elements, respectively of finite elementary regions of equal probability, is applied to each of the rotating molecules separately in a corresponding way as PLANCK does for an oscillator. As, however, the rotatory motion of a molecule, in the absence of a directing force and therefore of a potential energy coming into play in this motion, differs in principle from the motion of a PLANCK's oscillator, the immediate transfer of PLANCK's considerations to the rotatory motion of each of the molecules separately does not seem to me to be very obvious.

<sup>1)</sup> This question is also of importance for the thermal equation of state, cf. Suppl. No. 25 § 3 f (Sept. 1912).

<sup>2)</sup> A. EINSTEIN and O. STERN. Ann. d. Phys. (4) 40 (1913), p. 551.

<sup>3)</sup> Cf. M. PLANCK. Wärmestrahlung, 2te Aufl., p. 140.

<sup>4)</sup> O. SACKUR. Jahresber. der Schles. Ges. für vaterl. Cultur. Febr. 1913.

<sup>5)</sup> P. EHRENFEST. Verh. d. D. physik. Ges. 1913, p. 451.

It seems to me to be rather indicated to derive the amount of temperature energy (cf. Suppl. N<sup>o</sup>. 30a § 1), which the molecules possess at a temperature  $T$  on account of their rotations, from a consideration of the equilibrium of the system of rotating molecules with black radiation of that temperature, and for the latter to regard PLANCK's formula as given, in the way as is done for the translatory motion in the gas in Suppl. N<sup>o</sup>. 30a. EINSTEIN and STERN also start from the consideration of this equilibrium. Addition of the zero-point-energy forms then a new hypothesis which is justified by the results <sup>1)</sup>.

Instead of resolving the molecular rotatory motion of a gas considered as a whole into the rotations of the separate molecules one can also, imitating JEANS and DEBIJE, resolve it into a system of stationary waves. The elementary motions which come to appearance in that way entirely correspond in properties with that of a PLANCK's oscillator with definite frequency. It seems to me that the consideration of the equilibrium between black radiation and molecular rotatory motion in a way corresponding to that followed in Suppl. N<sup>o</sup>. 30a for the translatory motion, leads to the result that to each of such principal modes of vibration in the system PLANCK's formula has to be applied This is done in § 2.

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<sup>1)</sup> The result obtained by EHRENFEST i.e., that with his distribution of rotation frequencies without the hypothesis of a zero-point energy a good representation of the results obtained by EUCKEN at the lowest temperatures can be given, is remarkable. In the mean time in the observations no indication of the not monotone course of the specific heat, which is found by him at higher temperatures, is present. On the other hand a further investigation based on the assumption of a zero-point energy is justified by the indications for its existence which have since appeared in other fields also: cf. M. PLANCK, i.c. p 455 note 3, for the molecular translatory motion in gases: H. KAMERLINGH ONNES and W. H. KEESOM, Communication to the WOLFSKEHL congress, Göttingen 1913, W. H. KEESOM, Suppl. N<sup>o</sup>. 30a (May '13), for the free electrons in metals: W. H. KEESOM, Suppl. N<sup>o</sup>. 30b (May '13), concerning the deviations from CURIE's law for paramagnetic substances: E. OOSTERHUIS, Suppl. N<sup>o</sup>. 31 (June '13), concerning the spontaneous magnetization of ferromagnetic substances: this communication I, concerning the dependence on temperature of the molecular magnetic moment of ferromagnetic substances above the CURIE point this communication II, to which as perhaps pointing in the same direction, although in the mean time less definitely, the following can be added: the behaviour of the dielectric constant of aethyloether (cf. a following paper), the deviation at low temperatures from J. BECQUEREL's law concerning the width of some absorption bands (cf. J. BECQUEREL and H. KAMERLINGH ONNES, Comm. N<sup>o</sup>. 103 § 5, Febr. '08), the behaviour of the viscosity coefficient of gases at low temperatures, W. H. KEESOM, Suppl. N. 25 § 6 (Sept. '12), H. KAMERLINGH ONNES, C. DORSMAN and SOPHUS WEBER, Comm. N<sup>o</sup>. 134 a, b, c (March, April '13).

Comparison of the expression obtained there for the energy of the molecular rotations with the experimental data concerning the specific heat of hydrogen shows, as far as the general course is concerned, an agreement which is just as good as that found by EINSTEIN and STERN. For the ordinary and the not very low temperatures, for which EUCKEN's results have been confirmed by SCHFEL and HEUSE, now also deviations are found, which, just as those found by EINSTEIN and STERN cannot be ascribed to experimental errors. The deviations found here differ from those found by EINSTEIN and STERN in these respects: they are all in the same direction, *viz.* so that the experimental value is larger than the calculated one<sup>1)</sup>, and they increase regularly with the temperature. These points seem to be in favour of the suppositions made in § 2, in so far as it seems easier to account for deviations showing this course by introducing the hypothesis of the "appearance of a new degree of freedom" than for deviations such as were found by EINSTEIN and STERN. On the other hand the possible inequality of the two principal moments of inertia which govern in this region of temperature the contribution of the rotatory motion to the specific heat of hydrogen in the supposition that the third principal moment of inertia is so small that the contribution furnished by the rotation round the corresponding axis is not perceivable or only very small, may, perhaps also have as a consequence deviations such as found by EINSTEIN and STERN in supposing those two moments of inertia to be equal.

Before introducing one of these new hypotheses it seemed to me to be preferable to put the expression for the energy of the molecular rotations derived in § 2 to the test with the aid of other phenomena. As according to LANGEVIN's theory the molecular rotatory energy has a determining influence on the magnetization of paramagnetic substances, the latter can be used for the purpose. Dr. OOSTERHUIS, who applied with good success the quantum-theory with introduction of the zero-point energy following EINSTEIN and STERN for the explanation of the deviations which the susceptibility of some paramagnetic substances show from CURIE's law, was so kind at my suggestion as to put to the test the expression derived in § 2 also<sup>2)</sup>. He found that those deviations are not represented very much better with the aid of that expression than with that of the simpler expression given by EINSTEIN and STERN. A clear decision between the two expressions was not obtained.

<sup>1)</sup> The same is true for the deviations found by SACKUR *l.c.*

<sup>2)</sup> E. OOSTERHUIS, *Comm. Suppl.* N<sup>o</sup>. 31 (June 1913), § 7.

It then occurred to me that perhaps the spontaneous magnetization of ferromagnetic substances might furnish a still more sensitive criterion for putting the expression given in § 2 for the energy of the molecular rotations to the test. For this the result obtained in § 2 is introduced in § 3 into WEISS's theory for ferromagnetic substances. In doing this it is to be taken into consideration that the energy of the molecular rotations is changed by the presence of a directing field (§ 3*b*). In § 4 the results of a comparison with the observations are communicated. In a further chapter II (Suppl. N<sup>o</sup>. 32*b*) some general remarks follow, to which the application of the quantum-theory with introduction of the zero-point energy leads, particularly for the state of excited ferromagnetism. Here it should be kept in mind that several of those general remarks are not dependent on the special value which in §§ 2 and 3 is given for the rotatory energy, but follow from the general change of that energy with temperature, such as is given by the formulae of those sections. In how far this is the case for each remark in particular the reader will easily decide himself.

§ 2. *The energy of molecular rotations in the absence of a directing force.* If the velocity of the molecular rotations of a group of molecules in a gas is changed, the modification in the motion will be transferred from the centre of disturbance to the other molecules. The same is true for a solid, in which we provisionally suppose the molecules to rotate freely. There is no doubt that for the description of the propagation, considered as a molar process, of the disturbance of equilibrium with appropriate simplifying suppositions a differential equation of the same form holds as for the propagation of a wave motion in an elastic medium.

As also the boundary conditions<sup>1)</sup> agree with those which are valid for the propagation of a wave motion in an elastic medium (eventually a gas), as regards the rotatory motion conditions of stationary wave motion will be possible which correspond to those which occur with acoustical motions. In particular the number of possible principal modes of vibration with frequencies between  $\nu$  and  $\nu + d\nu$  will be determined by a formula such as equation (3) of Suppl. N<sup>o</sup>. 30*a*.

The molecular rotatory motion in the substance can be resolved into a system of such wave motions. For the determination of the number of these wave motions for a finite number of molecules we

<sup>1)</sup> If the molecules can rotate freely at the boundary, a loop occurs there, if their rotatory motion is impeded or strongly damped, a node.

again suppose DEBYE's method to be approximately valid. According to that method the "spectrum" is determined without taking account of the molecular structure, and then it is cut off on the side of the high frequencies at a value  $\nu_{\max}$  which is found by putting the total number of such modes of vibration equal to the number of degrees of freedom.

We may imagine that the energy of the radiation is transferred to the molecular rotations by means of the radiation pressure and hence and by analogy with the molecular translatory motion (cf. Suppl. N<sup>o</sup>. 30a § 2) suppose, that we have to take energy elements of magnitude  $\frac{1}{2} h\nu^2$ , if  $\nu$  is the frequency of the considered mode of vibration. A different supposition concerning the coefficient of  $h\nu$  would, moreover, not cause any change in the general results of this communication.

As was done for the translatory motion (Suppl. N<sup>o</sup>. 30a § 3) we will for this free rotatory motion suppose, that the velocity of propagation  $c$  of the wave motions considered here, for the small wavelengths which are the most important, at states which deviate only little from the state of thermodynamic equilibrium, is for each mode of vibration proportional to the square root of the energy  $u_r$ ,<sup>2)</sup> of that mode of vibration. We then obtain as in Suppl. N<sup>o</sup>. 30a § 4:

$$u_r = \frac{1}{2} \left\{ \frac{h\nu}{\frac{e^{kT}}{1} - 1} + \frac{1}{2} h\nu \right\} \dots \dots \dots (1)$$

This expression is adopted also by EINSTEIN and STERN for the energy of rotation with "frequency"  $\nu$  for one degree of freedom. The supposition concerning  $c$  may provisionally be further justified by the remark that by it we obtain that for high temperatures the ratio of the energy for one degree of freedom to  $\frac{1}{2} kT$  approaches to 1, as must be the case for these free rotations.

We will suppose that in this communication, where the contrary is not mentioned explicitly, we have to deal with the rotations round two equivalent axes. For the mean energy of rotation for these two degrees of freedom we then find

$$u_r = \frac{3}{\nu_{\max}^3} \int_0^{\nu_{\max}} \left\{ \frac{h\nu}{\frac{e^{kT}}{1} - 1} + \frac{1}{2} h\nu \right\} \nu^2 d\nu, \dots \dots \dots (2)$$

1) Cf. also P. EHRENFEST l. c., p. 453, note 1.

2) The index r will indicate that the quantity relates to the rotatory motion.

Further we suppose as in equations (5)<sup>1)</sup> and (7) of Suppl. N<sup>o</sup>. 30a)  $c = u_r^{1/2}$ . Hence (cf. formula (3) of Suppl. N<sup>o</sup>. 30a):

$$v_{\max} = u_1^{1/2} \dots \dots \dots (3)$$

This supposition causes (with the assumption of a zero-point energy as in (1)), that at sufficiently high temperatures  $u_1$  becomes  $k(T + \Delta)$ , where  $\Delta$  is a constant, and this OOSTERHUIS<sup>2)</sup> found suitable to explain the behaviour of the susceptibility of different paramagnetic substances.

Introducing as in Suppl. N<sup>o</sup>. 30a):

$$\xi = \frac{h\nu}{kT}, \quad x = \frac{h\nu_{\max}}{kT}, \quad \theta = \frac{h\nu_{\text{rot}}}{k}, \quad \theta_0 = \frac{h\nu_{\max_0}}{k} \dots (4)$$

we can write<sup>3)</sup>

$$\left. \begin{aligned} \left(\frac{u_1}{u_{r_0}}\right)^{1/2} &= 1 + \frac{8}{x^4} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \\ \frac{T}{\theta_0} &= \frac{1}{x} \cdot \left(\frac{u_r}{u_{r_0}}\right)^{1/2} \end{aligned} \right\} \dots \dots \dots (5)$$

These equations determine  $u_1$  as a function of  $T$  if there is no directing force<sup>4)</sup>. They contain the energy of rotation at  $T=0$ :

$$u_{r_0} = \frac{3}{8} k\theta_0 \dots \dots \dots (6)$$

<sup>1)</sup> In this equation the supposition is made that in the state of thermodynamic equilibrium the velocity of propagation for the different frequencies is the same.

<sup>2)</sup> E. OOSTERHUIS. Suppl. N<sup>o</sup>. 31 (June 1913)

<sup>3)</sup> The appearance of the constant  $\theta_0$  is characteristic of the introduction of the quantum-theory in the theory of this communication. This constant is connected with the moment of inertia of the molecule or of the part of it which rotates freely, in such a way that to a small value of the moment of inertia a large value of  $\theta_0$  corresponds and the reverse. We may therefore expect that for elements with monatomic molecules  $\theta_0$  is relatively large, and that for compounds with relatively heavy and extensive molecules  $\theta_0$  is relatively small. The deviations from the equipartition laws run parallel to that, as in fact OOSTERHUIS found regarding the deviations which paramagnetic substances show from CURIE's law.

<sup>4)</sup> Appropriate developments for the first of the equations (5): for the greater values of  $x$ :

$$\left(\frac{u_r}{u_{r_0}}\right)^{1/2} = 1 + \frac{8\pi^4}{15} \frac{1}{x^4} - 8 \sum_{n=1}^{n=\infty} e^{-nx} \left( \frac{1}{nx} + \frac{3}{n^2 x^2} + \frac{6}{n^3 x^3} + \frac{6}{n^4 x^4} \right),$$

for the smaller values of  $x$ :

$$\left(\frac{u_r}{u_{r_0}}\right)^{1/2} = \frac{8}{3} \frac{1}{x} \left\{ 1 + \frac{1}{20} x^2 - \frac{1}{1680} x^4 + \frac{1}{90720} x^6 - \frac{1}{4435200} x^8 \dots \right\}.$$

§ 3. *a. Introduction of the quantum-theory into WEISS's theory for the ferromagnetic state.* We suppose that the introduction of the quantum-theory only brings this change in the statistics of the orientations of the elementary magnets under the influence of the magnetic field, that in the relations which LANGEVIN <sup>1)</sup> has deduced for it  $kT$  has to be replaced by the value  $u_r$  for the rotation energy which is now valid <sup>2)</sup>.

According to LANGEVIN the magnetic moment  $M_m$  of unit of mass under the influence of the magnetic field  $H$  is:

$$M_m = n\mu \left\{ \frac{Ch a}{Sh a} - \frac{1}{a} \right\}; \dots \dots \dots (7)$$

$n$  is the number of freely rotating molecular <sup>3)</sup> magnets in the unit of mass,  $a$  is the molecular magnetic moment;  $a$  is determined by

$$a = \frac{\mu H}{u_r} \dots \dots \dots (8)$$

The value of  $u_r$ , which may be changed by the magnetic field is treated in this section under *b*.

From (7) and (8) follows for the susceptibility of paramagnetic substances, as long as no saturation <sup>4)</sup> begins to be appreciable:

$$\chi = \frac{n\mu^2}{3u_r} \dots \dots \dots (9)$$

OOSTERHUIS has also accepted this relation.

<sup>1)</sup> P. LANGEVIN. Ann. chim. phys. (8) 5 (1905), p. 70.

<sup>2)</sup> In the application to solids we imagine the molecules to rotate freely, or at least to be so weakly bound to a definite equilibrium orientation that the maximum increase, which the potential energy can undergo by the deviation of a molecule from the equilibrium orientation is still small compared with the mean kinetic energy of rotation which the molecule has at the temperatures at which we consider the magnetization. In cases in which the changes in potential energy are appreciable more intricate relations appear. Cf. P. WEISS, C.R. 156 (1913), p. 1674, 1836, for a treatment of such cases in the assumption of the equipartition value for the rotation energy.

<sup>3)</sup> Under "magnetic molecule" we understand in this communication the elementary particle which rotates freely as a whole and has a magnetic moment; at present we do not enter into the question whether it is the same as the chemical molecule or not. According to WEISS each chemical molecule  $Fe_3O_4$  would contain 3 magnetic molecules.

<sup>4)</sup> It deserves to be noticed that in the assumption of a zero-point energy saturation phenomena at low temperatures are to be expected to make their appearance at higher values of  $H$  than according to LANGEVIN's theory, in which  $a$  is determined by the value of  $\frac{H}{T}$ .

According to WEISS's<sup>1)</sup> theory for the ferromagnetic state:

$$H = H_e + H_m, \quad \dots \dots \dots (10)$$

where  $H_e$  is the external magnetic field and

$$H_m = N_m I_m \dots \dots \dots (11)$$

the molecular field.  $I_m$  = the magnetization per unit of volume =  $\varrho M_m$ , if  $\varrho$  = the density. WEISS supposes the coefficient of the molecular field  $N_m$  to be constant.

The spontaneous magnetization  $\sigma$ , which belongs to  $H_e = 0$ , is obtained by WEISS's construction in a  $\sigma, a$ -diagram by determining the point of intersection of the curve

$$\sigma = n\mu \left\{ \frac{\text{Ch } a}{\text{Sh } a} - \frac{1}{a} \right\} \dots \dots \dots (12)$$

with the straight line

$$\sigma = \frac{u_1}{N_m \varrho \mu} a \dots \dots \dots (13)$$

which corresponds to the chosen value of  $T$ .

If

$$u_{10} > \frac{N_m n \varrho \mu^2}{3}, \dots \dots \dots (14)$$

none of the straight lines (13) has another point of intersection with the curve (12) than the point  $a = 0$ . Hence in the assumption of a zero-point energy for the molecular rotatory motion *ferromagnetic substances*, characterised according to WEISS by their possessing a molecular field, *without the specific ferromagnetic properties*: spontaneous magnetization, hysteresis, remanent magnetism, are possible. We come back to this in § 6 (Suppl. N<sup>o</sup>. 32b).

If on the contrary

$$u_{10} < \frac{N_m n \varrho \mu^2}{3}, \dots \dots \dots (15)$$

to each temperature  $T < T_c$ , the temperature of the CURIE-point, which is determined by

$$u_{1c} = \frac{N_m n \varrho \mu^2}{3} \dots \dots \dots (16)$$

( $u_{1c}$  = the rotation energy at the CURIE point), a spontaneous magnetization belongs, which we may consider to be determined by (12) and

$$\sigma = n\mu \cdot \frac{1}{3} \frac{u_1}{u_{1c}} \dots \dots \dots (17)$$

<sup>1)</sup> P. WEISS. J. de phys. (4) 6 (1906), p. 661. Physik. ZS. 9 (1908), p. 358. Les idées modernes sur la Constitution de la matière (Conférences Paris 1912), p. 332.

b. *Influence of the magnetic field on the rotational energy* As according to the quantum-theory the rotational energy of the molecular magnets depends upon the frequencies which occur in the body considered, and as these frequencies may be changed under the influence of the magnetic field, the rotational energy may depend upon the field. The way of dependence can be deduced thermodynamically, if the energy in the absence of a field is known as a function of temperature (cf. § 2).

The heat which at an infinitely small reversible change has to be supplied to a ferromagnetic body, of which the state may be determined by  $T$  and  $M_m$ , is given per unit of mass by <sup>1)</sup>

$$dQ = dU_1 - HdM_m, \dots \dots \dots (18)$$

in which  $U_1$  also refers to the unit of mass, and  $H$ , as in this section under  $a$ , represents the total field acting on each magnetic molecule, the molecular field being included. The second law of thermodynamics then gives

$$\left(\frac{\partial U_1}{\partial M_m}\right)_T = H - T \left(\frac{\partial H}{\partial T}\right)_{M_m} \dots \dots \dots (19)$$

Following the supposition mentioned in the beginning of this section under  $a$  we may write

$$H = nu_{1m}f(M_m) \dots \dots \dots (20)$$

where  $f(M_m)$  is determined by (7) and (8). The index  $m$  in  $u_{1m}$  indicates that the rotation energy has been changed by the field,  $u_1$ , as in § 2, will indicate the rotational energy in the absence of the field. With  $U_1 = nu_{1m}$  (19) becomes

$$\frac{1}{f(M_m)} \left(\frac{\partial u_{1m}}{\partial M_m}\right)_T = u_{1m} - T \left(\frac{\partial u_{1m}}{\partial T}\right)_{M_m} \dots \dots \dots (21)$$

The general solution of this partial differential equation is

$$\frac{u_{1m}}{T} = \varphi \left( T e^{-\int_0^{M_m} f(M_m) dM_m} \right) \dots \dots \dots (22)$$

<sup>1)</sup> This equation was deduced by me from a consideration of the energy which has to be supplied to one of the molecular magnets, of which the moment is supposed to be constant, when its rotation energy and its orientation with regard to the field  $H$  are changed. In this, following WEISS, I supposed the total interaction of the molecules to be included in the form of the molecular field in  $H$ . One obtains for the energy to be supplied  $du_1 - H du_H$ , if  $du_H$  is the change of the component in the direction of  $H$  of the magnetic moment. Summation over the unit of mass gives (18). Cf. the appendix to this communication II for a more detailed proof, which Prof. LORENTZ kindly communicated to me.

As the inferior limit in the integral 0 has been chosen, as the function  $\varphi$  may be determined by considering that for  $M_m = 0$   $u_{1m}$  is given as a function of  $T$ , viz. by equation (5). The two equations obtained in this way determine  $u_{1m}$  when  $T$  and  $M_m$  are given. The following form can be given to these equations. If we call  $u_r$  and  $T^r$  the values of  $u_1$  and  $T$  which according to (5) belong to a definite value of  $x$ , the following values of  $u_{1m}$  and  $T$  now correspond to it:

$$\left. \begin{aligned} u_{1m} &= u_1 \cdot \frac{a}{\text{Sh}a} e^{a \frac{M_m}{n\mu}} \\ T &= T^* \cdot \frac{a}{\text{Sh}a} e^{a \frac{M_m}{n\mu}} \end{aligned} \right\} \dots \dots \dots (23)$$

In these equations the integration which occurs in (22) has been carried out. It is easily seen that  $u_{1m}$  is greater than the value of  $u_1$  (for  $M_m = 0$ ) which belongs to the same value of  $T$ . So also that if  $u_r = kT^r$ ,  $u_{1m}$  is equal to the value of  $u_r$  (for  $M_m = 0$ ) at the temperature  $T$ .

For determining the spontaneous magnetization,  $M_m$  in (23) must be replaced by  $\sigma$ , and further it has to be remembered that between  $\sigma$ ,  $a$ , and  $u_{1m}$  according to (12) and (17) the following relations exist <sup>2)</sup>:

$$\frac{\sigma}{n\mu} = \frac{\text{Ch}a}{\text{Sh}a} - \frac{1}{a} = \frac{1}{3} a \cdot \frac{u_{rm}}{u_{1c}} \dots \dots \dots (24)$$

The calculations can be performed by calculating at a given value of  $\frac{\sigma}{n\mu}$  the corresponding value of  $T$ : (24) gives the values of  $a$  and  $\frac{u_{rm}}{u_{1c}}$  corresponding to  $\frac{\sigma}{n\mu}$ ; then according to (23)

$$u_{1m}^* = u_{1m} \frac{\text{Sh}a}{a} e^{-a \frac{\sigma}{n\mu}}; \dots \dots \dots (25a)$$

according to (5) by the aid of the equations

<sup>1)</sup> In LANGEVIN'S  $M_m, a$ -diagram this integral can be read as the surface which has the curve (7) and the  $M_m$ -axis as its boundaries.

<sup>2)</sup> It follows from equation (23) that the determination of the CURIE point by equation (16) is not changed as a consequence of the influence of the field on the rotational energy. This may also be deduced directly.

$$\left. \begin{aligned} \left(\frac{u_1^*}{u_{10}}\right)^{1/2} &= 1 + \frac{8}{\alpha^4} \int_0^x \frac{\xi^3 d\xi}{e^\xi - 1} \\ \frac{T^*}{\theta_0} &= \frac{1}{\alpha} \cdot \left(\frac{u_1^*}{u_{10}}\right)^{1/2} \end{aligned} \right\} \dots \dots \dots (26)$$

with a given value of  $\theta_0$  the value of  $T^*$  may then be derived; finally  $T$  follows from

$$T = T^* \cdot \frac{a}{\text{Sha}} e^{a \frac{\sigma}{n\mu}} \dots \dots \dots (25b).$$

§ 4. *The spontaneous magnetization of magnetite and of nickel.*  
 In Fig. 1 the data are represented for a comparison of the observations concerning the spontaneous magnetization of magnetite and

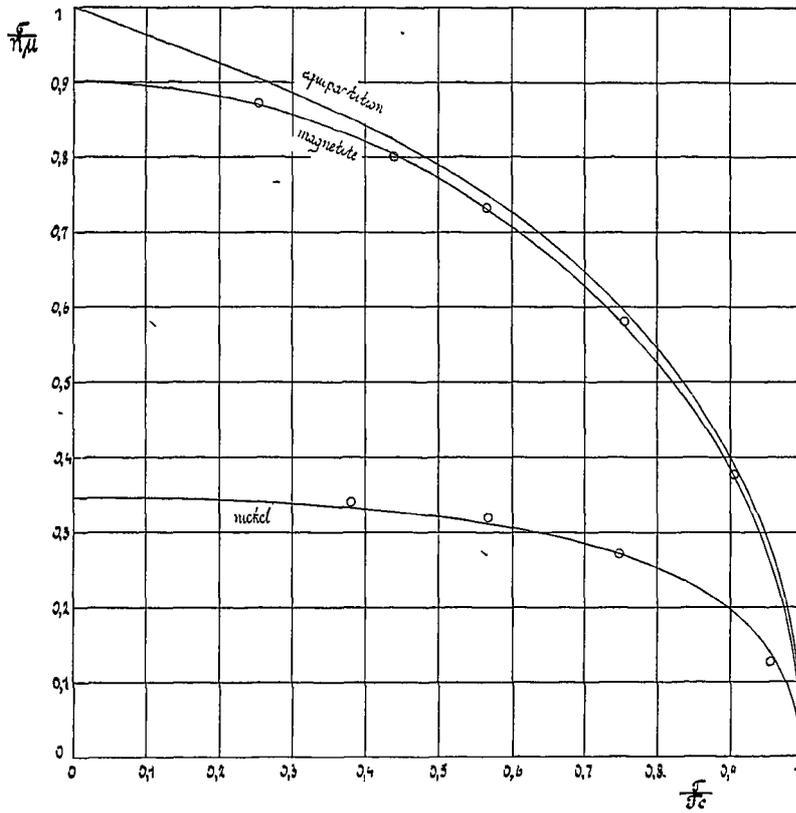


Fig. 1.

of nickel with the relations (23) to (26) of § 3.  $T_c$  is the temperature of the CURIE point. The curve marked "equipartition" has been

calculated from (24) with  $u_{im} = kT$ . The two other curves are taken from fig. 1, Pl. I, of Comm. N<sup>o</sup>. 114 by WRISS and KAMERLINGH ONNES (Febr. 1910)<sup>1)</sup> and represent the results of the observations concerning magnetite and nickel<sup>2)</sup>.

The points indicated by circles have been calculated with the equations (23) to (26). The following values of  $\theta_0$  were adopted<sup>3)</sup>

for magnetite  $\theta_0 = 75$

„ nickel  $\theta_0 = 2100$ .

The agreement between observation and calculation may be regarded as quite satisfactory for magnetite<sup>4)</sup>. This indicates that the application of the quantum-theory made here, corresponds in its principal features to reality in particular as regards the assumption of a zero-point energy.

For nickel the agreement is somewhat less satisfactory<sup>5)</sup>. Yet, I

<sup>1)</sup> A reading from the curve for magnetite published in Les idées modernes sur la Constitution de la Matière (Conférences Paris 1912) showed but insignificant differences from the readings from the figure in Comm. N<sup>o</sup>. 114.

<sup>2)</sup> The values of  $\frac{\sigma_0}{n\mu}$  have been calculated with the values of  $\theta_0$  given in the text.

<sup>3)</sup> Again the large difference in  $\theta_0$  between monatomic elements and compounds calls for attention. This difference corresponds to a similar difference (in the reverse sense) of the moment of inertia (cf. p. 460 note 3). It is connected with their high values of  $\theta_0$  (i. e. with their small moments of inertia), that the rotational energy at ordinary temperatures makes only a relatively small contribution to the specific heat of monatomic solids.

<sup>4)</sup> From the original of Fig. 1 the following data were read for magnetite:

$\frac{T}{T_c}$	$\frac{\sigma}{\sigma_{0,obs.}}$	$\times \frac{\sigma_0}{n\mu_{calc.}}$	$\frac{\sigma}{n\mu_{calc.}}$	O—C
0.253		0.871 <sup>5</sup>	0.873	— 0.001 <sup>5</sup>
0.439		0.802 <sup>5</sup>	0.800	+ 2 <sup>5</sup>
0.565		0.730 <sup>5</sup>	0.733	— 2 <sup>5</sup>
0.756		0.575 <sup>5</sup>	0.581	— 5 <sup>5</sup>
0.906		0.374 <sup>5</sup>	0.377	— 2 <sup>5</sup>

The agreement might still have been improved for the higher temperatures by choosing another  $\theta_0$ . This has not been done as presumably in the observational curve the correction for dilatation has not yet been applied. If this correction has still to be applied the agreement between observation and calculation lies, I think, within the degree of accuracy of the measurements.

<sup>5)</sup> For nickel the following data were read:

$\frac{T}{T_c}$	$\frac{\sigma}{\sigma_{0,obs.}}$	$\times \frac{\sigma_0}{n\mu_{calc.}}$	$\frac{\sigma}{n\mu_{calc.}}$	O—C
0.381		0.332	0.341	— 0.009
0.567		0.311 <sup>5</sup>	0.320	— 8 <sup>5</sup>
0.748 <sup>5</sup>		0.271 <sup>5</sup>	0.270 <sup>5</sup>	+ 1
0.955		0.138 <sup>5</sup>	0.127	+ 11 <sup>5</sup>

The correction for dilatation which possibly has still to be applied (cf. note 4) would in this case somewhat enlarge the deviation.

think, it may be still regarded as a confirmation of the principal features of the considerations of this paper. The divergences may then be attributed to the approximating character of some of the special assumptions of §§ 2 and 3.

If the assumptions made in this paper concerning the molecular rotational energy are adopted as being in the main right, the results obtained here may be regarded at the same time as a valuable confirmation of WEISS's theory regarding the molecular field.

It deserves notice that in the assumption of a zero-point energy the spontaneous magnetization at the absolute zero,  $\sigma_0$ , does not coincide with the "absolute saturation magnetization"  $n\mu$ , for which all magnetic moments are imagined to be directed parallel to each other. With the values of  $\theta_0$  given above one finds

$$\text{for magnetite } \frac{\sigma_0}{n\mu} = 0.906$$

$$\text{,, nickel } \frac{\sigma_0}{n\mu} = 0.346.$$

If these assumptions correspond to reality, this fact has to be taken into account in calculating the molecular magnetic moments from the saturation magnetization at low temperatures. With the above data one finds, taking the values for the saturation magnetisation <sup>1)</sup> at low temperatures from WEISS and KAMERLINGH ONNES, Comm. N<sup>o</sup>. 114, and applying the correction for dilatation as indicated there, for the magnetic moment of a gramme-molecule, resp. a gramme-atom: for magnetite 24402, for nickel <sup>2)</sup> 9734. Neither of these is approximately a whole multiple of the gramme-magneton 1123.5 adopted by WEISS. However, before somewhat definite results can be obtained regarding this point the further data concerning the absolute values of the saturation magnetization, particularly for magnetite, which WEISS has announced <sup>3)</sup>, must be awaited, and also calculations such as have been made for magnetite and nickel in this communication, have to be carried out for other substances (particularly for iron and cobalt).

<sup>1)</sup> It is assumed that nothing particular occurs in the saturation magnetization between the temperatures of liquid hydrogen and the absolute zero (cf. Comm. N<sup>o</sup>. 114 § 1b).

<sup>2)</sup> This number is less reliable in consequence of the agreement between observation and calculation being less close for nickel, particularly on the side of the low temperatures (cf. also this Communication II p. 470 note 2).

<sup>3)</sup> For instance Comm. N<sup>o</sup>. 114 (Febr. 1910), p. 769 note 1.

**Physics.** — “On the magnetization of ferromagnetic substances considered in connection with the assumption of zero-point energy. II. On the susceptibility in the excited ferromagnetic state”. By Dr. W. H. KEESOM. Supplement N<sup>o</sup>. 32b to the Communications from the Physical Laboratory at Leiden. Communicated by Prof. H. KAMERLINGH ONNES.

§ 5<sup>1)</sup> *The susceptibility of ferromagnetic substances above their CURIE-point.* According to WEISS's theory ferromagnetic substances above their CURIE-point, before eventually adopting the paramagnetic state, pass into a state (eventually a succession of different states) in which just as below the CURIE-point the magnetization produces a molecular field. In that case, however, spontaneous magnetization does not occur any more; hence the molecular field only comes into action when it is excited by the external field. We assume in this section that the condition (15) for the existence of a CURIE-point is satisfied. For states, in which saturation is not yet appreciable<sup>2)</sup>, follows from equation (7), which then simplifies to  $M_m = \frac{1}{3} n\mu a$ , with (8), (10), (11) and (16) for the specific susceptibility (for unit of mass):

$$\chi = \frac{n\mu^2}{3(u_1 - u_{1c})}, \dots \dots \dots (27)$$

hence

$$\chi^{-1} \sim (u_1 - u_{1c}) \dots \dots \dots (28)$$

In the first approximation, *viz.* for equipartition, as well as in the second approximation, *viz.* when in the development according to positive powers of  $x$  of the second member of the first of the equations (5) only the first two terms need to be considered<sup>3)</sup>, (28) passes into WEISS's law for the susceptibility above the CURIE-point:

$$\chi^{-1} \sim (T - T_c) \dots \dots \dots (29)$$

In fig. (2) is shown how the curve which gives  $\chi^{-1}$  as a function of temperature, is derived from  $u_1$  as a function of  $T$ . According to

1) The §§, equations and figures of this paper are numbered as continuations of those in Suppl. No. 32a.

2) For these states no account has to be taken of the change of  $u_1$  under the influence of the field, which has been treated in § 3b.

3) With an accuracy of 1% in  $u_1$  this is the case for  $T > 1.2 \Theta_0$ , with one of 1% for  $T > 4 \Theta_0$ .



from the point at the highest temperature the  $\chi^{-1}, T$ -curve graphed by them in Fig. I, pl. 1, i.e., for nickel<sup>1)</sup> has just the form which would be expected from Fig. 2<sup>2)</sup>,

§ 6. *The possibility of the existence of ferromagnetic substances without CURIE-point.* It was pointed out in § 3a that on the assumption of a zero-point energy for the molecular rotations the existence must be considered possible of ferromagnetic substances (substances with a molecular field), which do not show the specific ferromagnetic properties. The condition for it was given in (14). Such a substance will have to be looked for in the first instance among those which have a large zero-point energy of rotation (a small moment of inertia) and a small molecular magnetic moment, and, also a weak molecular field.

From (7) follows, for states in which saturation has not yet become appreciable, with (8), (10) and (11) for the susceptibility

$$\chi^{-1} \sim u_r \sim v \text{ with } v = \frac{N_m n \rho u^2}{3} \dots \dots (30)$$

In Fig. 3 are united the different cases which are possible for different values of the constant  $v$ , compared with  $u_{10}$ . In this figure for the different values of  $v$   $\chi^{-1}$  has to be measured from the corresponding horizontal line.

If at constant molecular magnetic moment and constant zero-point energy the molecular field increases from 0, we subsequently meet with the following cases:

$v = v_1$ . At sufficiently high temperatures  $\chi (T + \Delta_1) = \text{const.}$

<sup>1)</sup> Similar results they find for cobalt and iron.

<sup>2)</sup> The observations by WEISS and FOEX concerning the susceptibility of nickel above of the CURIE-point can up to 870° C. be reasonably well represented with the value  $\Theta_0 = 2100$  of § 4 and with the magnetic moment of the gramme-atom = 8552. This latter value differs from that derived in § 4 for the state below the CURIE-point. On account of provisional calculations it seems, however, probable to me that for nickel the spontaneous magnetization *below the CURIE-point as well as* the susceptibility in the excited ferromagnetic state *above the CURIE-point* up to the temperature mentioned above, according to the measurements by BLOCH, Thesis Zürich (Techn. Hochsch.) 1912, presumably even up to about 1200° C., can be represented with *the same value of  $\Theta_0$  and with the same value of the magnetic moment per atom*, and likewise with *the same value of the molecular field*. In a following paper I hope to communicate the results of further calculations regarding this point. If these calculations lead to a confirmation of that expectation, the significance of WEISS's theory of the molecular field (completed by the assumption made in this communication regarding the thermal equilibrium of these molecular rotations) will become even considerably greater.

(with positive  $\Delta_1$ ). This class of substances could be called *quasi-paramagnetic*: the presence of the molecular field only becomes

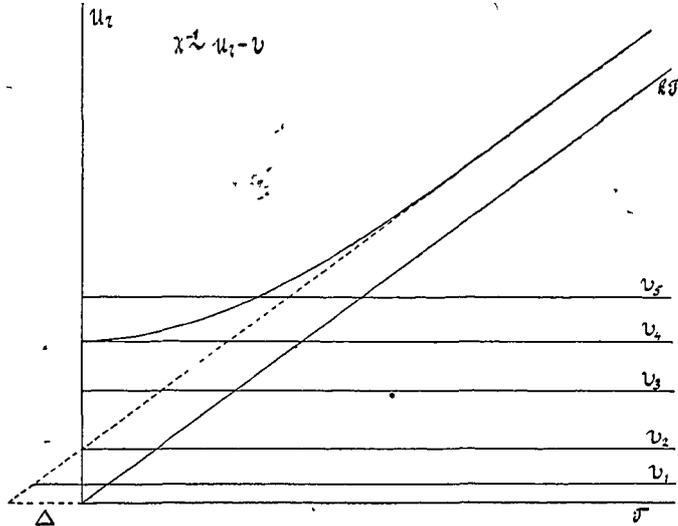


Fig. 3.

apparent, as far as the susceptibility is concerned, in this that these substances deviate from the law of corresponding states, which in accordance with the supposition made by KAMERLINGH ONNES and PERRIER<sup>1)</sup> and found confirmed in OOSTERHUIS' theory<sup>2)</sup> is valid for purely paramagnetic substances (without molecular field) with constant magnetic moment.

$v = v_2$ . The substance follows over a large region CURIE'S law ( $\Delta_2 = 0$ ). At low temperatures the  $\chi^{-1}$ ,  $T$ -graph is curved, a region with definite  $\Delta$ <sup>2)</sup> cannot, however, be indicated.

$v = v_3$ . State of excited ferromagnetism, characterised by a positive value of  $\Delta_3$  in  $\chi(T - \Delta_3) = \text{const.}$  for sufficiently high temperatures. The substance has, however, no CURIE-point.

$v = v_4$ . Also no CURIE-point. If we abstract from saturation phenomena,  $\chi$  would continually increase on approaching  $T = 0$ . It is for such a substance or one which differs little from it ( $v$  little less than  $v_4$ ) that one should in the first instance expect the appearance of saturation phenomena at low temperatures.

$v = v_5$ . Ferromagnetic substance with CURIE-point.

<sup>1)</sup> H. KAMERLINGH ONNES and ALB. PERRIER, Comm. N<sup>o</sup>. 124a (Dec. 1911), § 3. Cf. E. OOSTERHUIS, Suppl. N<sup>o</sup>. 31, These Proceedings p. 440, note 4.

<sup>2)</sup> Cf. E. OOSTERHUIS, l. c.

§ 7. *Increase of the molecular magnetic moment with temperature.*  
 In the discussions of this and the former paper the molecular magnetic moment has always been supposed to be constant and the magnetic axis to be a fixed axis in the magnetic molecule. The simplest hypothesis is that the electron or the electrons, whose motion (for instance in a circular orbit) causes the magnetic moment, are bound to a definite place in the molecule. In this manner one is led to the hypothesis, that a magnetic molecule owes its magnetic moment to the fact, that it rotates round a definite axis, which then is the magnetic axis, one or more electrons being situated at a distance from it. As long as the rotational velocity is constant and the distances of these electrons from the axis remain the same, the magnetic moment is constant. The question naturally arises, whether this rotation (round the magnetic axis) also participates in the thermal equilibrium. In the affirmative case the fact that the velocity of rotation does not change appreciably from low temperatures upwards over a large region of temperatures would point to a large value of the constant  $\theta$ , which corresponds to this rotation, and should be attributed to a particularly small moment of inertia about the corresponding axis.

We may resume this as follows: a magnetic molecule would be a molecule (or part of it) which has a small moment of inertia round a definite axis, so that with zero-point energy it rotates with great velocity round this axis, and contains at least one electron which is bound to a place in the molecule situated at a distance from that axis.

According to this hypothesis about the participation of the rotation which we now consider in the thermal equilibrium, at higher temperatures the magnetic moment will begin to increase with temperature, at first slowly, later on more rapidly. WEISS<sup>1)</sup> has actually been led by the observations above the CURIE-point for magnetite, to the hypothesis of a magnetic moment increasing with temperature. A difference with WEISS's views lies in this, that WEISS adopts a discontinuous increase of the molecular magnetic moment in rational proportions, whereas from the above hypothesis one would rather expect a continuous increase of the molecular magnetic moment with temperature. A further investigation will have to show, whether the measurements by WEISS and FOËX regarding this matter cannot be interpreted in this way, in particular for instance with application of the developments of § 3a to the rotational energy which here comes into play.

<sup>1)</sup> P. WEISS, Arch. sc. phys. et natur. (4) 31 (1911) p. 402, § 12.

If we keep in mind that for other substances the moments of inertia about different axes possibly do not differ from each other to such a degree as this seems to be the case with ferromagnetic substances, and that with different ratios of the moments of inertia very different cases can occur for paramagnetic substances also, and if in addition we take into consideration the possibility that according to § 6 there exist substances which possess a molecular field, but not a CURIE-point, there seems room for the further interpretation of different cases met with by DU BOIS, HONDA, and OWEN<sup>1)</sup> in their investigations regarding the susceptibility of elements, and which cannot according to OOSTERHUIS be represented with the assumption of a constant magnetic moment without molecular field.

#### A P P E N D I X.

The following proof of equation (18) of this Communication I was kindly communicated to me by Prof. LORENTZ.

In this appendix the references to sections and equations relate to the article V 14, "Elektronentheorie", in the Math. Encyklopädie. Some notations in this appendix differ from those used in the foregoing communication.

In considering the energy of a magnetized body one can start from two different points of view, viz. one can assume:

A. that the molecular magnets really are permanent magnets (hence that the magnetic moment is not due to rotations or to the circulation of electric charges), or

B. as in § 48e, that the magnetic moment is due to a rotation or to the circulation of electric charges round a definite axis in the molecule.

In both cases the magnetic energy may be put equal to  $\frac{1}{2} \int H^2 dS$ , the integration being taken over the whole space, including the space within the magnets.  $H$  is not the same for the hypotheses A and B. On the assumption A we have to imagine "magnetism" distributed over the magnets, and to calculate the magnetic force due to this magnetism. To this eventually the magnetic force due to electric currents is to be added. On the assumption B we have to deal with the force  $H$ , which, according to the equations of the electron theory, is due to the circulating electricity.

<sup>1)</sup> H. DU BOIS and K. HONDA. Proceedings. Jan. 1910, p. 547. K. HONDA. Ann. d. Phys. (4) 32 (1910), p. 1027. Science Reports Tôhoku University Sendai 1 (1912), p. 1. M. OWEN. Proceedings. Dec. 1911, p. 637. Ann. d. Phys. (4) 37 (1912), p. 657.

Concerning the molecular field we will assume that it consists of couples due to mutual actions of the molecules which are not magnetic actions, and that on the assumption B it is out of the question that the molecular field could change the moment of a magnet by induction. The energy per unit of volume due to the molecular field may be written as

$$-\frac{1}{2} kM^2,$$

if  $kM$  represents the molecular field.

We now follow the reasoning of § 52*a*. Hence we consider a physically infinitely small sphere of volume  $B$  within the magnetized body. The field within it, due to what lies outside it, is indicated by 2, the field due to what lies inside the sphere by 1.

The energy within the sphere due to 2 may be called:  $Ba$ ,  
 that „ „ „ „ „ the superposition of 2 and 1:  $Bb$ ,  
 „ „ „ „ „ „ 1 :  $Bc$ .

In calculating the latter we distinguish:

the own energy of each elementary magnet contained in  $B$  individually; the sum of these may be called  $Bp$ ;

the energy due to the superposition of the fields of the different elementary magnets:  $Bq$ .

We calculate  $p$  and  $q$  for the whole space (outside  $B$  only ether being assumed) and then have to subtract from this sum the energy in the outside space furnished by the elementary magnets that are inside the sphere. Let this be  $Br$ .

Then

$$c = p + q - r.$$

Let further  $BU$  be the energy of the (rotatory) heat motion, which opposes the directing of the particles ( $U$  is reckoned here per unit of volume).

Then the whole energy per unit of volume is:

$$U = a + b + p + q - r - \frac{1}{2} kM^2 + U,$$

By the own energy  $p$  is to be understood that which is due to the constitution of the elementary magnet and to its own field. As on the assumption A nothing ever changes of the elementary magnet,  $p$  is an absolute constant which need not be further considered.

On the assumption B, by  $p$  is understood the energy (magnetic and eventually ordinary kinetic) which corresponds to the rotation round the axis  $a$  (§ 48*e*). This energy is supposed not to be included in  $U$ . As the velocity of that rotation changes by induction,  $p$  is not an absolute constant on this assumption.

According to A as well as to B (cf. § 52*a*):

$$a = \frac{1}{2} \left( H + \frac{1}{3} M \right)^2, \quad r = \frac{1}{9} M^2.$$

In calculating  $b$  and  $q$  we have to distinguish between A and B: Assumption A. In this case formulae are valid which correspond to those which are valid for electrically polarized particles, viz.:

$$b = -\frac{1}{3} M \left( H + \frac{1}{3} M \right), \quad [\text{cf. (150)}]$$

whereas in calculating  $q$  we have to take for each particle [cf. (152)]

$$-\frac{1}{2} (\mathbf{m} \cdot \mathbf{h}_{11}),$$

here  $h_{11}$  is the magnetic force which at the place occupied by one particle is brought about by the remaining particles situated inside the sphere  $B$ ,  $\mathbf{m}$  the magnetic moment of that particle, considered as a vector,  $(\mathbf{a}, \mathbf{b})$  representing the scalar product of two vectors  $\mathbf{a}$  and  $\mathbf{b}$ . If we take the sum for all particles inside  $B$ , we can write

$$q = -\frac{1}{2} M h_{11}.$$

Assumption B. Now [cf. (151)]

$$b = \frac{2}{3} M \left( H + \frac{1}{3} M \right).$$

In calculating  $q$  we have to take for each particle

$$\frac{1}{2} (\mathbf{m} \cdot \mathbf{h}_{11}). \quad [\text{cf. § 52 } a, \gamma].$$

This gives

$$q = \frac{1}{2} M h_{11}.$$

On the assumption B we still have to consider the term  $\nu$ .

For the own energy of a magnet we may write (§ 48*e*)

$$\frac{1}{2} Q g^2,$$

but we must take into consideration, that the angular velocity  $g$  according to equation (140) differs from  $g_0$ . From (140) follows

$$\frac{1}{2} Q g^2 = \frac{1}{2} Q g_0^2 - \frac{g_0 \bar{k} |\bar{\mathbf{h}}| \cos \vartheta}{c},$$

if the second power of the last term in (140) is omitted (if we retained this we should take account of a term which is even smaller than the energy of the weak diamagnetism, which always occurs as a consequence of the appearance of the field and which is superposed on the paramagnetism, respectively ferromagnetism).

To distinguish it from the coefficient of the molecular field the quantity  $k$  of (140) is indicated here by  $\bar{k}$ .

From the formulae of § 15 one finds for the moment of the particle

$$\frac{1}{c} g_0 \bar{k};$$

hence the last term in the above expression becomes

$$-(\mathbf{m} \cdot \mathbf{h}).$$

Here  $\mathbf{h}$  is the whole magnetic force acting on the particle, viz. the LANGEVIN force  $H$  (see below) with the exception of the molecular field  $kM$ . Omitting the constant term  $\frac{1}{2} Qg_0^2$  we find

$$p = -M(H - kM) = -HM + kM^2.$$

Collecting the different terms we obtain according to:

Assumption A.

$$\begin{aligned} U &= \frac{1}{2} \left( H + \frac{1}{3} M \right)^2 - \frac{1}{3} M \left( H + \frac{1}{3} M \right) - \frac{1}{2} M h_{i_1} - \frac{1}{9} M^2 - \frac{1}{2} kM^2 + U_r \\ &= \frac{1}{2} H^2 - \frac{1}{6} M^2 - \frac{1}{2} M h_{i_1} - \frac{1}{2} kM^2 + U_r. \end{aligned}$$

If we write  $H = H + \frac{1}{3} M + h_{i_1} + kM$  for the total force which is to be put into LANGEVIN'S formula, we can also write

$$U = \frac{1}{2} HB - \frac{1}{2} HM + U_r.$$

Assumption B:

$$\begin{aligned} U &= \frac{1}{2} \left( H + \frac{1}{3} M \right)^2 + \frac{2}{3} M \left( H + \frac{1}{3} M \right) - HM + kM^2 + \frac{1}{2} M h_{i_1} \\ &\quad - \frac{1}{9} M^2 - \frac{1}{2} kM^2 + U_r \end{aligned}$$

With the aid of the above expression for  $H$  we find again

$$U = \frac{1}{2} HB - \frac{1}{2} HM + U_r$$

We may combine the different terms of  $H-H$  to one and write it in the form  $k'M$ . There will be no objection to this, if we consider that the term  $k'M$  is by far preponderating. Then

$$H = H + k'M.$$

With this we find

$$U = \frac{1}{2} H^2 - \frac{1}{2} k'M^2 + U_r.$$

The work done on the body at an infinitely small change is

$$H dB$$

The heat to be supplied is then

$$dQ = dU - H dB.$$

This gives

$$\begin{aligned} dQ &= H dH - k'M dM + dU_r - H dB \\ &= -H dM - k'M dM + dU_r \\ &= dU_r - H dM, \end{aligned}$$

which relation agrees with equation (18) of the preceding communication.

**Physics.** — “*Isothermals of monatomic substances and their binary mixtures. XV. The vapour pressure of solid and liquid argon, from the critical point down to  $-206^{\circ}$ .*” By C. A. CROMMELIN. (Communicated by Prof. H. KAMERLINGH ONNES). Comm. N<sup>o</sup>. 138c from the physical Laboratory at Leiden.

§ 1. In this paper the completed results are given of all the observations that I have so far made concerning the vapour pressure

T A B L E I.					
Date	N <sup>o</sup> .	$\theta$ (Celsius in Kelvin degrees)	$p_{\text{coex.}}$ in int. atm.	$p_{\text{coex.}}$ in cm. merc.	
1910. 14 Febr.	X	— 122.44	47.996	3645.1	critical point
14 "	IX	— 122.49	47.890	3637.1	liquid—vapour
12 "	VIII	— 122.70	47.503	3607.7	
9 "	II	— 125.49	42.457	3224.5	
9 "	III en IV	— 129.83	35.846	2722.4	
10 "	V	— 134.72	29.264	2222.5	
10 "	VI	— 140.80	22.185	1684.9	
1912. 29 May	XI	— 150.57	13.707	1041.0	
24 "	XIa	— 161.23	7.4332	564.53	
16 Dec.	XII	— 183.01	1.3369	101.53	
16 "	XIII	— 184.25	1.1794	89.574	
16 "	XIV	— 185.42	1.0451	79.371	triple point
16 "	XV	— 185.90	0.99379	75.475	
17 "	XVI	— 186.98	0.88575	67.270	solid—vapour
17 "	XVII	— 189.30	0.67896	51.565	
18 "	XIX	— 191.36	0.51917	39.429	
18 "	XX	— 194.58	0.33051	25.101	
18 "	XXI	— 197.62	0.21526	16.348	
18 "	XXII	— 206.04	0.088443	6.717	

For the boiling-point of argon under atmospheric pressure, by linear interpolation between observations XIV and XV we find:

$$\theta = -185.84.$$

of solid and liquid argon, besides some results which may be deduced from these observations.

The experimental material now at our disposal is put together in table I. (see p. 487).

The determinations in Febr. 1910 have already been published<sup>1)</sup>, and are only included here to facilitate the complete survey of all the vapour pressure determinations, and because we shall need them in the following discussion of the results.

The observations in May 1912 were made on the occasion of the determinations of the straight diameter<sup>2)</sup>; as regards the apparatus we can therefore refer to the papers concerning this. We need only remark that the pressure determinations were made with an open standard manometer<sup>3)</sup>.

The measurements in Dec. 1912 were made with the apparatus already described<sup>4)</sup> for the determination of vapour pressure at low pressures, which on this occasion also proved highly satisfactory.

As regards this last series of measurements we make the following remarks. Before we proceeded to a measurement we waited until the constancy of the pressure showed that the equilibrium between the phases was established. During this period the temperature was of course kept as carefully as possible constant. The measurement then consisted in reading the manometer and barometer several times alternately. As a rule the pressure in the apparatus remained almost completely constant during a measurement.

The values given for the temperature of the bath of liquid oxygen, boiling under atmospheric and under reduced pressure, in which these measurements were made, were based upon a new comparison of the standard platinum resistance thermometer  $P_{11}$  with the hydrogen and the helium thermometers, shortly to be published by KAMERLINGH ONNES and HOLST. This gives results that differ slightly from the former calibration<sup>5)</sup> but for none of the temperatures are they more than 0.05 and they are of a completely systematic character. The cause of this difference is not yet clear. A direct determination of the difference between the boiling point of argon and of oxygen will throw more light upon it.

<sup>1)</sup> C. A. CROMMELIN, Proceedings May 1910, Comm. No. 115, and Thesis Leiden, 1910.

<sup>2)</sup> E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proceedings Oct. 1912, Comm. No. 131a.

<sup>3)</sup> H. KAMERLINGH ONNES, Proceedings Nov. 1898, Comm. No. 44.

<sup>4)</sup> H. KAMERLINGH ONNES and C. BRAAK, Proceedings Oct. 1908, Comm. No. 107a.

<sup>5)</sup> H. KAMERLINGH ONNES and J. CLAY, Proceedings Sept. 1906, Comm. No. 95c and II. KAMERLINGH ONNES, C. BRAAK and J. CLAY, Proceedings Dec. 1907, Comm. No. 101a.

My thanks are due to Mr. G. HOIST, assistant at the Physical Laboratory, for making these temperature determinations, and for the calculations of the temperatures.

The determination of the triple point was made difficult by the undercooling phenomena which constantly appeared. If, while the temperature was just above the triple point, the temperature was slowly allowed to fall, it repeatedly happened that the whole mass of liquid argon crystallized out. By allowing the temperature to rise and fall with extreme slowness, and waiting patiently for the establishment of the equilibrium, I at last succeeded in establishing a temperature at which the three phases remained in equilibrium with each other for nearly two hours. During this period, the triple point was determined with an admirably constant pressure and temperature. This also gave me an opportunity of observing that the piece of solid argon sank in the liquid, and remained lying at the bottom of the tube, so that *in the triple point the density of solid argon is greater than that of liquid argon*. We shall presently be able to make use of this observation, although I had no opportunity to make a quantitative determination of the density of solid argon. Concerning the calculation of the observation there is nothing particular to remark. An atmosphere in Leiden is reckoned at 75.9488 cm. mercury.

## 2. Representation of the observations by formulae.

In order to get a useful representation of the observations by a formula, I first made use of RANKINE and BOSE's formula

$$\log p_{\text{coex}} = a_{\text{RB}} + b_{\text{RB}} T^{-1} + c_{\text{RB}} T^{-2} + d_{\text{RB}} T^{-3}$$

for the field of liquid-vapour as well as for that of solid-vapour. The result of the testing of the values of the pressure calculated from these formulae by the values observed, are found in table II.

As can be seen in the table, the correspondence is fairly satisfactory, especially in the part liquid-vapour, while it might be further improved for instance by the application of the method of least squares.

In the second place I have tried to apply to my observations NERNST's<sup>1)</sup> vapour pressure formula. We may regard it as a purely empirical formula with 4 coefficients, written in the form

$$\log p = \frac{A}{T} + BT + D \log T + C$$

and then calculate the coefficients which correspond best to the observations, without troubling about the theoretical significance of

<sup>1)</sup> W. NERNST, Göttinger Nachr. 1906, p. 1.

the coefficients. The result of a calculation of this kind is found in table III. The correspondence is considerably better than with RANKINE and BOSE's formula.

In the field of liquid-vapour the correspondence is less good, so that we have omitted the calculation of the results.

TABLE II.				
Liquid-vapour. $a_{RB} = +4.85033$ . $b_{RB} = -634.391$ . $c_{RB} = +30769.09$ . $d_{RB} = -1076464$ .				
$\theta$	$p_{\text{koex. (O)}}$	$p_{\text{koex. (C)}}$	O—C abs.	O—C in %
-122.44	47.996	67.886	+ 0.110	+ 0.23
122.49	47.890	47.797	+ 0.093	+ 0.19
122.70	47.503	47.422	+ 0.081	+ 0.17
125.49	42.457	42.646	- 0.189	- 0.45
129.83	35.846	35.908	- 0.062	- 0.17
134.72	29.264	29.264	0.000	0.00
140.80	22.185	22.289	- 0.104	- 0.47
150.57	13.707	13.707	0.000	0.00
161.23	7.4332	7.3961	+ 0.0371	+ 0.50
183.01	1.3369	1.3397	- 0.0028	- 0.21
184.25	1.1794	1.1825	- 0.0031	- 0.26
185.42	1.0451	1.0470	- 0.0019	- 0.18
185.90	0.99379	0.99492	- 0.00113	- 0.11
186.98	0.88575	0.88473	+ 0.00102	+ 0.12
189.30	0.67896	0.67896	0.00000	0.00
Solid-vapour. $a_{RB} = +8.48993$ $b_{RB} = -849.4767$ . $c_{RB} = -4204.71$ . $d_{RB} = +122.3163$ .				
- 189.30	0.67896	0.68126	- 0.00230	- 0.34
191.36	0.51917	0.51105	+ 0.00812	+ 1.56
194.58	0.33051	0.32861	+ 0.00190	+ 0.58
197.62	0.21526	0.22016	- 0.00490	- 2.28
206.04	0.088443	0.088028	+ 0.000415	+ 0.45

For practical use in the field of liquid-vapour therefore in our case, RANKINE-BOSE'S formula is preferable to NERNST'S. At the same

TABLE III. Solid—vapour.			
$A = + 9034.32. B = - 1.42112. C = - 1014.0278.$			
$D = + 533.0275.$			
$\theta$	$p(O)$	$p(C)$	$O-C$ in %
-189.30	0.67896	0.67764	+0.19
191.36	0.51017	0.51809	+0.21
194.58	0.33051	0.33197	-0.45
197.62	0.21526	0.21526	0.00
206.04	0.088443	0.087942	+0.57

time the following calculation will show that NERNST'S formula, also in the field of liquid-vapour is capable of representing the observations as far as the critical point in a fairly satisfactory way, and in many cases, where the accuracy required is not so very great, may be a convenient help in calculation. I wrote the formula in the more usual form

$$\log p = - \frac{\lambda}{4.571 \cdot T} + 1.75 \log T - \frac{\varepsilon}{4.571} T + C$$

and took for the chemical constant  $C$  in accordance with SACKUR<sup>1)</sup> the value 0.35, so that there now only remain two constants that are to be determined by the observations. With the value of the constants

$$\lambda = + 1385 \quad \text{and} \quad \varepsilon = + 0.01446$$

we get a fairly good correspondence from the critical point down to the triplepoint, in which the deviations in  $p$  are all less than 2%.

Finally I have tried to calculate all the terms of the formula, which SACKUR deduces from the heat theorem of NERNST, from the available calorimetric data, as SACKUR has done for some vapour pressure determinations by RAMSAY and TRAVERS<sup>2)</sup>.

SACKUR writes the vapour pressure formula in the following form

<sup>1)</sup> O. SACKUR, Ann. d. Physik (4) 40 (1913) p. 80.

<sup>2)</sup> W. RAMSAY and M. W. TRAVERS, Phil. Trans. (A) 197 (1901) p. 47.

$$\log p = -\frac{\lambda}{2.3 RT} + \frac{c_p}{R} \log T - \frac{1}{2.3} \int_0^T \frac{c}{T} dT + C + \frac{c_p}{2.3 R}$$

in which  $\lambda$  means the heat of evaporation at the temperature  $T$ ,  $c$  the specific heat of liquid or solid,  $c_p$  the specific heat of the vapour and  $R$  the gas constant (all for a grammolecule of the substance).

I have only made calculations from this formula for the field of solid-vapour. The reason for this will be seen presently.

The measurements of DITTENBERGER<sup>2)</sup> and PIER<sup>3)</sup> both give the value of 4.91 for the molecular specific heat at constant pressure, of gaseous argon at higher temperatures. As in many cases it has been shown that this quantity is conspicuously independent of the temperature, we shall make use of it also for low temperatures.

For  $R$  we assume the value 1.985.

Concerning the value of  $c$  nothing is known experimentally. In order to arrive at a rational estimation, in spite of this, of the integral

$\int_0^T \frac{c}{T} dT$  I calculated the frequency  $\nu$  from LINDEMANN'S<sup>4)</sup> formula.

$$\nu = 2.80 \times 10^{13} \sqrt{\frac{T_0}{Mv_0^{2/3}}}$$

(in which the index 0 refers to the melting point) and then values for  $c$  at the various temperatures by the formulae of NERNST-LINDEMANN<sup>5)</sup> and of DEBIJE<sup>6)</sup>. In the field of temperature with which we have to deal, it makes no difference which of the two formulae we use<sup>7)</sup>.

Finally the values of the integral were determined by the graphic method.

Naturally these calculations could only be made for solid argon, as NERNST-LINDEMANN'S and DEBIJE'S formulae only apply to solid substances.

<sup>1)</sup> l. c. p. 80.

<sup>2)</sup> W. DITTENBERGER, In. Diss. Halle 1897.

<sup>3)</sup> M. PIER, Zeitschr. f. Electrochemie 15 (1909) p. 536.

<sup>4)</sup> F. A. LINDEMANN, Physik. Zeitschr. 11 (1910) p. 609 and W. NERNST and F. A. LINDEMANN, Berl. Sitz. Ber. 1911 p. 494.

<sup>5)</sup> l. c.

<sup>6)</sup> P. DEBIJE, Ann. der Physik. (4) 39 (1912) p. 789.

<sup>7)</sup> Tables for the calculation of  $c$  are published: for the formula of NERNST-LINDEMANN by F. POLLITZER, Die Berechnung chemischer Affinitäten nach dem NERNST'schen Wärmetheorem, Enke, Stuttgart, 1912, p. 162 sqq; for the formula of DEBIJE by W. NERNST, Berl. Sitz. Ber. 1912 p. 1172.

If we take the value 1630 for the molecular heat of evaporation for all the temperatures in the field considered, a value which is chosen with a view to obtaining the best correspondence, and which is not contrary to an extrapolation of the values of  $\lambda$  for the liquid given below then we find the following.

TABLE IV.			
$\theta$	$p(O)$	$p(C)$	O-C in % of O
- 189.30	0.6790	0.6433	+ 5.3
191.36	0.5192	0.5050	+ 2.7
194.58	0.3305	0.3385	- 2.4
197.62	0.2153	0.2351	- 9.2
206.04	0.0884	0.0617	+30.0

The correspondence obtained in this way, may be considered on the whole satisfactory.

I have to thank Mr. W. H. KEESOM for many useful suggestions in connection with these calculations.

### § 3. The triple point.

The triple point constants as observed are given in Table I. Calculation showed that the break of the two curves in argon is in the usual direction. In order to determine the values of  $\left(\frac{dp}{dT}\right)_{\text{coex. vap. liq.}}$  and  $\left(\frac{dp}{dT}\right)_{\text{coex. vap. sol.}}$  at the triple point as sharply as possible, I calculated for the triple point and for the two points lying immediately above and below it, the constants in the formula of WREDE-RANKINE-KEESOM  $\log p_{\text{coex}} = a_{\text{RK}} + b_{\text{RK}} T^{-1} + c_{\text{RK}} T^{-2}$  and by differentiation of this formula, the values of the differential coefficients.

In this way I found

$$\left(\frac{dp}{dT}\right)_{\text{coex. vap. liq.}} = 0.08162; \quad \left(\frac{dp}{dT}\right)_{\text{coex. vap. sol.}} = 0.08623.$$

As may be seen from these values there is a break in the usual direction although very slight.

From the observation already mentioned, that in the triple point

the density of solid argon is greater than that of liquid argon, we may conclude, upon the ground of the general thermodynamical rules<sup>1)</sup>, about the triple point, that the melting curve from the triple point and in the immediate neighbourhood of it will run in the direction of the higher temperatures and pressures.

#### 4. Calculation of the heat of evaporation at different temperatures.

As the density of the liquid and of the saturated vapour is known along by far the greater part of the vapour pressure curve<sup>2)</sup>, we were able to calculate the heat of evaporation for a number of temperatures by the well known equation of CLAPEYRON-CLAUSIUS:

$$\lambda_{\text{liq. vap}} = T \left( \frac{dp}{dT} \right)_{\text{coex.}} (v_{\text{vap.}} - v_{\text{liq.}})$$

For the simplification of the calculations those temperatures were chosen at which the vapour pressure determinations were made. The derivation of the liquid and vapour densities to these temperatures was made by the aid of the formulae that KEESOM<sup>3)</sup> has given for the curve of these densities. They are

$$\begin{aligned} \rho_{\text{liq}} &= \rho_k \{1 + A(1-t) + B(1-t)^2\} \\ \rho_{\text{vap}} &= \rho_k \{1 + A(1-t) - B(1-t)^2\}. \end{aligned}$$

With the constants

$$A = + 0.744537; B = + 1.76408; \lambda = 0.341571$$

and the critical density  $\rho_{\text{crit}} = 0.53078$ <sup>3)</sup> they give a very satisfactory correspondence with the observations, except for the vapour densities at the lowest temperatures, where the percentual deviations become very large. As, however, at these temperatures the vapour densities can be calculated by the ordinary gaslaws, this gives no difficulty.

The values of  $\left( \frac{dp}{dT} \right)_{\text{coex.}}$  were calculated by the formula of RANKINE-BOSE already mentioned.

All quantities were expressed in *C. G. S.* units, and then the whole expression for the heat of evaporation divided by the mechanical equivalent, in order to get the result in calories per degree. The results are shown in table III.

<sup>1)</sup> Cf. H. W. BAKHUIS ROOZEBOOM, Die heterogenen Gleichgewichte, erstes Heft, p. 94.

<sup>2)</sup> E. MATHIAS, H. KAMERLINGH ONNES and C. A. CROMMELIN, Proceedings Oct. and Dec. 1912 and Jan. 1913. Comm. No. 131a.

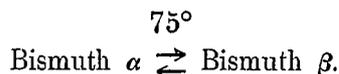
<sup>3)</sup> W. H. KEESOM, Proceedings April 1902. Comm. No. 79. See also J. E. VERSCHAFFELT, Zittingsversl. June 1896, Comm. No. 25 and Proceedings April 1900, Comm. No. 55.

TABLE V. Heat of evaporation of argon.			
$\theta$	$q_{\text{Fvap.}}$	$q_{\text{Flq.}}$	$\lambda_{\text{liq. vap. in cal.}}$
— 125.49	0.28727	0.78303	12.916
— 129.83	0.21451	0.88342	17.821
— 134.72	0.16621	0.96258	21.014
— 140.80	0.12115	1.04134	24.105
— 150.57	0.06854	1.13680	29.672
— 161.23	0.03723	1.22414	33.005
— 183.06	0.00814	1.37338	35.001

In conclusion I offer my hearty thanks to Prof. KAMERLINGH ONNES for the interest which he has taken in my work.

**Chemistry.** — “*The Allotropy of Cadmium.*” I. By Prof. ERNST COHEN and W. D. HELDERMAN.

1. In a paper which will be published in the *Zeitschrift für physik. Chemie* one of us (C.) proved in collaboration with Mr. A. L. TH. MOESVELD, that bismuth is capable of existing in more than one allotropic modification and that there is a transition temperature at  $75^\circ$  of the enantiotropic transformation



In that paper we mention that we had found in a publication of MATTHIESSEN and VON BOSE<sup>1)</sup> (on the electric conductivity of metals, published in 1862) certain indications which justified the presumption that other metals which till now are only known in one modification would show the same behaviour as bismuth (and tin). The following clauses may be quoted from MATTHIESSEN and VON BOSE's paper as referring specially to the metal cadmium:

“Die nach mehrtägigem Erhitzen auf  $100^\circ$  erhaltenen Veränderungen in der Leitungsfähigkeit der Drahte, sind unglücklicher Weise verloren gegangen. Es mag bemerkt werden, dass die Veränderungen sehr gering waren und dass eine Abnahme in der

<sup>1)</sup> POGGENDORFF's *Ann.* **115**, 353 (1862).

Leitungsfähigkeit stattfand", and "Wenn reines Kadmium über 80°C. erhitzt wird, so wird es äusserst spröde, ja, es kann sogar in einem heissen Mörser mit der grössten Leichtigkeit gepulvert werden. Wir würden die Bestimmungen der Drähte nicht haben ausführen können, wenn sie nicht überfirnisst gewesen wären, da sie sonst durch das Bewegen des Oeles beim Umrühren in Stücke zerfallen wären. Es ist bemerkenswert, dass diese Aenderung in der molekularen Beschaffenheit der Drähte nicht irgend erheblich in der Leitungsfähigkeit sichtbar wird."

These remarks formed the starting point of the following research.

2. The experiments on tin and bismuth had proved that metals may show very great retardation in undergoing molecular changes, at temperatures either above or below their transitionpoints. This reluctance to undergo change is doubtless one of the reasons why the allotropy of the metals mentioned above, which play an important role in industry, remained undiscovered until so late a period.

Anticipating our results with cadmium, we state that the same may be said about this metal. Cadmium gives at 65°C. an allotropic (enantiotropic) modification; the very strongly marked retardations have concealed the allotropic change from the numerous investigators who studied this metal in different directions.

3. Until the present we have used two methods of investigation.

*a. Experiments with the Pycnometer.*

The details of these determinations will be described in our paper in the *Zeitschrift für physikalische Chemie*.

We used a form of pycnometer which has already been described (volume about 25 cc.). The thermometers which could be read with an error not exceeding 0°.01 had been compared with a standard of the Phys. Techn. Reichsanstalt at Charlottenburg—Berlin. Generally we used water as a liquid in the pycnometer, but as a control we sometimes substituted paraffineoil for it.

All determinations we carried out in duplicate (using 16—30 grains of the metal). The difference between two of these never exceeded three units in the third decimal place. The metal (Cadmium—"Kahlbaum") was purchased from KAHLBAUM—Berlin. We were not able to detect any impurity in 100 grams of the material. We received it in two consignments (flat rods) which we shall distinguish by the letters  $K_1$  and  $K_2$ .

The density of  $K_1$  we found to be:

$$d_{\frac{25^\circ}{4^\circ}} 8.635; 8.632; 8.633; 8.633 \text{ mean } \mathbf{8.633}$$

in independent determinations, taking fresh quantities each time.

For  $K_2$  we found:

$$d \frac{25^\circ}{4^\circ} 8.641; 8.644; 8.642, \text{ mean } 8.643$$

4. After heating  $K_1$  at a temperature of  $150^\circ$  during 95 hours in a current of dry carbon-dioxide which was freed from oxygen, we found:

$$d \frac{25^\circ}{4^\circ} 8.630 \text{ and } 8.633.$$

These figures show that the density of the metal had not been changed by the heating.

5. As there was a possibility that we had passed a transition point, but that cadmium showed similar retardations to those which we had found in the case of bismuth (and tin), we heated a certain amount of  $K_2$  ( $d \frac{25^\circ}{4^\circ} = 8.643$ ) during 3 days and nights at  $100^\circ$  in contact with a dilute solution of cadmiumsulphate. After this time the metal was chilled (at  $0^\circ$ ) and washed with water, dilute hydrochloric acid (these liquids had been cooled) alcohol and aether. It was then dried at  $30^\circ$ . Two determinations of the density gave:

$$d \frac{25^\circ}{4^\circ} = 8.633 \text{ (and } 8.633)$$

This experiment showed, that by heating at  $100^\circ$  a change had been produced in the metal which lowered its density (measured at  $25^\circ.0$ ) by 10 units in the third decimal place; our duplicate determinations prove that this difference exceeds considerably our experimental errors.

6. In order to determine if a change of density takes place at temperatures below  $100^\circ$ , we warmed the metal ( $d \frac{25^\circ}{4^\circ} 8.633$  and  $8.633$ ) again in contact with a solution of cadmiumsulphate during 14 hours at a temperature of  $60^\circ$ — $70^\circ$ . After the manipulation the metal was chilled, washed, and dried in the manner described above. Its density was now:

$$d \frac{25^\circ}{4^\circ} 8.620,$$

which proves that there occurs at  $60^\circ$ — $70^\circ$  a diminution of the density of 11 units in the third decimal place.

7. We repeated the experiment described in § 6 with the specimen the density of which was now  $d \frac{25^\circ}{4^\circ} 8.620$ , keeping it this time

during 24 hours at 40°. We found:

$$d \frac{25^\circ}{4^\circ} 8.642 \text{ and } 8.643.$$

Its density (taken at 25°.0) showed an increase of 22 units in the third decimal place.

8. The experiment of § 6 was repeated again with the metal that had now a density of  $d \frac{25^\circ}{4^\circ} 8.642$  (8.643) (Vide § 7). After having kept it during 24 hours at 60—70° in a solution of cadmium-sulphate, we found (after chilling, washing etc.):

$$d \frac{25^\circ}{4^\circ} 8.631 \text{ and } 8.633.$$

At 60—70° there has been again a *decrease* of 10 units in the third decimal place.

9. The experiments of § 5—8 prove that there is a transition-temperature between 40° and 70°.

10. In order to fix this temperature more closely, we carried out the following

*b. Experiments with the Dilatometer.*

In order to measure as accurately as possible the changes of volume which the metal undergoes within short times, we used 360 grams of our metal  $K_3$ .

After having reduced the metal to turnings, we heated it during 24 hours in contact with a solution of cadmiumsulphate. The metal was then chilled and washed and transferred into a dilatometer which was then filled with paraffineoil. This had been heated for some hours at 200° (under reduced pressure) in contact with finely divided cadmium, until there was no more evolution of gasbubbles.

In order to reduce as far as possible the quantity of this oil the expansion of which would have made the measurements more troublesome, a quantity of small glass-beads was put into the bulb.

11. The dilatometer was now kept at different but constant temperatures by means of an electrically heated thermostat which we shall describe in full later. The temperatures at which the readings of the meniscus were made, remained constant within 0.002 degrees. (A BECKMANN-thermometer was used in the thermostat). By this device the dilatometer becomes an instrument of precision.

The results are given in the following tables<sup>1)</sup>.

<sup>1)</sup> The capillary tube (diameter of bore 1 mm.) was bent into a horizontal position.

T A B L E I.

Temperature	Duration of the observations in hours.	Rise of the level of oil in mm.	Rise in mm. per hour
49°60	10½	— 1500	— 140
59.60	5	— 233	— 46
60.45	3½	— 66	— 19
62.40	9½	— 74	— 8
64.90	4	0	0
66.90	16½	+ 53	+ 3
84.40	6	+ 267	+ 44

With a second dilatometer we got the following results:

T A B L E II.

Temperature	Duration of the observations in hours.	Rise of the level of oil in mm.	Rise in mm. per hour
62.4°	5½	— 246	— 44
64.7	9	— 59	— 7
64.8	15	— 57	— 4
65.0	4½	+ 32	+ 7

The transition temperature has thus been fixed at **64°.9** within 0.1 degree.

12. It may be pointed out here that the expansion which accompanies the transition of Cadmium- $\alpha$  into Cadmium- $\beta$  (at 64°.9) explains the disintegration of cadmium wires observed at 80° by MATTHIESSEN and VON BOSE.

13. We hope to be able to give shortly the details and conclusions of our research, as well as the values of the density for the two pure modifications of cadmium.

*Utrecht*, October 1913.

VAN 'T HOFF-Laboratory.

(November 27, 1913).

## E R R A T U M.

In the paper *on canonical elements* by Prof. W. DE SITTER in the Proceedings for September:

pages 290—291: From page 290 line 19: “In the same way . . .”  
to page 291 line 21: “We then have”

should be inserted on page 289 between the lines 19 and 20, after  
“...already quoted”.

KONINKLIJKE AKADEMIE VAN WETENSCHAPPEN  
TE AMSTERDAM.

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PROCEEDINGS OF THE MEETING  
of Saturday November 29, 1913.  
VOL XVI.

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*President:* Prof. H. A. LORENTZ.

*Secretary:* Prof. P. ZEEMAN.

(Translated from: Verslag van de gewone vergadering der Wis- en Natuurkundige  
Afdeling van Zaterdag 29 November 1913, Dl. XXII).

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- J. BÖESEKEN and K. H. A. SILLEVIS: "The stability of cyclo hydrocarbons in connection with their configuration. The transformation of cyclo-hexene into benzene and cyclo-hexane." (Contribution to the knowledge of catalytic phenomena). (Communicated by Prof. A. F. HOLLEMAN), p. 499.
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**Physiology.** — “*On hearing-apparatus examined after Lord RAYLEIGH's mode of arrangement.*” By Prof. H. ZWAARDEMAKER.

(Communicated in the meeting of September 27, 1913).

In an earlier publication <sup>1)</sup> we were guided by the principle that, before endeavouring to find a fitting apparatus for a diseased organ of hearing, we should first of all examine its auditory range in the zone  $a_1$  to  $e_3$ . The apparatus has to supply the deficiency of the organ. The experimental part of our previous researches was performed with a microphone (in camera plumbica <sup>2)</sup>) and a string-galvanometer. Lord RAYLEIGH's mode of arrangement is unquestionably a better method.

§ 1. *Non-resonating arrangement.*

ZERNOV placed Lord RAYLEIGH's small mirror<sup>3)</sup> obliquely to the sound-wave and encircled it by a gauze screen. In this way all resonance is prevented; however, the sensitiveness is relatively small. That was why I took an afferent tube of the dimensions of the auditory canal and drew up before it a funnel, whose tone of resonance lies beyond the speechzone and whose mouth corresponds in width with the auricle. Hereby resonance is excluded, except such as the human ear is always subject to. The place where the measuring mirror is suspended corresponds to that of the tympanic membrane, with this difference that in the case of stationary waves, there is always a node on the membrane and a loop on the mirror, for the former is strongly damped by the auditory ossicles, whereas the latter is damped only by the air <sup>4)</sup>.

The width of the artificial auditory canal is 6 mm., the diameter of the mirror, used in the experiment, is 4 mm. It is placed at an angle of 45° immediately in front of the canal. To keep off the streams of air a small plug of cotton-wool is put in the afferent tube. The stopped wooden pipes, sounded with maximum power without causing a deflection or an anomalous vacillation, yield the following results as registered at 1 m's distance in the camera silenta (mirror completely stationary; absence of resonance; the wall of the

<sup>1)</sup> “On hearing-apparatus” Nederl. Tijdschr. v. Geneesk. 1912. II. p. 1101.

<sup>2)</sup> “Eine Camera plumbica für Mikrophone”. Zeitschr. für biol. Technik. Bd. II. S. 340.

<sup>3)</sup> ZERNOV used a magnet to ensure a constant position of rest. I adopted a simpler method by applying a flat Wollaston fibre. (See these Procs. XVI p. 195.

<sup>4)</sup> VIOLLE, Acoustique, 1892, p. 108.

room thickly padded with horsehair):  $a_1$  3 (5),  $ais_1$  5,  $b_1$  1 (3),  $c_1$  1 (5),  $cis_2$  2 (3),  $d_2$  1 (2),  $dis_3$  1,  $e_2$  1,  $f_2$  1,  $fis_2$  1,  $g_2$  3 (2),  $gis_2$  2 $\frac{1}{2}$  (1),  $a_2$  4 (2),  $ais_2$  3 (2),  $b_2$  2,  $c_2$  2,  $cis_3$  1,  $d_3$  1,  $dis_3$  1 (2),  $c_3$  4 (6)<sup>1</sup>.

The procedure is quite simple. At a distance of 1 m. the organ pipe is sounded twice, tone for tone, once with the hearing apparatus, another time with the comparison-funnel. The reinforcement is expressed in the ratios of both numbers.

§ 2. *Hearing-apparatus with selection, without the aid of foreign energy.*

In the publication alluded to above, an endeavour was made to classify hearing apparatus as follows: 1. contrivances substituting a deficient conducting apparatus, 2. apparatus bringing the sound generator nearer to the listener, 3. apparatus affording an enlarged receiving capacity, 4. apparatus reinforcing a certain group of tones, 5. apparatus reinforcing through foreign energy.

For shortness sake only the last two groups are discussed in the present paper.

Most of the ear-trumpets used by deaf people belong to the apparatus mentioned sub 4. In them the reinforcement is occasioned not only by selection, but also by the widening of the receiving surface and by shortening the distance from the speaker. This is a peculiar feature of GUYE'S apparatus, which is largely used in our country. Tested by Lord RAYLEIGH'S mode of arrangement it yields the following results, illustrating the reinforcement of every single tone: (see table 494).

The most reliable of these determinations is the one in the first column. With the old method the results were liable to be misleading in virtue of undue selection of certain tones. With our method this is out of the question, there being no other resonance than that which is always present in the human ear itself (meatus, auricle).

The specimen of GUYE'S apparatus that we examined this time, reinforces the discant of the speechzone; the one investigated in 1912, acted similarly upon the bass as we found by electric measurement. An improved specimen of modern type (copper spiral along the border of the inner receiver, the inside of the latter being covered with velvet) also intensifies the discant more than the bass. It appears that the new models are discant-intensifiers and that their influence is distributed evenly over a wide range. To make assurance double sure, I subjoin the results of a measurement in the camera *silenta*, i.e. free from all room-resonance.

<sup>1</sup>) The figures in brackets apply for determinations made in another room.

GUYE's hearing-apparatus New model of large size (receiving funnel 191 cm<sup>2</sup>).

Table showing how many times the sound is reinforced as compared with a receiving funnel of about the width of the auricle (21 cm<sup>2</sup>).

	Free from resonance. In a common room.	Insertion of an oblique membrane of Japanese rice-papier.	With the aid of micro- phone and string-galvano- meter compared with a circular aperture of 1 cm. diameter.
$e_3$	8	1	25
$dis_3$	19	9	49
$d_3$	50	29	36
$cis_3$	60	14	25
$c_3$	30	11	4
$b_2$	35	11	2
$ais_2$	22	20	2
$a_2$	18	40	2
$gis_2$	20	27	2
$g_2$	30	20	16
$fis_2$	20	23	9
$f_2$	5	4	9
$e_2$	5	9	49
$dis_2$	5	1	12
$d_2$	3	33	9
$cis_2$	2	9	1
$c_2$	2	4	2
$b_1$	3	5	1
$ais_1$	8	6	1
$a_1$	10	3	1

In theory it is especially the average that exceeds considerably the amount of reinforcement generated by enlargement of the receiver. To all appearance this is due to the distribution of the energy and to the peculiar faculty of the resonator to attract sound. This phenomenon is most distinct when we choose hearing-apparatus whose receiver has the width of the comparison-funnel i.e. the width of the auricle.

GUYE's hearing apparatus tested in the camera silenta (its reinforcement compared with a funnel whose width is nine times smaller).

$e_3$ 10	$fis_2$ 62
$dis_3$ 19	$f_2$ 65
$d_3$ 21	$e_2$ 20
$cis_3$ 6	$dis_2$ 2
$c_3$ 30	$d_2$ 2
$b_2$ 34	$cis_2$ 5
$ais_2$ 13	$c_2$ 2
$a_2$ 14	$b_1$ 6
$gis_2$ 18	$ais_1$ 4
$g_2$ 29	$a_1$ 4
average 18	

N.B. Considering the size of the receiver of GUYE's apparatus we could have looked only for a ninefold reinforcement. The actual reinforcement, however, is eighteenfold. This is accounted for partly by the shorter distance from the sound-generator to the measuring apparatus, to a great extent it is attributable also to resonance.

Reinforcing influence of German hearing-apparatus (pleophone n<sup>o</sup>. 2). The receiver has the same width as the comparison funnel. (21 cm<sup>2</sup>).

Measurement in an ordinary room.	
$e_1$ 1	$fis_2$ 6
$dis_1$ 1	$f_2$ 18
$d_3$ 5	$e_2$ 13
$cis_3$ 9	$dis_2$ 10
$c_3$ 33	$d_2$ 4
$b_2$ 25	$cis_2$ 3
$ais_2$ 2	$c_2$ 5
$a_2$ 1	$b_1$ 3
$gis_2$ 2	$ais_1$ 2
$g_2$ 10	$a_1$ 3

N.B. Average reinforcement 7.8 times. However, not nearly so regular as in GUYE's apparatus.

Less conspicuous, but still very distinct is the resonance reinforcement with a number of hearing apparatus I examined some time ago by means of microphone and string-galvanometer and which I have now measured again by Lord RAYLEIGH's mode of arrangement.

Reinforcing influence of German apparatus, compared with that of a control-funnel of 21 cm<sup>2</sup>.

(Measurement in the camera silentia).

	Pleophone N <sup>o</sup> . 3 (receiver 28 cm <sup>2</sup> .)	Cornet	Continophone (width = control- funnel)	Rex (receiver 34 cm <sup>2</sup> .)	Ideal- Taschen
<i>e</i> <sub>3</sub>	1	1	1	1	1
<i>dis</i> <sub>3</sub>	2	2	1	1	1
<i>d</i> <sub>3</sub>	1	1	2	1	1
<i>cis</i> <sub>3</sub>	1	1	1	2	1
<i>c</i> <sub>3</sub>	1	2	1	5	3
<i>b</i> <sub>2</sub>	3	3	1	10	4
<i>ais</i> <sub>2</sub>	5	3	1	<b>16</b>	1
<i>a</i> <sub>2</sub>	9	2	3	15	3
<i>gis</i> <sub>2</sub>	<b>16</b>	1	5	9	3
<i>g</i> <sub>2</sub>	8	6	<b>7</b>	5	13
<i>fts</i> <sub>2</sub>	3	5	2	1	<b>37</b>
<i>f</i> <sub>2</sub>	1	2	3	1	1
<i>e</i> <sub>2</sub>	1	1	4	1	1
<i>d.s</i> <sub>2</sub>	2	10	1	1	1
<i>d</i> <sub>2</sub>	4	<b>70</b>	3	6	1
<i>cis</i> <sub>2</sub>	8	<b>70</b>	5	13	2
<i>c</i> <sub>2</sub>	15	40	18	<b>31</b>	2
<i>b</i> <sub>1</sub>	<b>17</b>	2	<b>27</b>	7	1
<i>ais</i> <sub>1</sub>	13	2	14 5	5	
<i>a</i> <sub>1</sub>	17	5	10 3	3	?
Average	6.4	11.4	5.5	6.7	4

It is remarkable that two maxima of resonance occur in all these apparatus. I suppose there is still a third, very low or very high, and therefore lying beyond the lower or the upper limit of the speechzone. If this is the case it would fall in with the fact that such an apparatus is always composed of two resonating cavities, which invariably yield three maxima, as I pointed out elsewhere <sup>1)</sup>.

As stated before the same apparatus was tested in 1912 with the aid of microphone and string-galvanometer. The reinforcements then detected were of the same order and the resonance-maxima were generally found at the same points (only Ideal-Taschen showed considerable deviation). The common average of electric measurements I found to be 14; of non-resonance measurements 10 in an ordinary room and 7 in the camera silentia.

As to uniformity the reinforcement is far from satisfactory, because the amount of damping of these resonators must not be excessive, of course: considerable damping would destroy the reinforcing faculty.

### § 3. *Hearing-apparatus with foreign energy.*

The average reinforcement produced by resonating hearing-apparatus cannot be strong even without any damping. For a strong intensification electric energy is required. The sound is made to impact on the microphone, which is in circuit with the telephone; hereby the electric energy is converted into acoustic energy. The gain thus effected is sometimes so great, that by potent damping we are enabled to expand the resonance of the membrane, which we have to take to boot.

Thus in a perfect way we readily obtain the average reinforcement of Gurn's apparatus. The following table shows the results of a comparison with the usual control-receiver, whose width is precisely equal to that of the ordinary microphone of aural surgery. The width of the opera-aurophone is  $2\frac{1}{2}$  times as great, because a funnel is placed before the microphone.

Far more striking results can be obtained. Then, however, a noise of "boiling" often reveals itself in the microphone, which is immediately associated with too extensive amplitudes of the sound-vibrations at the highest resonance of microphone- and telephone-membranes, in tune with each other. During the measurement this disturbance expresses itself in a restless to- and fro motion of the mirror. As yet no damping contrivance has been devised to overcome this disorder.

<sup>1)</sup> "Multiple resonance" Ned. Tijds. v. Geneesk. 1913 II p. 647. When trying to detect the 3<sup>rd</sup> maximum in the pleophone I found it lying rather beyond  $e_3$ .

Reinforcement of electric apparatus, determined in  
non-resonant arrangement.

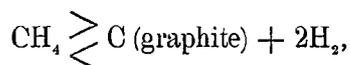
	Megalophone of FLATAU	Opera-aurophone
<i>e</i> <sub>3</sub>	35	100
<i>dis</i> <sub>3</sub>	35	50
<i>d</i> <sub>3</sub>	25	60
<i>cis</i> <sub>3</sub>	25	75
<i>c</i> <sub>3</sub>	25	100
<i>b</i> <sub>2</sub>	25	150
<i>ais</i> <sub>2</sub>	15	156
<i>a</i> <sub>2</sub>	1	140
<i>gis</i> <sub>2</sub>	15	40
<i>g</i> <sub>2</sub>	10	165
<i>fis</i> <sub>2</sub>	2	110
<i>f</i> <sub>2</sub>	7	80
<i>e</i> <sub>2</sub>	10	140
<i>dis</i> <sub>2</sub>	17	120
<i>d</i> <sub>2</sub>	13	120
<i>cis</i> <sub>2</sub>	16	34
<i>c</i> <sub>2</sub>	25	24
<i>b</i> <sub>1</sub>	18	30
<i>ais</i> <sub>1</sub>	13	70
<i>a</i> <sub>1</sub>	11	23
Average:	17.5	80

Together with the so-called accessory noises (crackling) it materially limits the use of the electric hearing-apparatus.

**Chemistry.** — “*The stability of cyclo hydrocarbons in connection with their configuration. The transformation of cyclo-hexene into benzene and cyclo-hexane.*” (Contribution to the knowledge of catalytic phenomena). By Prof. J. BÖESEKEN and K. H. A. SILLEVIS. (Communicated by Prof. A. F. HOLLEMAN.)

(Communicated in the meeting of October 25, 1913).

1. When studying the stability of hydrocarbon compounds below 400° and in the presence of catalysts account must be taken of the fact that under those circumstances there is only one real stable equilibrium<sup>1)</sup> namely



which, below 400°, is practically situated entirely at the methane side.

Hence, if this gas is generated from an arbitrary hydrocarbon, this will be a proof that the catalyst employed is capable of causing the real equilibrium under the conditions of the experiment.

Experience has now taught that under the influence of definite conditions, transformations may occur and equilibria be possible without methane being evolved or carbon being separated.

All these latter equilibria are metastable and the possibility of their realization is closely connected with a judicious choice of conditions and catalyst. In order to choose properly we must first ask which catalysts are the most suitable for definite changes.<sup>1)</sup>

In the hydrocarbons we are dealing with three kinds of bonds: the C-C-, the C-H-, and the H-H-bond. In order to attain the real equilibrium the catalyst must be able to exert an action on all bonds (to effect a dislocation<sup>2)</sup>) which is only possible when, under the conditions of the catalysis, it does not unite to form stable compounds with the elements or combinations thereof which are to be “activated”.

On the other hand they should be substances which, under somewhat modified conditions, can unite with carbon as well as with hydrogen (H. J. PRINS).<sup>3)</sup>

<sup>1)</sup> M. MAYER and V. ALTMAYER, B **40**, 2134 (1907); v. WARTENBERG Z. ph. Ch. **61**, 366 (1908) **63**, 269 (1909).

<sup>2)</sup> I refer to the dissertation from H. J. PRINS, Delft 1912, wherein, supported by the principle of reciprocity, he has endeavoured to give an explanation of the catalytic phenomena.

<sup>3)</sup> Recueil **29**, 86 (1910).

Substances which are most suitable for this purpose are metals which form carbides as well as hydrides. Their catalytic action will be the most powerful<sup>1)</sup> in the region where these combinations exist in a condition of dissociation, where, consequently the "activation" is greatest without the catalyst being paralyzed by too great a chemical action.

To these metals appear to belong in the first place nickel and cobalt (MAYER and ALTMAYER l.c.); to their action must be attributed the fact that during the hydrogenations according to SABATIER and SENDERENS<sup>1)</sup> considerable quantities of methane are often formed.

The activating power of a catalyst will, however, have to be unequal, under the same conditions, for each of the bonds, because the dissociation regions of the carbides and the hydrides will not as a rule coincide, and experience has taught that nickel is eminently suited for the hydrogenation of hydrocarbons without methane being evolved, if only we keep below  $\pm 240^\circ$ .

Hence, the C-C-activation of nickel at the ordinary pressure only appears to become appreciable above that temperature, which we may call the catalytic limit for that bond. Little is known of the limit of the hydrogen activation of nickel, which seems to be greatly dependent on the condition of the metal, anyhow the temperatures at which this activation becomes important and the hydrocarbon activation limit do not diverge greatly.

In the case of other metals these limits may differ more seriously. This is shown in a very convincing manner from the research of ZELINSKY<sup>2)</sup>. He demonstrated that palladium black, which at  $0^\circ$  is an excellent hydrogen "activator" did, at  $300^\circ$ , resolve cyclo-hexane into benzene and hydrogen only; the catalytic limit of palladium black for the C-C-bond of cyclo-hexane is therefore situated above  $300^\circ$ .

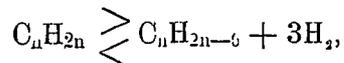
Hence, if we wish to study the resolving or combining reactions of a hydrocarbon and hydrogen, palladium black is the catalyst *per excellence*.<sup>3)</sup>

<sup>1)</sup> Compare Ann. Ch. et Ph. [8] 4, 336 (1905).

<sup>2)</sup> B 44, 3122 (1911); 45, 3678 (1912).

<sup>3)</sup> In reality, at least two bonds are activated simultaneously, for instance the C-H and the H-H bond or the C-C and the other bonds; in order not to become too prolix we will distinguish provisionally the carbon and hydrogen activation only. Under carbon activation I, therefore, understand here the influence which is not limited to causing a dislocation but leads to a dissociation of the saturated carbon-carbon bond. Before this point is attained some activation still takes place but this can lead at most to linking and splitting off of hydrogen; hence to simplify matters I am speaking in that case only of hydrogen activation.

2. By this happy choice of catalyst, ZELINSKY showed that benzene and cyclo-hexane, at  $\pm 200^\circ$  and at the ordinary pressure, are related according to the mobile equilibrium:



which, above  $300^\circ$  is shifted entirely in the direction of benzene and hydrogen, and below  $170^\circ$  wholly in the direction cyclo-hexane.

From this follows that at  $300^\circ$  cyclo-hexane is *supersaturated*, that six carbon atoms which are linked together are no longer *tetravalent* but *trivalent* in regard to the hydrogen. It is true the benzene at the ordinary temperature is unsaturated for hydrogen, but if we take into consideration that the decomposition of cyclo-hexane starts at  $170^\circ$  that unsaturation cannot be considerable.

The knowledge of this equilibrium enables us to understand why the aromatic compounds are reduced with difficulty and why they behave somewhat like saturated hydrocarbons; without a catalyst like palladium black we could not have elucidated the matter experimentally.

Nickel would have been less suitable because below  $100^\circ$  it is but little hydrogen-active and also because not far above  $300^\circ$  it becomes too much carbon-active.

One of us <sup>1)</sup> has pointed out that the great general stability of the aromatic compounds, to which belongs this little-pronounced unsaturation, can be deduced from the "Werner principle of affinity distributed evenly in space" when we take into consideration the extraordinary favourable steric distribution of the atoms. This stability can differ very little from that of the hydroaromatic compounds because the distribution in space is more favourable.

He also considered the question why, in substitutions in the benzene nucleus the additive products to be expected have as yet not been isolated. These ought to be derivatives of di- or tetrahydrobenzene.

If we consider these hydrocarbons themselves we notice that here is found an unequal distribution of the unsaturation as well as of the atoms in space; in the presence of suitable catalysts they ought to be converted more readily into benzene or cyclo-hexane than the two latter into each other.

Guided by these considerations we have studied in the first place the behaviour of cyclo-hexene. As stated above, this hydrocarbon

<sup>1)</sup> Proc. March 1912.

will not only be much more unsaturated than benzene, which fact has long been known, *it must also be much more supersaturated than cyclo-hexane and be converted into benzene under conditions where cyclo-hexane does not yet lose hydrogen* thus, for instance at 180° and in the presence of a suitable catalyst. For this purpose we have passed cyclo-hexene over nickel at 180° in a current of carbon dioxide and indeed obtained a considerable quantity of benzene (with cyclo-hexane)<sup>1)</sup>.

The labile cyclo-hexene will begin to split into benzene and hydrogen :



but this hydrogen will subsequently form cyclo-hexane with the still undecomposed cyclo-hexane; the whole process thus progresses:



Hence, according to this equation a mixture of 33.3% of benzene and 66.6% of cyclo-hexane should have formed; in reality we found about 40% of benzene while 2 à 4% of cyclo-hexene had remained unchanged; the remainder consisted of cyclo-hexane.

The fact that too much benzene has been found here may be due to different causes. First of all, the decomposition of cyclo-hexane into benzene and hydrogen starts already at 180° (ZELINSKY l.c.); true, we have found no hydrogen in the reaction products but we found CO, which may have been generated by reduction of the CO<sub>2</sub>.

This formation of CO points, however, to the fact that, in this case, the CO<sub>2</sub> must not be looked upon as an indifferent gas, so that the experiments will have to be repeated in a current of nitrogen. Although the vapours evolved were cooled by means of solid carbon dioxide and alcohol there is still a chance that a little has been lost by evaporation which may also be a possible source of an excess of benzene.

*In any case the supersaturation of the system C<sub>6</sub>H<sub>10</sub> in regard to C<sub>6</sub>H<sub>6</sub> + 2 H<sub>2</sub> has been proved sufficiently.*

It now speaks for itself that, in the hydrogenation of benzene according to SABATIER and SENDERENS, substances like cyclo-hexane — even supposing them to be actual intermediate products — cannot be retained. When they are converted almost completely into benzene and cyclo-hexane in an atmosphere of CO<sub>2</sub> nothing is to be expected, in presence of an excess of hydrogen, but cyclo-hexane mixed

<sup>1)</sup> For this we have chosen for practical reasons nickel and not palladium particularly because, as a matter of fact, we kept far below 240°.

At the ordinary temperature Pd. and Pt. were not active enough to promote the transformation.

eventually with benzene (if working above 180°) and with methane if working above 240°.

3. As regards the experimental part, the cyclo-hexane was prepared from cyclo-hexanol<sup>1)</sup> by slowly distilling this, according to BRUNEL<sup>2)</sup>, with dried and powdered KHSO<sub>4</sub> (80 grams to 200 grams of C<sub>6</sub>H<sub>11</sub>OH) from a flask with a high adapter and then fractionating the distillate:

A liquid Bp.<sub>76</sub> = 82°.5—83°.5 ; D<sub>4</sub><sup>20</sup> = 0.8120 ; n<sub>D</sub><sup>18</sup> = 1.44617 was obtained.

In glacial acetic acid it rapidly took up bromine so that in presence of benzene and cyclo-hexane it could be titrated with the same.

260,4 mg. of cyclo-hexene mixed with 1 gr. of C<sub>6</sub>H<sub>6</sub> and 2 gr. of C<sub>6</sub>H<sub>12</sub>,  
consumed 510 mg. of Br<sub>2</sub> calculated 508 mg.  
298.6 gr. with 1.5 gr. of C<sub>6</sub>H<sub>6</sub> and 1 gr. of C<sub>6</sub>H<sub>12</sub>,  
consumed 584.5 mg. of Br<sub>2</sub>, calculated 582 mg.

Subsequently a certain weight was passed slowly and in a feeble current of CO<sub>2</sub> over active nickel heated at 180°. We used the apparatus that had been employed for the decomposition of oenanthol<sup>3)</sup> with this understanding, however, that the CO<sub>2</sub> was first carefully freed from oxygen and that the vapours leaving the electric oven were first cooled by ice and salt and then by alcohol and solid carbon dioxide to be finally drawn into an aspirator. The cyclo-hexene was dropped at the beginning of the oven from a small capillary pipette in such a manner that the minute droplets arrived in the tube at the spot where the carbon dioxide was introduced.

First of all, the products obtained were tested qualitatively.

The liquid obtained had a pronounced odour of benzene, whereas the characteristic odour of the hexene had all but disappeared; it was cautiously nitrated with a mixture of sulphuric and nitric acid, the product obtained after being washed was fractionated; the fraction passing over below 100° was freed from nitrobenzene by means of tin and hydro-chloric acid; it now distilled at 80°, solidified at 5°,5 and had the agreeable odour of cyclo-hexane.

The fraction boiling above 100° was converted into aniline and identified as such.

A few quantitative determinations were then made, that is to say, it was determined how much bromine was taken up in a glacial

<sup>1)</sup> This latter according to HOLLEMAN Recueil 24, 21 (1905).

<sup>2)</sup> Bull. [3] 33, 270, also WILLSTÄTTER B. 45, 1464 (1912).

<sup>3)</sup> Recueil 32, 27 (1913).

acetic acid solution in order to ascertain the content of unchanged cyclo-hexene; the hydrogenation figure was then determined according to WILLSTATTER'S method, with active-platinum in glacial acetic acid from which, after deducting the hydrogen required for the reduction of the cyclo-hexene, the benzene content could be deduced, and finally the density and refraction were determined by way of control.

The subjoined table gives a survey of the results obtained.

T A B L E.

Substance	Bromine number expressed in mg. P. gram of substance	Reduction number expressed in cc. H <sub>2</sub> per gr. of substance	Condition of the product calculated therefrom			$d_4^{20}$		$n_D^{20}$	
						found	calculat.	found	calcul.
Cyclohexene	1950	270	—			0.8120		1.44617	
Benzene	0	852	—			0.8790		1.50042	
Cyclohexane	0	0	—			0.7810		1.42691	
			C <sub>6</sub> H <sub>10</sub>	C <sub>6</sub> H <sub>6</sub>	C <sub>6</sub> H <sub>12</sub>				
Reaction prod. I	68	345	3.5%	39.4%	57.1%	0.8194	0.8207	1.46161	1.4564
" " II	77	376	4.0%	41.7%	54.3%	0.8189	0.8231	1.46310	1.4583
" " III	95	—				0.8153		1.45962	

The gas drawn into the aspirator contained considerable quantities of carbon monoxide; methane was not present.

4. In our general consideration we have assumed that at 180° and in the absence of an excess of hydrogen, benzene and cyclo-hexane only could be present in admixture with methane; we must, however, also keep account of the presence of methylcyclo-pentane, the isomer of cyclo-hexane with the stable saturated 5-ring.

Nothing is known as to the relation of these two isomers at the ordinary pressure.

ASCHAN<sup>1)</sup> certainly has found that from 70 grams of C<sub>6</sub>H<sub>12</sub>, after this had stood for two days with 140 grams of anhydrous AlCl<sub>3</sub> and was then boiled for 48 hours — were obtained 2.5 grams of a fraction boiling below 78°, which fraction was saturated and possessed the general formula C<sub>n</sub>H<sub>2n</sub>; from this we can at most draw the conclusion that it may have contained methylcyclo-pentane and that the two isomers may be capable of existing for

<sup>1)</sup> Ann. 324, 12 and 85 (1902).

some time in the presence of an immense excess of aluminium chloride.

A transformation of cyclo-hexane or of a mixture of benzene and hydrogen into methylcyclo-pentane at a high pressure and temperature has been observed, however by IPATIEV and KIZNER.

IPATIEV<sup>1)</sup> heated quantities of 40 grams of  $C_6H_{12}$  with 3 grams of  $Al_2O_3$  at 500—510° and under a pressure of 70 atm. and could liberate from a total of 700 grams a little of the cyclo-pentane derivative; in addition a great many aromatic compounds and unsaturated hydrocarbons had formed.

Also this experiment does not say much more but that the hydrocarbons are possible in presence of each other which, moreover, does not signify much as, like in ASCHAN's investigation, there is here no question whatever of an equilibrium attained. Both experiments prove that  $Al_2O_3$  and  $AlCl_3$  are bad catalysts for the saturated carbon-carbon bond, which could not be expected to be otherwise<sup>2)</sup>.

Of much more importance is the observation that benzene is converted into methylcyclo-pentane when it is heated at 280° in a sealed tube with an excess of HI<sup>3)</sup> because from this it follows that at 280° and under pressure the cyclo-pentane derivative is more stable than the cyclo-hexane or the mixture of  $C_6H_6$  and hydrogen.

Of a pure catalysis there is, however, also no question in this case as a very large excess of III and I, has been employed here; moreover, this superior action of iodine over  $AlCl_3$  is in harmony with the fact that the element can unite with hydrocarbons as well as with hydrogen to form dissociable compounds under conditions which are not far removed from that of the discussed transformation (H. J. PRINS l.c.)

In order to study the relation of the two isomers at the ordinary pressure we will have to choose in any case a C-C-activator such as nickel even if we run the risk that a part of the system attains the methane equilibrium.

The fact that not much methylcyclo-pentane can have formed in the transformation of the cyclo-hexene into benzene and cyclo-hexane at 180° as studied by us, is, moreover, shown from the

<sup>1)</sup> B. 44, 2987 (1911).

<sup>2)</sup> On the other hand the large quantities of higher condensation products of an aromatic character show that  $AlCl_3$ , in particular, activates the unsaturated bonds. As soon as a saturated hydrocarbon begins to lose hydrogen, under the influence of  $AlCl_3$  this property must lead to the actually observed complications.

<sup>3)</sup> N. N. KIZNER. Cent. Bl. 1897 II, 344.

figures found for density and refraction. These are for the naphthène:  $d_4^{19.5} = 0.7488$  and  $n_D^{19.5} = 1.4096$  <sup>1)</sup>, hence, much smaller than that of cyclo-hexene.

Now, the densities found by us are certainly somewhat below the calculated ones, but on the other hand the indices of refraction are somewhat higher. Moreover, the product freed from benzene by nitration had almost the true solidifying point of cyclo-hexane whereas this suffers a very strong depression by the presence of admixtures <sup>2)</sup>. Hence, after the nitration, these cannot have been present in quantities exceeding 1 %.

### S U M M A R Y.

1. Cyclo-hexene at 180° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and cyclo-hexane.
2. Cyclo-hexane at 300° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and hydrogen (ZELINSKY). Six cyclo-combined carbon atoms are then trivalent in regard to the hydrogen.
3. Cyclo-hexene at 180° and ordinary pressure is metastable in regard to the corresponding mixture of benzene and hydrogen.
4. Cyclo-hexene is more strongly *supersaturated* with hydrogen than cyclo-hexane.
5. Probably, methylcyclo-pentane at 280° and under pressure is more stable than the corresponding mixture of benzene and hydrogen or cyclo-hexane.
6. Nickel is, in the first place, a hydrogen activator; the carbon activation becomes only considerable at 240°; at 180° this latter action in regard to the first may be neglected.
7. Palladium is an excellent hydrogen activator, the carbon activation may still be neglected at 300° (ZELINSKY).
8. Iodine at 280° and under pressure is presumably a strong hydrogen and a feeble carbon activator <sup>3)</sup>.

<sup>1)</sup> ZELINSKY. B. 35, 2684—86 (1902).

<sup>2)</sup> MASCARELLI states a molecular depression of about 200 (Atti R [5] 16 I 924 (1907); this value we obtained also in the determination of the melting line of the system  $C_6H_6-C_6H_{12}$  which consequently takes a very asymmetric course.

<sup>3)</sup> See Pat. Kl-o 250236 3/8 1910, Zentr. Bl. 1912 II 1084.

**Meteorology.** — “*On the relation between the cloudiness of the sky and the duration of sunshine*”. By Dr. J. P. VAN DER STOK.

(Communicated in the meeting of September 27, 1913).

1. The subject, mentioned in the title, has but rarely and then cursorily been discussed in meteorological textbooks, periodicals and monographs, and the fact that the sum of degree of cloudiness and duration of sunshine, expressed in percentages and considered for monthly or seasonal means, differs little from 100, is then regarded as a satisfactory result concerning both methods of observing the covering of the sky.

From observations taken during many years and for three European stations in different climates we find:

	Hamburg <sup>1)</sup>		Pola <sup>2)</sup>		Potsdam <sup>3)</sup>		Ham- burg	Pola	Pots- dam
	B	S	B	S	B	S	T	T	T
Winter	79%	14%	56%	37%	63%	31%	93%	93%	94%
Spring	63	33	49	49	63	36	96	98	99
Summer	66	31	34	69	59	45	97	103	104
Autumn	71	22	49	48	64	30	93	97	94
Year	70	25	47	51	65	33	95	98	98

B = Cloudiness, S = Duration of Sunshine, T = B + S.

In fact it does seem natural that, to a certain extent, the one factor is complimentary to the other; if the degree of cloudiness is a hundred or zero, the duration must certainly be resp. zero and a hundred, and as in temperate climates these extreme cases often occur, it is natural that the sums do not differ much from 100. From monthly means of cloudiness and duration of sunshine we find for the five Dutch stations the numbers of table I, calculated from or reduced to the period 1900—1911.

From these results it appears that, in general, the sum increases with the sun's height; in summer the sum is nearly a hundred, in winter not more than 86 and only at Helder it remains considerably

<sup>1)</sup> KÖNIG. Dauer des Sonnenscheins in Europa. Nova Acta, K. Leip. Car. D. Ak. d. Naturf. Bd. 67, n<sup>o</sup> 3, 1896.

<sup>2)</sup> FRIEDEMANN. Bewölkung und Sonnenschein des Mittelmeergebietes. Aus dem Arch. d. D. Seewarte. Bd. 36, 1913.

<sup>3)</sup> MEISZNER. Das Wetter. 1907 en 1910.

TABLE I.

Sums of cloudiness and duration of sunshine, Monthly means.

	De Bilt	Helder	Groningen	Vlissingen	Maastricht	Mean
January . . .	90	80	90	83	86	85.8
February . . .	90	83	94	87	90	88.8
March . . .	93	80	91	89	87	88.0
April . . . .	97	84	99	93	91	92.8
May . . . . .	100	88	102	94	95	95.8
June . . . . .	99	89	99	94	92	94.6
July . . . . .	99	88	98	92	92	93.8
August . . . .	101	90	99	93	95	95.6
September . .	95	82	94	90	88	89.8
October . . . .	92	80	90	86	88	87.2
November . . .	91	80	91	80	86	85.6
December . . .	88	80	90	82	86	85.2
Year . . . . .	97	86	97	91	92	92.6

behind the full percentage in every month. However, it is well known, (as an inspection of the hourly values given in annals also proves) that the sunshine-recorders do not register until some time after sunrise and leave off registering before sunset, so that all average values (but mostly those of the wintermonths when the total amount of sunshine is small) must be too low and that to a considerable extent.

Monthly means therefore are certainly not likely to give a proper idea of the relation between cloudiness and duration of sunshine so that in order to come to a better understanding we employ observations taken at a time when we are sure of the undisturbed influence of the sun; as the cloudiness is observed at 8 a.m., 2 p.m and 7 p.m, it is the afternoon observation which is indicated for this investigation.

As shown by tables II and III, the sum is then considerably higher than 100% for all five stations with the exception of winter for Helder and of December for all stations.

From the fact that in June and July, when the sun is highest, the sums are almost equal for all stations, we may conclude that individual conceptions in estimating the cloudiness play a subordinate

TABLE II.  
Mean Cloudiness and duration of sunshine, 2 p m, 1909—1911.

	Helder		Groningen		De Bilt		Vlissingen		Maastricht	
	Clouds	Sun								
January . . .	66 <sup>0</sup> / <sub>100</sub>	25 <sup>0</sup> / <sub>100</sub>	78 <sup>0</sup> / <sub>100</sub>	27 <sup>0</sup> / <sub>100</sub>	70 <sup>0</sup> / <sub>100</sub>	35 <sup>0</sup> / <sub>100</sub>	74 <sup>0</sup> / <sub>100</sub>	30 <sup>0</sup> / <sub>100</sub>	75 <sup>0</sup> / <sub>100</sub>	28 <sup>0</sup> / <sub>100</sub>
February . . .	69	27	76	28	70	33	73	34	78	26
March . . .	66	37	77	32	70	46	70	36	75	37
April . . .	57	54	73	42	64	55	60	55	67	51
May . . .	46	65	65	61	60	60	50	69	67	48
June . . .	61	52	72	41	71	45	65	48	76	37
July . . .	57	56	75	39	69	48	64	50	72	38
August . . .	53	57	70	50	59	63	53	61	62	51
September . . .	62	47	74	42	66	52	62	50	63	50
October . . .	69	32	74	34	66	48	67	40	71	37
November . . .	72	19	76	32	72	33	71	25	78	25
December . . .	78	10	83	10	79	22	79	16	79	15
Year . . .	63	40	74	36	68	45	66	43	72	37

TABLE III.  
Sum of Cloudiness and duration of sunshine, 2 pm., 1909—1911.

	Helder	Groningen	De Bilt	Vlissingen	Maastricht	Mean
January . . .	91	105	105	104	103	101.6
February . . .	96	104	103	107	104	102.8
March . . .	103	109	116	106	112	109.2
April . . .	111	115	119	115	<b>118</b>	115.6
May . . .	111	<b>126</b>	<b>120</b>	<b>119</b>	115	118.2
June . . .	113	113	116	113	113	113.6
July . . .	113	114	117	114	110	113.6
August . . .	110	<b>120</b>	<b>122</b>	114	<b>113</b>	115.8
September . . .	109	116	118	112	113	113.5
October . . .	101	108	114	107	108	107.6
November . . .	91	108	105	96	103	100.6
December . . .	88	93	101	95	94	94.2
Year . . .	103	111	113	109	109	108.9

part and that the differences as shown in these tables must be ascribed rather to the nature of the clouds than to this reason.

When treated in this way several peculiarities are observed which remain concealed when daily means are used e.g. the fact that near Helder the cloudiness is smaller than at de Bilt, whereas de Bilt shows 5 % more of sunshine.

Furthermore these tables show that in wintertime also, when the sun's elevation is very small (in January for 52° L. N. and 2 p. m. the sun's height is only 12.25°), the sums mostly exceed 100 %.

If we do not wish to ascribe the different relations at de Bilt and Helder, characterized by a difference of 10 % in the sums for the whole year, on the one hand to a difference in the estimate of cloudiness or, on the other hand, to instrumental unequalities, an explanation of these phenomena is required.

That the sum of cloudiness and duration of sunshine is more than 100 % and that this fact is not shown in monthly means because two opposite causes neutralize each other, has also been remarked by others e.g. by BESSON and COEURDEVACHE<sup>1)</sup>.

We can now take a further step and, from the frequent occurrence of extreme values, conclude that also the numbers of tables II and III cannot be considered as a proper measure for the relation between cloudiness and duration of sunshine and we may expect that the sums must be considerably larger for average values of cloudiness.

This conclusion is fully confirmed by the data of tables IV and V, giving the results of a classification of percentages of sunshine's duration according to those of cloudiness. Table V is printed as an example of the way in which different combinations may occur.

Although the numbers of table IV do not everywhere show a regular course, they clearly demonstrate that the sums of cloudiness and duration of sunshine may amount in summer to more than 130, in winter to more than 110 %.

In this communication the disagreements between different stations are not taken into consideration and the question is restricted to the problem: how to explain the absolute values, the differences between summer and winter and the position of the maxima as shown in table IV for the station de Bilt only.

2. In order to find a possible relation between the results of both methods of observing the covering of the sky, it is in the first place necessary to consider, what is understood by the term "degree

<sup>1)</sup> Ann. Soc. Météor. de France, 56, 1908 (73).

TABLE IV

Sums of cloudiness and duration of sunshine in percentages  
De Bilt, 2 pm. 1900—1911

Cloud- iness	Jan. Dec.	Febr. March	April May	June July	Aug. Sept.	Oct. Nov.
0	89	98	100	100	100	99
1	108	107	110	110	108	105
2	111	104	119	118	119	110
3	107	117	123	128	126	115
4	94	119	125	131	130	109
5	92	116	125	127	127	107
6	98	112	124	124	122	111
7	93	110	124	118	120	102
8	91	97	103	103	102	97
9	94	97	96	100	99	95
10	101	101	104	102	104	101
Mean	98	104	112	114	114	103
Number observ.	738	714	732	732	732	730

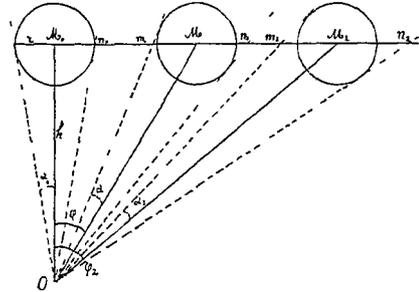
TABLE V.

Frequency of cloudiness and duration of sunshine.  
De Bilt 2 pm. 1900—1911. June and July.

Cloud- iness	Duration of sunshine.										Number	Mean duration of sunshine		
	0	1	2	3	4	5	6	7	8	9			10	
0	—	—	—	—	—	—	—	—	—	—	—	15	15	100.0 %
1	—	—	—	—	—	—	—	—	—	—	—	32	32	100.0
2	—	—	1	—	—	—	—	—	1	—	—	46	48	97.9
3	—	—	—	—	—	—	1	1	—	3	—	58	63	98.4
4	—	—	—	1	—	1	4	—	7	5	—	32	50	90.6
5	1	2	2	1	3	3	3	4	7	9	—	23	58	77.4
6	5	4	5	5	5	4	7	8	5	8	—	22	78	64.0
7	13	8	9	11	4	4	16	3	15	6	7	—	96	47.5
8	38	11	17	11	5	6	3	4	—	5	1	—	101	22.7
9	58	9	5	3	4	4	2	—	1	—	—	—	86	9.8
10	91	9	4	—	1	—	—	—	—	—	—	—	105	2.0
Sum	206	43	43	32	22	22	36	20	36	36	236	732		51.2

Mean cloudiness 62.6 %

of cloudiness", and, if possible, to substitute a simpler definition, suitable for mathematical treatment, for this evidently complicated conception.



In fig.(1) the plane of the drawing represents a plane going through the observer in  $O$  and the zenith in  $M_0$ ; the circles are projections of spherical clouds upon this plane, the diameter of the clouds is denoted by  $d$ , their mutual distance by  $\Delta$ .

Fig. 1.

The apparent proportion of white to white and blue in the sky will be different according to the part of the arc  $\varphi_1, \varphi_2 - \varphi_1, \varphi_{n+1} - \varphi_n$  considered; obviously the apparent cloudiness of the  $n^{\text{th}}$  order is

$$\frac{\alpha_{n+1} + \alpha_n}{\varphi_{n+1} - \varphi_n}$$

As we have here to do with proportions, and angular values are unsuitable for mathematical treatment, we substitute for the projection upon the sky-arc the projection upon the straight line  $M_0 M_1 \dots M_n$ ; then the apparent cloudiness is defined as:

$$S_n = \frac{M_{n+1} m_{n+1} + M_n n_n}{M_{n+1} M_n} = \frac{d \cos(\varphi_{n+1} - \alpha_{n+1}) + \cos(\varphi_n + \alpha_n)}{\Delta 2 \cos(\varphi_{n+1} - \alpha_{n+1}) \cos(\varphi_n + \alpha_n)}$$

Here  $\frac{d}{\Delta}$  denotes the true cloudiness  $W$  of the sky, the cloudiness being defined as a proportion between linear quantities. When the spheres are not very large we can assume an average value for  $n$  and  $n + 1$ , and the apparent cloudiness of the  $n^{\text{th}}$  order becomes:

$$S_n = W \frac{\cos \varphi_n \cos \alpha_n}{\cos^2 \varphi_n - \sin^2 \alpha_n}$$

or, as  $\sin \alpha_n = \sin \alpha_0 \cos \varphi_n$

$$\cos^2 \varphi_n = \frac{1}{1 + n^2 q^2} \quad q = \frac{\Delta}{h}$$

$$S_n = W \frac{\sqrt{n^2 q^2 + \cos^2 \alpha_0}}{\cos^2 \alpha_0}$$

If the clouds are not large so that  $\cos^2 \alpha = 1$  may be assumed as equal to unity, this expression becomes, owing to the relation  $nq = \tan \varphi_n$ ,

$$S_n = \frac{W}{\cos \varphi_n}$$

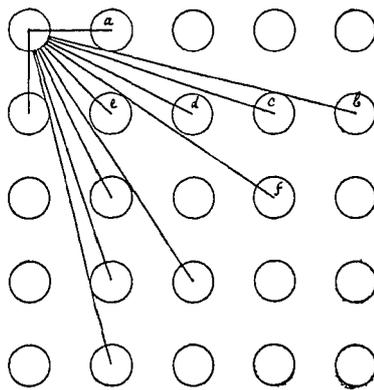
As  $\cos^2 6 = 0.99$ , this will hold good for pretty large clouds which, when seen in the zenith, are measured by an angular value of  $12^\circ$ .

At a zenith's distance

$$\varphi = \text{arc cos } (W)$$

the apparent cloudiness becomes equal to unity, i.e. the cloudbank begins there, which is always more or less manifest when the clouds are regularly spread over the sky.

In the foregoing considerations the true cloudiness ( $W$ ) is regarded as a proportion of linear quantities, whereas in reality the proportion between white and blue in the plane going through  $M_0 M_1 M_2$  and at right angle to the plane of the drawing of fig. (1) ought to be considered, and the question arises in how far it is permissible to substitute a fictitious linear repartition along a line for a real cloudiness as measured in a plane.



In fig. (2) the clouds, assumed to be spherical, are projected upon the plane going through their centra and an observer, looking at this plane from a point  $O$  below the origin of coordinates, will notice totally different proportions between white and blue in different directions.

If, as in fig. (2), the mutual distance  $\Delta$  is equal to twice the diameter  $d$ , he will notice six different degrees of cloudiness within an angular distance

of  $45^\circ$ , as denoted by full lines, and the alignments  $a$  and  $e$  will be repeated 4 times, the other 6 times over the whole sky.

The average cloudiness derived from this regular arrangement is then

$$\frac{1}{20} \left[ 1 + \frac{\sqrt{2}}{2} + \frac{2\sqrt{5}}{5} + \frac{2\sqrt{10}}{10} + \frac{2\sqrt{13}}{13} + \frac{2\sqrt{17}}{17} \right] = 0.214.$$

From the proportion between the surface of the circles and the total surface of the corresponding plane we find for the true cloudiness, according to the formula :

$$Cl. = \frac{\pi d^2}{4 \Delta^2} = \frac{\pi}{16} = 0.196$$

showing a difference of 1.8 %.

Although this calculation (given as an example, not as a proof) is applicable only to moderate and small degrees of cloudiness, because a cloudiness 10 cannot be represented by circles, we may conclude from this example that it is permissible to substitute a linear for a surface-cloudiness of which it is impossible to give a final definition because a given proportion of white and blue in a plane can be represented in very different ways.

3. In the following calculations we assume the clouds to have the shape of an ellipse rotating about a vertical axis and that these clouds, if average values derived from many observations are used, may be considered as small so that the tangents, drawn to the ellipse in a vertical plane, may be regarded as parallel. The well known fact that the dimensions of all objects (mountains, constellations, sun, moon) when seen near the horizon appear strongly exaggerated, is taken into account by introducing a physiological factor  $f(\varphi)$ .

The relation between true and apparent cloudiness in a point at a zenith's distance  $\varphi$  then becomes :

$$W_s = W f(\varphi) \sqrt{1 + k^2 \tan^2 \varphi}, \dots \dots \dots (1)$$

where  $k$  denotes the proportion between the vertical and horizontal axes of the ellipsoid i. e. greater than unity when pointed upwards, smaller than unity when oblate.

We further assume that an object at the horizon is seen twice as large as in the zenith, and as  $f(\varphi)$  must satisfy the condition that  $f = 1$  for  $\varphi = 0$ , the simplest forms which this function can be given are :

$$f_1 = 1 + \sin \varphi, f_2 = 2 - \cos^2 \varphi, f_3 = 2 - \cos \varphi.$$

Of these functions the first corresponds with the greatest, the last with the smallest augmentation for values of  $\varphi$  near  $45^\circ$ .

The value of the angle  $\beta$ , the zenith's distance where, apparently, the blue disappears out of the sky and the perspective cloudbank begins, is then determined by the formula :

$$W \cdot f(\beta) \cdot \sqrt{1 + k^2 \tan^2 \beta} = 1 \dots \dots \dots (2)$$

and the sum of the cloudiness in the arc  $\varphi = 0$  to  $\varphi = \beta$  becomes :

$$IW = W \int_0^\beta f(\varphi) \cdot \sqrt{1 + k^2 \tan^2 \varphi} d\varphi \dots \dots \dots (3)$$

The apparent cloudiness corresponding to the true cloudiness  $W$  is then :

$$W_s = 1 - 2/\pi \cdot (\beta - IW) \dots \dots \dots (4)$$

If  $Z$  denotes the duration of sunshine as registered at the same time, then the expression holds good :

$$1 - Z = R = W \sqrt{1 + k^2 \tan^2 \varphi} \quad . . . . . (5)$$

where  $\varphi$  is the sun's zenith's distance.

$W_s$  and  $R$  being known by observation, it is, theoretically, possible to calculate the two unknown quantities  $W$  and  $k$  from (4) and (5) with the help of (2) and (3).

Practically the only possibility to come to a result is to give  $k$  different values and to calculate  $W$  and  $R$  for a series of values of the auxiliary quantity  $\beta$ .

In the following calculations the zenith's distance of the sun at 2 p.m. has been assumed to be in summer (June—July)  $37^\circ 42'$ , in winter (December—January)  $78^\circ 37'$ .

Table VI shows the results of the calculation for the summer-months and spherical clouds ( $k=1$ ); it appears then that, starting from the assumed supposition an explanation can be given of the results of observation concerning the magnitude of the sum or cloudiness and duration of sunshine. The first augmenting factor,  $1 + \sin \varphi$ , leads to values which are somewhat too large; the second,  $2 - \cos^2 \varphi$ , to an exact maximum; the last,  $2 - \cos \varphi$ , to a value somewhat smaller than 130.

The position of the maximum is less satisfactory; it corresponds in table IV to an apparent cloudiness of 4, whereas in Table VI the greatest values correspond to an apparent cloudiness of 6.5 and 5.5. The augmenting factor  $2 - \cos \varphi$  gives the best results because then the calculated duration of sunshine for the heavy cloudiness 7—8 is smaller than in the foregoing tables and shows a better agreement with the numbers of table IV.

For this reason the latter augmenting factor is chosen in calculating the cloudiness and duration of sunshine for three values of  $k$  viz. 1.305, 1.5 and 2, all greater than unity and therefore corresponding with clouds pointed upwards. For values smaller than unity the shifting of the maximum would certainly occur in the wrong direction i. e. to the side of the heavy cloudiness.

In fact these increased values of  $k$  lead to an improvement of the results, the maximum now corresponding with an apparent cloudiness of 5.

As might have been expected, the influence of a variation of  $k$  upon the position of the maximum is not great when the value of  $\varphi$  is small, because in that case  $R$  varies little with  $m$ .

A more complete agreement between calculation and observation

might be obtained, but only by using a more complicated augmenting factor.

When the sun's height decreases or  $\varphi$  increases, the influence of  $k$  is much stronger; values as  $k = 0.5$  or  $k = 0.12$  appeared to be of no use in calculating the duration of sunshine in winter and, after some trials, only the value  $k = 0.25$  proved to give satisfactory results.

As for the summermonths the factor  $2 - \cos \varphi$  appeared to be the best, although the maximum value happens to be somewhat too small; on the other hand the position of the maximum is almost accurate, corresponding with an apparent cloudiness of 2.

For the wintermonths, therefore, an almost complete agreement between calculation and observation might be obtained by increasing the augmenting factor and assuming e.g.  $2.5 - 1.5 \cos \varphi$ , which would agree with the experiment, the augmentation near the horizon being certainly more than twice.

The integration-constants  $1 + k$  and  $+1$  in the formula for  $I_1$  (table VIII) had to be added in order to ensure the condition:

$$I_1 = 0 \text{ for } x = 0$$

In calculating the elliptical integrals in the expressions for  $I_3$ , the "Funktionentafeln mit Formeln und Kurven von JAHNKE und EMDE". Teubner 1909, have been made use of.

4. The results of this inquiry can be summed up as follows; it is possible to explain the relation between cloudiness and duration of sunshine as found by experiment by means of theoretical reasoning and simple assumptions. In this way a numerical measure of the specific influence of the cloudiness upon radiation, received and emitted, can be obtained according to the nature of the clouds in different seasons.

In the considerations made use of in treating this problem, it is assumed that in calculating the estimated cloudiness  $W_s$  and also the apparent cloudiness  $R$ , as derived from the duration of sunshine, the same value  $W$  of the true cloudiness obtains.

This supposition is certainly not quite justified; the former observation is made with incident rays, or more accurately diffuse reflection, the latter with transmitted light and probably (at least for Cirri, Pseudo-cirri and Fracto-Cumuli) the loose, flocky clouds and cloud-borders transmit some light, whereas, with reflected light, they make the impression of an entire covering of that cloudy part of the sky; on the other hand the sunshine-recorders readily discontinue registering when the sun's rays are absorbed. The fact also that the sun's image as formed by the glass sphere or the slit of the sun-

shine-recorder not being small with respect to the time-scale, may give rise to a smaller value of  $W$  than is derived from the estimated cloudiness, because a more or less continuous discoloration can be observed when light and shadow are in reality varying in a discontinuous way. It will be difficult to take into account either factor as they are dependent on the velocity of the cloudmotion by which the possibility of a registration of relatively feeble rays of light is determined. The influence of these factors can be determined only by experiment, which however would be difficult to carry out. It would be necessary to extend it to a great number of different cases and, in order to inquire in how far compensation happens to occur between too large a percentage of sunshine in the case of slowly moving clouds and too small a percentage when the clouddrift is more rapid, the experiment would have to be extended to a great number of different cases.

Finally it may be noticed that the fact that clouds generally show a flat base and a pointed apex, might be taken into account by considering the upper half of ellipsoids, the equatorial plane being situated in the plane  $M_s M_1 \dots M_n$ . Then the duration of sunshine corresponding to a given value of  $W$  increases, but as, on the other hand, the apparent cloudiness decreases, the sums remain nearly the same.

TABLE VI.  
Calculation for spherical clouds.  
De Bilt, June + July,  $\alpha = 37^\circ 42' 5$

$\beta$	$W$	$W_s$	$Z$	$W_s + Z$	
30°	0.577	0.922	0.270	119.2	$k = 1$
35	0.521	0.894	0.342	123.6	
40	0.466	0.862	0.411	127.3	$1 = \frac{1 + \sin \beta}{\cos \beta} W$
45	0.414	0.824	0.476	130.0	
50	0.364	0.781	0.540	132.1	$R = \frac{W}{\cos \beta}$
55	0.315	0.732	0.601	133.3	
60	0.268	<b>0.677</b>	0.661	<b>133.8</b>	$I_1 = \frac{1}{2} \ln \frac{1 + \sin \beta}{1 - \sin \beta} - \ln \cos \beta$
65	0.222	0.611	0.720	133.1	
70	0.176	0.538	0.777	131.5	
75	0.132	0.450	0.833	128.3	
80	0.088	0.345	0.889	123.4	
85	0.044	0.211	0.945	115.6	

$\beta$	$W$	$W_s$	$Z$	$W_s + Z$	
30°	0.693	0.931	0.124	105.5	
35	0.616	0.899	0.221	112.0	
40	0.542	0.861	0.315	117.6	$I = \frac{2 - \cos^2 \beta}{\cos \beta} W$
45	0.471	0.817	0.405	122.2	
50	0.405	0.769	0.488	125.7	$R = \frac{W}{\cos \beta}$
55	0.343	0.714	0.566	128.0	
60	0.286	0.655	0.638	129.3	
65	0.232	<b>0.589</b>	0.707	<b>129.6</b>	$I_2 = \ln \frac{1 + \sin \beta}{1 - \sin \beta} - \sin \beta$
70	0.182	0.515	0.770	128.5	
75	0.134	0.430	0.831	126.1	
80	0.088	0.329	0.889	121.8	
85	0.044	0.202	0.944	114.6	

30	0.764	0.947	0.035	98.2	
35	0.694	0.919	0.123	104.2	
40	0.621	0.883	0.215	109.8	$I = \frac{2 - \cos \beta}{\cos \beta} W$
45	0.547	0.841	0.309	115.0	
50	0.474	0.791	0.401	119.2	$R = \frac{W}{\cos \beta}$
55	0.402	0.734	0.492	122.6	
60	0.333	0.670	0.579	124.9	$I_3 = \ln \frac{1 + \sin \beta}{1 - \sin \beta} - \beta$
65	0.268	<b>0.598</b>	0.661	<b>125.9</b>	
70	0.206	0.518	0.739	125.7	
75	0.149	0.427	0.812	123.9	
80	0.095	0.322	0.880	120.2	
85	0.046	0.194	0.942	113.6	

TABLE VII

Calculation for clouds pointed upwards:  $k > 1$ . De Bilt, June—July,  $\nu = 37^{\circ}42'5$ .

$\beta$	$W$	$W_s$	$Z$	Sum	
30°	0.704	0.933	0.002	93.50%	$k = 1.305$
35	0.625	0.900	0.114	101.4	$1 = \sqrt{1+m^2 \sin^2 \beta} \frac{2-\cos \beta}{\cos \beta} W$
40	0.547	0.860	0.225	108.5	
45	0.470	0.814	0.333	114.7	$R = \frac{\sqrt{1+m^2 \sin^2 \rho}}{\cos \rho} W$
50	0.399	0.761	0.435	119.6	$I_3 = k \ln \frac{\sqrt{1+m^2 x^2 + kx}}{\sqrt{1+m^2 x^2 - kx}}$
55	0.332	0.701	0.530	123.1	
60	0.270	0.639	0.618	125.7	
65	0.213	<b>0.567</b>	0.698	<b>126.5</b>	$-m \ln \frac{\sqrt{1+m^2 x^2 + mx}}{\sqrt{1+m^2 x^2 - mx}}$
70	0.162	0.492	0.770	126.2	
75	0.116	0.406	0.836	124.2	$-\int_{\pi/2-\beta}^{\pi/2} d\varphi \sqrt{1-n^2 \sin^2 \varphi}$
80	0.073	0.307	0.896	120.3	
85	0.035	0.189	0.967	115.6	$m^2 = k^2 - 1 \quad n^2 = \frac{k^2 - 1}{k^2} \quad x = \sin \beta$
30°	0.667	0.925	0.000	92.50%	
35	0.584	0.889	0.106	99.5	
40	0.504	0.847	0.228	107.5	$f_3 = 2 - \cos \varphi$
45	0.429	0.800	0.343	114.3	
50	0.360	0.749	0.449	119.8	
55	0.297	0.688	0.546	123.4	$k = 1.5$
60	0.245	0.625	0.633	125.8	
65	0.188	<b>0.556</b>	0.711	<b>126.7</b>	
70	0.142	0.481	0.782	126.3	
75	0.101	0.397	0.845	124.2	
80	0.064	0.301	0.902	120.3	
85	0.030	0.183	0.953	113.6	

$\beta$	$W$	$W_s$	$Z$	Sum	
30°	0.577	0.905	0.000	90.50%	
35	0.492	0.866	0.094	96.0	$f_3 = 2 - \cos \beta$
40	0.415	0.821	0.236	105.7	
45	0.346	0.768	0.363	113.1	
50	0.285	0.719	0.475	119.4	$k = 2$
55	0.232	0.662	0.573	123.5	
60	0.185	0.601	0.659	126.0	
65	0.144	<b>0.536</b>	0.735	<b>127.1</b>	
70	0.108	0.464	0.801	126.5	
75	0.076	0.384	0.860	124.4	
80	0.048	0.292	0.911	120.3	
85	0.023	0.179	0.958	113.7	

TABLE VIII.

Calculation for flat clouds:  $k < 1 = 0.25$ .De Bilt. December + January,  $\alpha = 78^\circ 37'$ .

$\beta$	$W$	$W_s$	$Z$	Sum	
40	0.596	0.912	0.052	96.4	
45	0.568	0.888	0.094	98.2	$1 = \sqrt{1 - m^2 \sin^2 \beta} \frac{1 + \sin \beta}{\cos \beta} W$
50	0.543	0.875	0.135	101.0	
55	0.518	0.854	0.175	102.9	$R = \frac{\sqrt{1 - m^2 \sin^2 \beta}}{\cos \beta} W$
60	0.492	0.829	0.216	104.5	
65	0.462	0.798	0.263	106.1	$I_1 = \frac{k}{2} \ln \frac{\sqrt{1 - m^2 x^2} + kx}{\sqrt{1 - m^2 x^2} - kx}$
70	0.425	0.753	0.323	107.6	$+ m b g \sin(mx)$
75	0.372	0.683	0.407	109.0	
80	0.290	<b>0.563</b>	0.537	<b>110.0</b>	$+ k \ln \frac{\sqrt{1 - m^2 x^2} + k}{(1 + k) \sqrt{1 - x^2}}$
82°5	0.230	0.464	0.634	109.8	
85	0.166	0.353	0.736	108.9	$+ 1 - \sqrt{1 - m^2 x^2}$
87°5	0.086	0.202	0.863	106.5	$m^2 = k^2 - 1 \quad x = \sin \beta$

$\beta$	$W$	$W_s$	$Z$	$Sum$	
40	0.693	0.912	0.000	91.2	$1 = \sqrt{1 - m^2 \sin^2 \beta} \frac{2 - \cos^2 \beta}{\cos \beta} W$
45	0.647	0.886	0.000	88.6	
50	0.604	0.859	0.037	89.6	$R = \frac{\sqrt{1 - m^2 \sin^2 \rho}}{\cos \rho} W$
55	0.564	0.829	0.102	93.0	
60	0.524	0.797	0.164	96.1	$I_2 = k \ln \frac{\sqrt{1 - m^2 x^2} + kx}{\sqrt{1 - m^2 x^2} - kx}$
65	0.495	0.759	0.229	98.8	$-\frac{1}{2} x \sqrt{1 - m^2 x^2}$
70	0.438	0.710	0.302	101.2	
75	0.378	0.639	0.397	103.6	$+\frac{4m^2 - 1}{2m} bg \sin(mx)$
80	0.293	0.525	0.534	105.9	
82 <sup>5</sup>	0.235	0.441	0.625	106.6	$m^2 = k^2 - 1 \quad x = \sin \beta$
85	0.166	<b>0.331</b>	0.736	<b>106.7</b>	
87 <sup>5</sup>	0.086	0.202	0.863	106.5	

40	0.793	0.949	0.000	94.9	$1 = \sqrt{1 - m^2 \sin^2 \beta} \frac{2 - \cos \beta}{\cos \beta} W$
45	0.750	0.901	0.000	90.1	
50	0.706	0.890	0.000	89.0	
55	0.660	0.860	0.000	86.0	$R = \frac{\sqrt{1 - m^2 \sin^2 \rho}}{\cos \rho} W$
60	0.612	0.823	0.026	84.9	
65	0.559	0.778	0.109	88.7	$I_3 = k \ln \frac{\sqrt{1 - m^2 x^2} + kx}{\sqrt{1 - m^2 x^2} - kx}$
70	0.497	0.719	0.207	92.6	$+ 2m bg \sin(mx)$
75	0.420	0.637	0.341	97.8	$-\int_0^\beta d\varphi \sqrt{1 - m^2 \sin^2 \varphi}$
80	0.316	0.513	0.497	101.0	
82 <sup>5</sup>	0.249	0.421	0.603	102.4	$m^2 = k^2 - 1 \quad x = \sin \beta$
85	0.173	<b>0.315</b>	0.724	<b>103.9</b>	
87 <sup>5</sup>	0.088	0.178	0.860	103.8	

**Physics.** — “*Contribution to the knowledge of the string galvanometer.*” Communicated by Prof. J. K. A. WERTHEIM SALOMONSON.

(Communicated in the meeting of October 25, 1913).

I. *Intensity of the magnetic field with prismatic pole-pieces.* STEFAN (Wied. Ann. 38, 1889, p. 440) has shown that in an electro-magnet with a round core the number of the magnetic lines in the interferricum could considerably be increased, by giving the pole-pieces a conical form with a top-angle of about  $110^\circ$ . In the string galvanometer prismatic pole-pieces are used. What must be the top-angle in this case in order to obtain a maximal magnetization in the interferricum?

STEFAN admits in his calculation, which is afterwards also used by P. WEISS (Soc. fr. d. Phys. 1907, p. 132) that the lines of force in the magnetically saturated iron core are parallel to the axis, and that at the surface of the cone free magnetism is extant. We divide the conical surface into a succession of infinitely narrow circular strips standing perpendicularly to the axis. Each point situated on such a strip, exercises on a point placed at the summit of the cone an attraction, inversely proportional to the square of the distance. The axial component of this force may be represented by an expression proportional to  $\frac{\cos \alpha}{l^2}$  in which  $l$  represents the distance, and

$\alpha$  half the topangle. If we put  $l = \frac{r}{\sin \alpha}$  in which  $r$  indicates the radius of the circular strip, then the axial force becomes proportional to  $\frac{\cos \alpha \sin^2 \alpha}{r^2}$ .

This expression has a maximum for  $\cos \alpha = \sqrt{\frac{1}{3}}$  or  $\alpha =$  about  $55^\circ$ .

What holds for one definite point of the circular strip, holds for every point of any other circular strip situated on the conical surface. Consequently the most favourable top-angle for the cone amounts to about  $110^\circ$ .

We can apply a similar reasoning in the case of prismatical pole-pieces. In this case we divide the prismatic surface into infinitely narrow strips parallel to the rib.

We calculate in the first place the attraction, exercised by an infini.

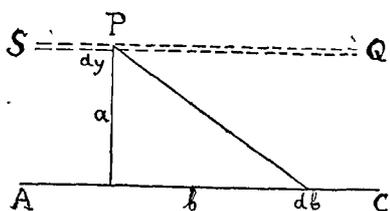


Fig. 1.

As the attraction of  $P$  on  $db$  is inversely proportional to the square of the mutual distance and proportional to the size of the part  $db$ , we may put:

$$K \propto \frac{db}{a^2 + b^2}.$$

We now obtain the total attraction of the part  $P$  on the whole line  $AC$  by integrating this expression between the limits  $+\infty$  and  $-\infty$

$$\int_{-\infty}^{+\infty} \frac{db}{a^2 + b^2} = \frac{1}{a} \operatorname{tg}^{-1} \frac{b}{a} \Big|_{-\infty}^{+\infty} = \frac{\pi}{a}.$$

The attraction of each part of the strip  $SQ$  on the whole line  $AC$  is consequently inversely proportional to their mutual distance. This holds for every other part of the strip and consequently for the entire strip  $SQ$ , and for every other strip running parallel to  $AC$ .

We shall now calculate the attractive force exercised in an axial direction by a strip  $SQ$ .

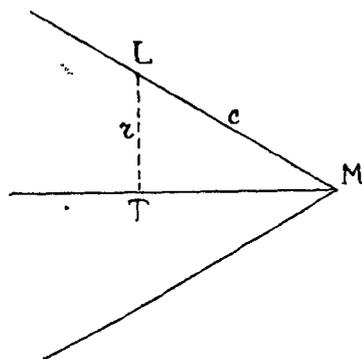


Fig. 2.

Be  $L$  a point of the strip  $SQ$ ,  $M$  a point situated in the rib, whilst we suppose that both  $L$  and  $M$  are situated in a plane, normal to the rib. We found that the attractive force of the strip running through  $L$  on the line situated in the rib  $M$ , is inversely proportional to their distance  $LM = c$ , consequently

$$K_1 \propto \frac{1}{c}.$$

If the distance from  $L$  to the line  $TM$  be  $= r$ , the axial component is

$$\frac{\cos \alpha}{c} \text{ and as } \frac{1}{c} = \frac{\sin \alpha}{r}$$

the axial fraction is proportional to  $\frac{\sin \alpha \cos \alpha}{r}$ .

This expression has a maximum for  $\alpha = 45^\circ$ .

As the same reasoning may be used for every other strip situated on the planes of the prism, we ought to cut the prism in such a way that the bi-plane-angle at the rib amounts to exactly  $90^\circ$ .

This is only true if the planes of the prisms terminate in the line of intersection. This case however never occurs: the planes are always cut off by a plane parallel to the ribs so that the interferricum is enclosed between two planes parallel to each other and perpendicular to the lines of force. In such a case we can, however, still calculate the maximal field-intensity at the line of intersection of the planes. The field is then formed by two different components, i.e. by the magnetic lines passing through the side-planes and by those issued by the two limiting planes. If these be  $H_1$  and  $H_2$ , we have for the total field:  $H = H_1 + H_2$ .

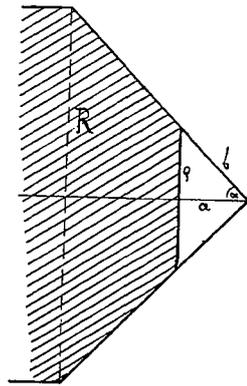


Fig. 3.

We found for each strip  $H_1$  the value of  $\frac{\sin \alpha \cos \alpha}{r}$ . In order to obtain an expression for the magnetization due to an entire side-plane we suppose that the breadth of the strip is  $dr$ , and that consequently its action is proportional to  $\sin \alpha \cos \alpha \frac{dr}{r}$ . If we integrate this expression between the limits  $q$  and  $R$ , in which  $q$  represents half the depth of the interferricum,  $R$  half the thickness of the magnet, we find the value looked for. It amounts to:

$$H_1 = \int_q^R \sin \alpha \cos \alpha \frac{dr}{r} = \sin \alpha \cos \alpha \ln \frac{R}{q}$$

In order to calculate the magnetic field caused by the free magnetism in the parallel boundary plane, we divide it again into length-wise strips.

The attraction exercised on the rib by each strip is inversely proportional to their mutual distance  $b$ , consequently  $\frac{1}{b}$ .

The axial attraction is  $\frac{a}{b^2}$ , if  $a$  represents half the length of the interferricum. If we integrate along  $b$  between the limits  $a$  and  $\sqrt{a^2 + \rho^2}$ , then we find

$$H_2 = 1 - \frac{a}{\sqrt{a^2 + \rho^2}} = 1 - \cos \alpha$$

Hence:  $H_1 + H_2 = 1 - \cos \alpha + \sin \alpha \cos \alpha \lg n \frac{R}{\rho}$ .

The maximal value of this expression depends on the magnitude  $R:\rho$ . If  $\rho$  is infinitely small, which means that the side-planes of the prism terminate in the natural rib, we find again  $\alpha = 45^\circ$ . With other values of  $R$  we find:

$R:r$	$\alpha$
$\infty$	$45^\circ$
100	$49^\circ 44'$
50	$51^\circ 38'$
25	$52^\circ 5'$
10	$55^\circ 29'$

In the string-galvanometer, as a rule,  $R:\rho$  will be somewhere between 25 and 50. By making the top-angle about  $51^\circ$  we obtain the maximal field-intensity. As however the value of the expression for  $H_1 + H_2$  does not vary much in the neighbourhood of the maximum, a little deviation in size of the angle will have no prejudicial consequences.

In general we can say that it is better to make the angle a little larger than the theoretical value, as in that case the field will become more homogeneous, whilst with a smaller angle the field-intensity will diminish more rapidly towards the rims. As a maximum perhaps  $53^\circ$ — $55^\circ$  may be taken; i.e. with a core of 5 cm. diameter the angle should be nearly  $55^\circ$  and with a core of 10 cm.  $53^\circ$  must not be surpassed.

II. *The magnetic field and the shape of the string in the EINTHOVEN-galvanometer.*

As soon as a constant current passes through the string of the galvanometer of EINTHOVEN the string assumes a curved shape. If we wished to draw this shape, we might use a well-known graphostatical method of construction. It is used e.g. to draw the shape of a chain of a suspension bridge.

Suppose the chain is suspended between  $A$  and  $B$  and the loads

$4_1, 3_1, 2_1, 1_1, 1_0, 2_0, 3_0, 4_0$  pulling on the chain in a vertical direction, perpendicularly to  $AB$ , then a diagram is drawn in the following

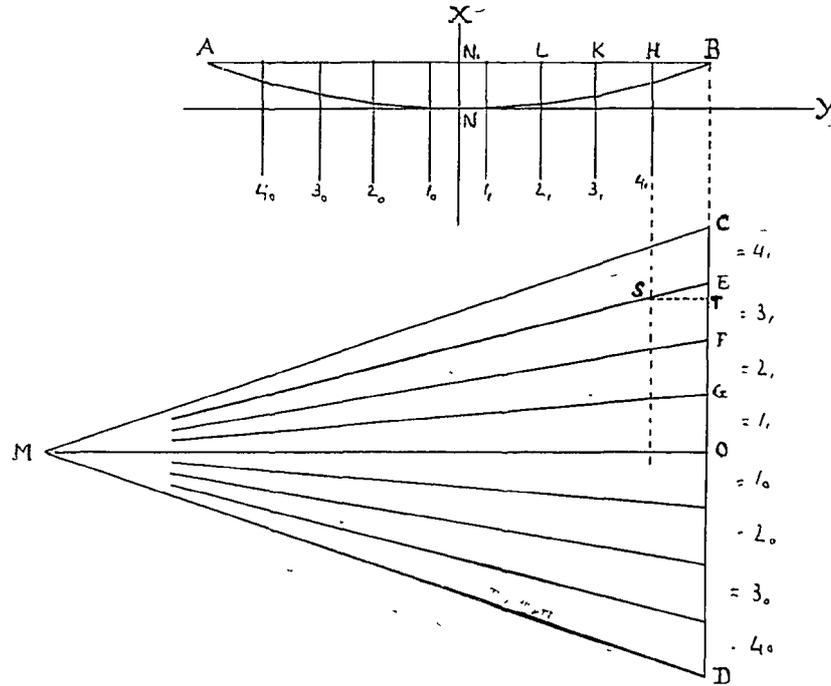


Fig. 4.

manner. Parallel to  $AB$  a line  $OM$  is drawn representing the longitudinal strain of the chain. Perpendicularly to the end of  $OM$   $OD$  is drawn, and on this line parts  $OG, GF, FE$  are taken representing the pulls  $4_1, 3_1$ , etc. to  $4_0$  on the same scale as has been used with  $OM$ . The points of division in the line  $DC$  are joined with  $M$ . From  $B$  a line is drawn, parallel to  $MC$ , till it intersects with  $H_1$ . From there a line is drawn, parallel to  $ME$ , till it intersects with  $K_3$ , etc. In this way we finally get the line  $BNA$ , which represents the shape of the chain.

Theoretically this construction would also be correct, if the number of the lateral loads were infinitely great and their distances infinitely small.

If we regard this method of construction more closely, we immediately see that the line  $OC$  represents the sum of all the lateral forces, if we start in the middle of the chain. We may consequently consider the distance from every point of that line to the point  $O$  as the integral of the lateral forces. If these be represented by the expression  $f(Z)$  and if the forces act at distances  $dl$  from each other, then  $\int f(Z)dl$  is an expression for the length of each part of the line  $OC$ , reckoned from the point  $O$ .

If we have drawn the line  $\int f(Z)dl$  and we join any divisional point with  $M$ , we find the slope of the chain on the place of the load, corresponding to the divisional point. So e.g. in figure 4 the slope at 3, will be represented by the line  $EM$ . To calculate the slope with regard to the  $Y$ -axis, we deduce from the congruency of the triangles  $SET$  and  $MEO$ , that the increase of height  $TE$  which we may indicate as  $\Delta h$ , is  $= \frac{EO}{OM} \times ST$ .

As  $EO$  represents the integral lateral pressure, consequently  $\int f(Z)dl$  and  $OM$  the total longitudinal tension  $P$ , whilst  $ST$  represents the length  $\Delta l$  of the chain of which the slope has been calculated, we can write, passing to infinitely small differences

$$dh = \frac{dl}{P} \int f(Z)dl$$

or integrating:

$$h = \frac{1}{P} \int \left( dl \int f(H)dl \right)$$

We may apply this reasoning to the string galvanometer. We find then that the lateral pressure which we called  $f(Z)$ , is proportional to the intensity of current in the string  $I$  and to the field-intensity  $H$  at every point which may be written  $f(IH)$ , or as  $I$  is constant over the length of the string,  $If(H)$ .

For the galvanometer we get the expression:

$$h = \frac{I}{P} \int \left( dl \int f(H)dl \right)$$

if the coordinate-system has its origin in the point  $N$ . If we take the point  $N_1$  i. e. the middle of the not-deviated string, this expression becomes:

$$h_1 = \frac{I}{P} \left\{ \int_0^l dl \left( \int_0^l f(H)dl \right) - \int dl \left( \int f(H)dl \right) \right\}$$

in which the definite integral has simply the meaning of the maximal deflection  $NN_1$  of the string at the existing intensity of current and tension.

If we keep to a coordinate system originating in  $N$ , we arrive at the conclusion that the shape of the string is related to the local intensity of the magnetic field in such a way, that we obtain an expression for the shape of the string by integrating twice successively the expression for the magnetic field.

As an example may serve the case that the magnetic field is homogeneous over its entire height. We can then write  $f(H) = H$ .

Then we obtain for the lateral pressure the well-known formula

$$z = I \int H dl = HIl$$

and for the form of the string

$$h = \frac{I}{P} \int H dl = \frac{1}{2} \frac{I}{P} Hl^2.$$

the length of the string being  $2l$ .

This last expression represents the vertex-equation of a parabola. In a homogeneous field the string takes the form of a parabola.

In these and also in the following considerations we assume that the longitudinal tension in the vertical string is everywhere the same, and that the weight of the string itself may be neglected, compared with its tension  $P$ .

The formula given above may also be applied in cases where the field, taken over the height, is not homogeneous. It may be applied, if we can express the local field-intensity either in figures or in a formula.

In the string-galvanometer where the pole-pieces are pierced, we can, as a first approximation, represent the intensity of field by the line  $I$  (fig. 5). Over the length  $l_1$  corresponding to half the width of

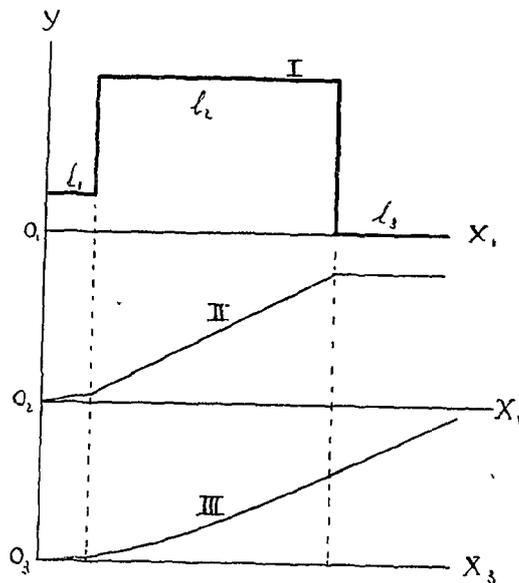


Fig. 5.

the central bore we have a constant field of an intensity  $H_1$ ; over the length  $l_2$  corresponding to the length of the strongest part, the field is also homogeneous and has a density  $H_2$ , whilst the string continues beyond this part over a distance  $l_3$  where the density of the field falls to nought. The entire length of the string is consequently  $2(l_1 + l_2 + l_3)$ . Now we integrate successively over the parts  $l_1$ ,  $l_2$  and  $l_3$ , and find for the lateral pressure:

$$\begin{aligned} \text{over } l_1 : z_1 &= IH_1 l_1 \\ \text{over } l_2 : z_1 z_2 &= I(\underline{H_1} l_1 + H_2 l_2) \\ \text{over } l_3 : z_1 z_2 z_3 &= I(\underline{H_1} l_1 + \underline{H_2} l_2) \end{aligned}$$

in which the underscoring indicates that we have no longer to do with a variable, but with a constant. The line answering to these integrals for the lateral pressure is represented by II.

For the form of the string we obtain after a second integration:

$$\text{in part } l_1 : h = \frac{1}{2} \frac{I}{P} H_1 l_1^2$$

$$\text{in part } l_2 : h = \frac{I}{P} \left( \frac{1}{2} \underline{H_1} l_1^2 + \underline{H_1} l_1 l_2 + \frac{1}{2} H_2 l_2^2 \right)$$

$$\begin{aligned} \text{and in part } l_3 : h &= \frac{I}{P} \left\{ \frac{1}{2} \underline{H_1} l_1^2 + \underline{H_1} l_1 l_2 + \frac{1}{2} \underline{H_2} l_2^2 + \underline{H_1} l_1 l_3 + \underline{H_2} l_2 l_3 \right\} \\ &= \frac{I}{P} \left\{ H_1 \left( \frac{1}{2} \underline{l_1}^2 + \underline{l_1} l_2 + \underline{l_1} l_3 \right) + H_2 \left( \frac{1}{2} \underline{l_2}^2 + \underline{l_2} l_3 \right) \right\} \end{aligned}$$

In the points between  $l_1$  and  $l_2$  and between  $l_2$  and  $l_3$  the line given by the last expression shows a gradual change of direction and not an abrupt one. This is proved by the fact that the value of  $\frac{dh}{dl}$  at the end of  $l_1$  is equal to  $\frac{dh}{dl}$  at the commencement of  $l_2$ , if  $l_2$  be made  $= 0$ . This equality of the differential coefficients holds likewise for the transition of  $l_2$  into  $l_3$ .

Though perhaps we might obtain a better approximation for the shape of the string by supposing

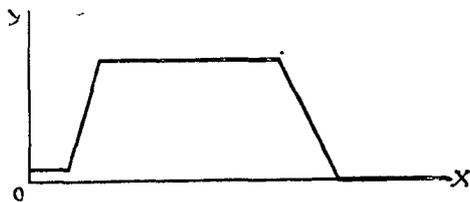


Fig. 6.

that the intensity of the magnetic field varies according to a line of the form represented in fig. 6, we can already obtain some practical result with the simple expression, graphically represented in fig. 5.

Let us first take the case that the string is not longer than the height of the field, in other terms that  $l_3 = 0$ .

The expression for  $h$  remains then :

$$h = \frac{I}{P} \left( \frac{1}{2} H_1 l_1^2 + H_1 l_1 l_2 + \frac{1}{2} H_2 l_2^2 \right) \\ = \frac{I}{P} \left\{ \frac{1}{2} H_1 (l_1 + l_2)^2 + \frac{1}{2} l_1^2 (H_2 - H_1) \right\}$$

If we give to  $l_1 + l_2$  the length of 50 millimeters, to  $H_1$  the value of 4000, to  $H_2$  the value of 20000 gausses, we obtain, if the bore possesses a radius  $l_1 = 10$  or 7 millimeters, deviations  $h$  bearing a proportion as 17.8 to 19.832. This means that the smaller bore of 14 millimeters diameter gives an increase of the sensibility of 11 % as compared with a perforation of 20 millimeters, the height of the field being in both cases 100 millimeters.

Since 1909 I have used a galvanometer in which the perforation has been reduced to 13.7 millimeters, for which the firm of ZEISS has constructed a special apochromatic objective. The Cambridge Instrument Cy. has of late likewise reduced the bore of their instruments.

With the formulae given above we can also approximately calculate the change in the sensibility if the height of the strongest part of the field is shortened whilst the length of the string remains constant.

Let us write for that purpose :

$$h \sim H_1 \left[ \frac{1}{2} l_1^2 + l_1 (l_2 + l_3) \right] + H_2 \left( \frac{1}{2} l_1^2 + l_2 l_3 \right).$$

If  $l_2 + l_3$  be constant, e.g. = 50, and if we give to  $l_2$  successively the values 50, 45, 40, 35, 30, whilst  $l_1$  remains = 7; if further  $H_1$  be 4000 and  $H_2 = 20000$ , we obtain for  $h$  26.47, 26.22, 25.47, 24.22 and 22.47. This means that a diminution of the height of the field of 10 % gives only a diminution of the sensibility of 0.8 %; a diminution of height of 20 % takes 3.8 %, one of 30 % 8.2 % away from the sensibility.

From this we may conclude that it is of no consequence, if the length of the string exceeds the height of the field by 10—15 %. On the other hand with a given length of the string the height of the field may be 10—15 % less, without causing an appreciable loss of sensitiveness. Now it is possible that with a given diameter of the iron-core a diminution of the height of the field might cause a slight increase of the density, by which even the slight loss caused by an excess of length of the string over the height of the field would be entirely compensated. I must add, however, that I have not given any further consideration to this question.

From our formulae we can obtain a better insight into the significance of the average *active* intensity, in a not homogeneous field. Active intensity means the intensity of a perfectly homogeneous field causing the same deviation  $h$  as can be obtained in the not homogeneous field. We get the expression:

$$H_w = \frac{H_1 l_1^2 + 2 H_1 l_1 l_2 + H_2 l_2^2}{(l_1 + l_2)^2} = H_1 + (H_2 - H_1) \left( \frac{l_2}{l_1 + l_2} \right)^2$$

Be again  $H_1 = 4000$ ,  $H_2 = 20000$ ,  $l_1 = 7$  mm. and  $l_2 = 43$  mm., then  $H_w$ , the active density, is 15843, whilst the arithmetic average, calculated as  $H_1 + (H_2 - H_1) \frac{l_1 + l_2}{l_2}$  amounts to 17760.

We may add here, that the average active value can also be obtained with sufficient accuracy by dividing the square of the average intensity by the maximal intensity:

$$H_w = \frac{H^2_{gem.}}{H_{maz.}}$$

In the example chosen, this empirical formula results in  $H_w = 15771$  instead of 15843, as first calculated, consequently an amount differing by less than  $\frac{1}{2}\%$  from the real value.

The mathematical connection between the shape of the string and the local field-intensity enables us either to calculate or to construct the shape of the string if the local intensity of the field be known with sufficient accuracy.

I have tried to measure the local field intensity by different methods. Firstly Prof. P. ZEMAN had the kindness to try his method depending on the resolution of the spectral lines into doubles in the magnetic field. As in the narrow and high interferricum the spectral tubes filled with Helium or with Hg vapours were destroyed in a few seconds, this method has not given practical results.

Therefore I had to apply other methods, viz. the bismuth-method, and the method with the magnetic balance of COTTON.

For the bismuth-method I used thin wires of pure bismuth furnished by the firm of HARTMANN-BRAUN. The measurements were made by means of a wire of 0.17 mm. diameter and a length of 12 mm. with a current of 1 milliamperè. The temperature of the wire was measured repeatedly by measuring its resistance, after the field had been reduced as near as possible to nought. The results were finally calculated by means of the formula:

$$H = 2060 + 8t + (120.9 + 2.4t)\Delta$$

which formula had been calculated from earlier measurements published by HENDERSON and later measurements of myself.

This formula in which  $t$  represents the temperature in centigrades,  $\Delta$  the procentual increase of resistance, gives, with an intensity of field greater than 4500 Gauss, results, that are accurate to within 1%, at least between the limits of temperature of 7°—25° Celcius. I obtained with this method, for the electromagnet of my EINTHOVEN galvanometer N°. II:

With a field-curr. of 0.40 Amp.	$H=5360$	in the strongest part of the field
„ „ „ „	1.53	„ „ „ „ „ „ „ „
„ „ „ „	2.39	„ „ „ „ „ „ „ „
„ „ „ „	3.49	„ „ „ „ „ „ „ „
„ „ „ „	8.54	„ „ „ „ „ „ „ „
„ „ „ „	8.54	„ „ „ „ „ „ „ „
	14150	„ „ „ „ „ „ „ „
		„ „ „ „ „ „ „ „

In these measurements I could not know whether the bismuth-wire had actually been in the strongest part of the field. Also it proved to be very difficult to measure the different parts of the field very accurately.

Therefore I have repeated the measurements with a balance of COTTON, which proved to give more accurate results with less difficulty and in less time.

My balance was provided with a rectilinear current carrying conductor of 19.057 mm. length; the arms of the balance were 304.25 resp. 304.48 mm. long. The constant was calculated at  $5151 \frac{P}{I}$  in which  $P$  represented the weight placed in the scale,  $I$  the current strength in Ampères. The sensitiveness of the balance was varied till I got about a 1 mm. deflection for 1 milligram. The balance was placed on a sliding support, so that it could easily be moved in the direction of the interferricum.

In my first measurements I found with the same magnet with a fieldcurrent of:

1.50 Ampère	$H = 19730$
3.48 „	27810
8.30 „	31695

which numbers probably differ less than 0.3% from the real value. They agree with the values obtained before.

With this magnetic balance I have tried to measure the local intensity at every point of the field, with a given magnetizing current, viz. 1.55 Ampère. The balance was arranged so as to place the current-carrying conductor exactly in the central part of the interferricum, symmetrically with regard to the perforation. After the

first measurement of the field-intensity the balance was moved along the field over a distance of 1.24 mm, this being one revolution of the micrometer-screw of the sliding support. The average intensity was measured again, and after each measurement the balance was moved along the field over the same distance, till at last the balance had passed through the entire field, and had come out of the interferricum.

In this series of experiments I found that the greater part of the field might be called absolutely homogeneous. Proceeding from this part the average intensity could now be calculated for each distance of 1.24 mm. Obviously the figures calculated for the weaker part of the field cannot be regarded as very accurate. By graphical interpolation I got figures which seemed to me to be more conform to the real value. In order to prove this, I recalculated from the values, for each part of 1.24 mm., average values over 19.05 mm. In table I we find in column I the calculated values for each part of the field of 1.24 mm. length. The second column gives the recalculated figures for each length of 19.05 mm., whilst in the 3<sup>rd</sup> column the figures as measured are given. The degree of agreement between the 2<sup>nd</sup> and the 3<sup>rd</sup> column indicates the degree of accuracy between the same. In general this correspondence is not unsatisfactory, only the values 2 and 3 show differences of 2% and 3.5%. For the rest the difference amounts to less than 1%. The curves of fig. 7 represent graphically the numbers given in the table.

With the figures obtained for the local intensity of field we can now draw the exact shape of the string, by means of the graphical construction described in the beginning, or we can calculate it. The calculation is made by two additions that serve as means of integration. The first addition produces the series of figures 0, 0+1, 0+1+2, 0+1+2+3 etc., consequently the values 0, 3600, 7250, 11050 etc., which indicate the integral values of the lateral pressure, at each point.

If these values be  $a, b, c, d$ , then a second addition in exactly the same way, gives us:  $a, a+b, a+b+c, a+b+c+d$ , etc. These last figures are given in column IV and show the relative deviation with regard to a  $Y$ -axis tangential to the point of maximal amplitude. They enable us to calculate with the field-current employed the relatively maximal deflections of any part of the string.

If e.g. the maximal deflection of a string of a length of  $2 \times 48$  parts of 1.24 mm. each with a given current were 191.8, then the deflection with the same current would be 41.5 for a string of the same material and tension, but only half the length. We see that in

	I	II	III	IV		I	II	III	IV
0	3600	8940	8940	0	25	20950	20930	20900	45.7
1	3650	8995	8950	0.036	26	"	20870	20860	50.2
2	3800	9305	9010	0.11	27	"	20660	20600	54.8
3	4000	9900	9570	0.22	28	"	20310	20200	59.7
4	6100	10890	11030	0.37	29	"	19850	19850	64.8
5	12000	12020	12000	0.58	30	"	19280	19200	70.1
6	16100	13165	13050	0.91	31	"	18620	18540	75.6
7	19600	14320	14400	1.40	32	"	17310	17850	81.3
8	20430	15475	15400	2.09	33	19800	16500	16350	87.2
9	20750	16630	16750	2.99	34	17700	15630	15400	93.3
10	20950	17770	17800	4.09	35	15750	14700	14600	99.6
11	"	18900	18600	5.40	36	14000	13720	13700	106.0
12	"	19890	19600	6.92	37	12500	12830	12700	112.6
13	"	20490	20600	8.64	38	11000	11590	11700	119.3
14	"	20810	20860	10.58	39	9900	10450	10530	126.1
15	"	20900	20900	12.7	40	8800	9340	9470	133.7
16	"	20935	20930	15.1	41	7900	8316	8320	140.1
17	"	20950	20930	17.6	42	7000	7010	7060	147.2
18	"	"	20950	20.4	43	6200		6060	154.3
19	"	"	"	23.4	44	5400		4860	161.5
20	"	"	"	26.6	45	4600		4020	169.7
21	"	"	"	30.0	46	3800		3440	176.1
22	"	"	"	33.6	47	3100		2780	183.4
23	"	"	"	37.4	48	2400		2340	191.8
24	"	"	"	41.5	49	1750		1910	198.2

reality the deflections are not proportional to the square of the length of the string, as would be the case in an absolutely homogeneous field. This is caused by the central weaker part of the field, which influence increases if the string is shorter.

We should try to minimise the influence of the bore. We have already considered one way of doing it, i.e. to make the bore as narrow as possible. It is however difficult to make the bore

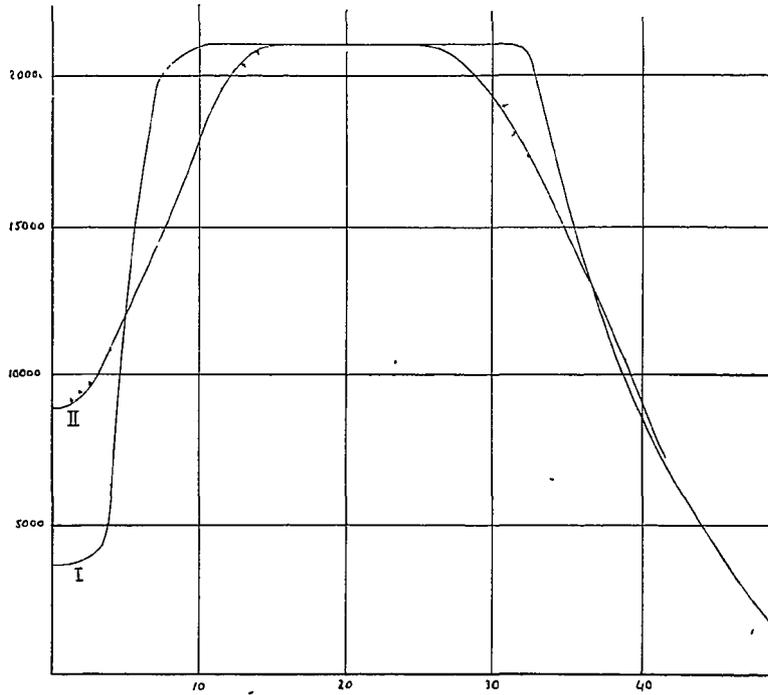


Fig. 7.

narrower than 13 m.m., as there are technical objections against the construction of apochromatical objectives of high aperture with an external diameter less than 12 m.m. Another way consists in increasing the field-current as much as possible. We have then a double advantage. Firstly the maximal field-intensity is increased as much as possible. Secondly with the more perfect magnetic saturation of the iron core, the magnetic leakage near the central bore pushes a relatively greater number of lines of force into the part of the field corresponding to the bore. The central part of the field increases thereby both absolutely and relatively. The direct measurement immediately confirms this.

Using the bismuth-method I found with the electro-magnet of galvanometer II in the weakest part a field with an average intensity of 14150 gauss, when the strongest part reached 31350 gauss. With a maximal field-strength of 20950 gauss the field in the central part fell to 5650 gauss.

With a new electro-magnet of a somewhat different form and size, which is wound for 25 ampère, I found:

at 21 ampère	maximal	39050	minimal:	23200
„ 10	„	36250	„	19760
„ 1	„	17010	„	7417

I may add here that with 25 ampère the field-strength increased to 40000 gauss. I intend to arm this electro-magnet with pole-pieces made of ferrocobalt, the new alloy of WEISS and hope to obtain with them a maximum of 43000 gauss.

### III. Determination of the active fieldstrength.

As active field-strength we indicated the intensity of a field homogeneous over the whole length of the string, which causes the same deflection as the not homogeneous field, the tension and the material of the string as well as the current passing through it, being the same.

EINTHOVEN has already given a method to measure the active intensity of the field. His method depends on the measurement of the electro-magnetical damping of the movement of the string.

Here follow two more methods which lead both to about the same result.

#### First Method.

If a current  $I$  passes through the string, it is subjected to a lateral pressure  $HI$  which causes the string to sway, and whereby a certain quantity of potential energy is stored. When the circuit is broken the string generally resumes its former position after a few damped oscillations. With every oscillation potential energy is changed into kinetical energy, and vice versa.

At the moment the string passes for the first time its final position of equilibrium, the total originally stored potential energy has disappeared, and nothing but kinetical energy remains. If the oscillations had been undamped, we might equal these two forms of energy. On account of the damping the value for the kinetical energy must first be corrected. We have then got an equation from which  $H$  can be resolved, and which gives an expression for the actual mean intensity of the magnetic field.

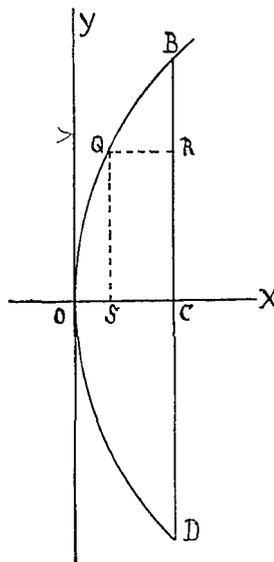


Fig. 8.

In our considerations we assume the field to be homogeneous and we neglect the elasticity and the weight of the string itself with regard to its strain. Under these circumstances the string takes, as we saw, a parabolic shape.

Be  $BQOD$  the deflected string, its centre being  $O$ . With regard to a system of coordi-

nates passing through  $O$ , where the  $y$ -axis touches the parabola, the form of the string is represented by the equation:

$$y^2 = 2px.$$

The potential energy of any small particle  $dy$  of the string amounts to:

$$\frac{1}{2} HI QR dy.$$

Now  $QR = h - x$  in which  $h$  represents the maximal deflection  $OC$  of the string, whilst  $x$  is the abscissa of the point  $Q$ . As  $x = \frac{y^2}{2p}$  we obtain for the potential energy of the part  $dy$ :

$$\frac{1}{2} HI \left( h - \frac{y}{2p} \right)^2 dy.$$

By integrating this expression between the limits  $O$  and  $\frac{1}{2}l$ ,  $l$  being the length of the string, we get half the potential energy. Hence the total energy amounts to:

$$E_{(pot.)} = 2 \times \frac{1}{2} \int_0^{\frac{1}{2}l} \left( h - \frac{y}{2p} \right)^2 dy = \frac{1}{3} lhHI.$$

In order to calculate the kinetical energy, each part of the string is assumed to perform a series of damped oscillations, which may be represented by the expression:

$$S = A e^{-\alpha t} \cos \omega t,$$

in which  $S$  be the place of the part at any moment with regard to the line  $BD$ ,  $A$  the maximal amplitude,  $\alpha$  the damping-constant,  $\omega$  the number of oscillations in  $2\pi$  seconds.

If we consider a particle of the string  $dy$  situated in  $Q$ , we have:

$$A = QR = h - \frac{y^2}{2p}.$$

The velocity at any moment is:

$$v = \frac{ds}{dt} = - \left( h - \frac{y^2}{2p} \right) \{ \omega \sin \omega t + \alpha \cos \omega t \} E^{-\alpha t}$$

which expression at the moment when the string passes through its final position of rest, becomes:

$$v_{max.} = - \left( h - \frac{y^2}{2p} \right) \omega e^{-\frac{\pi\alpha}{2\omega}}.$$

Hence in the formula for the kinetical energy

$$E_{(kin)} = \frac{1}{2} m v^2$$

the velocity  $v$  is known. The mass  $m$  of a part  $dy$  of the string is expressed by :

$$m = \pi r^2 g dy$$

in which  $r$  is half the diameter,  $g$  the specific weight of the string. We obtain finally for the kinetical energy of the part  $dy$

$$E_{(kin, dy)} = \frac{1}{2} \left( h - \frac{y^2}{2p} \right)^2 \omega^2 \pi r^2 g \epsilon^{-\frac{\alpha \pi}{2\omega}} dy.$$

Integrating over half the length of the string, and by multiplying by 2, the total kinetical energy of the string gives at its passage through the position of equilibrium

$$E_{(kin)} = 2 \int_0^{\frac{h}{2}} \frac{1}{2} \left( h - \frac{y^2}{2p} \right)^2 \omega^2 \pi r^2 g \epsilon^{-\frac{\pi \alpha}{2\omega}} dy = \frac{4}{15} \pi r^2 g l \omega^2 h^2 \epsilon^{-\frac{\pi \alpha}{2\omega}}$$

This value should have been equal to the value obtained for the potential energy, if the movement had been undamped. The damping makes the amount of the kinetical energy too small. The exact

amount is obtained by multiplication by  $\epsilon^{\frac{\pi \alpha}{2\omega}}$ .

As the expression of the potential energy is expressed in ergs, this must likewise be done with the kinetical energy, which causes the introduction of the factor 1.0197.

We obtain finally after the introduction of  $N = \frac{\omega}{2\pi}$  :

$$\frac{1}{3} H l h = 1.0197 \times \frac{4}{15} \pi r^2 g l \omega^2 h^2$$

and hence :

$$H = 32.2 \frac{N^2 h \pi r^2 g}{I}$$

2<sup>nd</sup> method.

We can calculate the lateral pressure on the string in its deviated position in different ways. Above we had already mentioned the expression  $H l l$  for it.

Proceeding from the graphostatical construction, discussed before, we see that the slope of the string at the point of suspension  $B$  corresponds with the inclination of the line  $MC$  (vide fig. 4). This slope is given by the tangent at the point, i.e. by the magnitude of

$\frac{dy}{dx}$  and on the other hand by the tangent of the angle  $CMO$ , consequently by  $\frac{CO}{OM}$ .

As the tangent at any point of a parabola is expressed by

$$\frac{dy}{dx} = \frac{y}{2x}$$

we get for the slope at the end of the string, where  $y = \frac{1}{2}l$  and  $x = h$ :

$$\frac{dy}{dx}(x = h) = \frac{l}{4h}.$$

As  $CO$  represents half the total lateral strain, consequently  $\frac{1}{2}Z$  and  $OM$  the total longitudinal strain  $P$  we may write:

$$\frac{l}{4h} = \frac{2P}{Z} \text{ or } Z = \frac{8h}{l}P.$$

The longitudinal strain of a string can be found from the formula for the vibration-frequency of a stretched string, given in KOHLRAUSCH'S Handbuch der prakt. Phys. (11<sup>th</sup> edition p. 245):

$$N = \frac{1}{2l} \sqrt{\frac{9.81 P}{p}}$$

in which  $N$  represents the frequency per second,  $l$  the length in meters and  $p$  the weight of 1 m. of wire. We obtain from this for the tension

$$P = \frac{4N^2 l^2 p}{9.81}.$$

By substituting this value of  $P$  in the equation for the lateral pressure, we find:

$$Z = \frac{8h}{l} \frac{4N^2 l^2 p}{9.81}$$

which value may be equalled to the lateral pressure calculated before:

$$Hl = \frac{8h}{l} \frac{4N^2 l^2 p}{9.81}.$$

As  $Hl$  indicates the pressure in dynes,  $p$ , the weight of 1 m. of string, must likewise be expressed in dynes, thus:

$$p = 9.81 \pi r^2 g.$$

We obtain finally after this substitution:

$$H = \frac{32 N^2 h \pi r^2 g}{l}.$$

**Chemistry.** — “*Equilibria in ternary systems.*” X. By Prof. F. A. H. SCHREINEMAKERS.

After having deduced in the previous communication the diagrams for a constant temperature (the saturation- and vapoursaturation-curves under their own vapourpressure), and for a constant pressure (the boilingpointcurves and their corresponding vapourcurves), we will deduce now the diagrams for a constant temperature and pressure. We may act for this in the same way as in communication I. For this we imagine for instance in figure 1 (I) besides the saturationcurve of the compound  $F$  also one of the compound  $F'$ . Both these saturationcurves may then be situated either outside each other or they may intersect each other, or the one may surround the other. We imagine both curves situated completely in the liquid-region.

Because the heterogeneous region shifts on decrease of pressure in such direction that the liquidregion becomes smaller and the vapour-region becomes greater, under a certain pressure the liquid-curve  $ed$  of the heterogeneous region will touch one of the saturationcurves. When it touches that of  $F$ , we obtain figure 2 (I) wherein the saturationcurve of  $F'$  is to be imagined. This is then still completely situated in the liquidregion and may be situated with respect to that of  $F$  in the abovementioned ways. Of all the solutions saturated with  $F$  or with  $F'$  at this pressure, therefore, only one exists, namely saturated with  $F$ , that can be in equilibrium with vapour.

On further decrease of pressure figure 3 (I) now arises; herein we imagine the second saturationcurve, still completely in the liquid-region, and whether or not intersecting that of  $F$ . Of all solutions saturated with  $F$  or with  $F'$  at this pressure now two liquids exist, saturated with  $F$  ( $a$  and  $b$ ) which may be in equilibrium with vapour ( $a_1$  and  $b_1$ ). On further decrease of pressure very many cases may now occur. At first we assume that both the saturation-curves are situated completely outside each other and rest also outside each other in the contemplated pressure-interval. On decrease of pressure the heterogeneous region shifts over the saturationcurve of  $F$ , attains at a certain pressure the saturationcurve of  $F'$ , and on further decrease of pressure shifts also over this.

We may distinguish for this two principal cases:

1. the saturationcurve of  $F$  is situated already completely outside the liquidregion before the liquidcurve  $ed$  of the heterogeneous region touches the saturationcurve of  $F'$ ;

2. the saturationcurve of  $F'$  is situated still partly in the liquid-

region, when the liquidcurve  $ed$  of the heterogeneous region touches the saturationcurve of  $F'$ .

In the latter case, therefore, there is a series of pressures under which at the same time two liquids saturated with  $F$  and two with  $F'$  may be in equilibrium with vapour. Solutions saturated with  $F+F'$  do not exist.

When both the liquidcurves intersect each other numberless cases are to be distinguished, of which we shall only discuss a few. Imagining for instance in fig. 3 (I) that the vapoursaturation curve of  $F'$  is also drawn, then we can obtain a diagram as fig. 1. The liquidline  $d-e$  of the heterogeneous region, intersects the saturation-

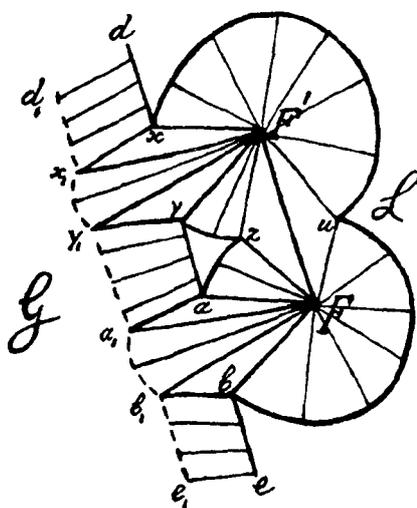


Fig. 1.

The liquids of branch  $dx$  may be in equilibrium with the vapours of  $d_1x_1$ ; the liquids of  $ya$  with the vapours of  $y_1a_1$ , the liquids of  $be$  with the vapours of  $b_1e_1$ . The solid phase  $F$  can exist together with the vapours of branch  $a_1b_1$ ; the solid phase  $F'$  together with the vapours of branch  $x_1y_1$ .

Further there are four liquids saturated with a solid phase which may be at the same time in equilibrium with a vapour. Therefore, there exist four threephasecomplexes: solid + liquid + vapour, nl.  $F$  + liquid  $a$  + vapour  $a_1$ ,  $F$  + liquid  $b$  + vapour  $b_1$ ,  $F'$  + liquid  $x$  + vapour  $x_1$ , and  $F'$  + liquid  $y$  + vapour  $y_1$ . Besides the great liquidregion, indicated by  $L$  we find also in the figure the small liquidregion  $az y$ .

On decrease of pressure figure 1 may pass now into figure 2. The points  $a$ ,  $y$ , and  $z$  of figure 1 coincide in figure 2 in the point  $f$ , the points  $a_1$  and  $y_1$  of fig. 1 coincide in fig. 2 in the point  $f_1$ .

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The metastable part  $bx$  of curve  $de$  must therefore go through point  $f$  and the metastable part  $x_1b_1$  of curve  $d_1e_1$  must go through the point  $f_1$ . Fig. 2 may also be imagined to have arisen from fig. 1 in that the threephasetriangles  $FF'z$ ,  $Faa_1$  and  $Fyy_1$  move until they touch along one side.

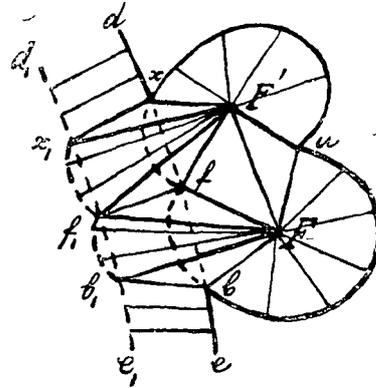


Fig. 2.

Of the two solutions  $u$  and  $f$ , saturated with  $F + F'$ , the latter may be in equilibrium with the vapour  $f_1$ ; at the temperature and under the pressure to which fig. 2 applies, therefore, the fourphaseequilibrium  $F + F' + \text{liquid } f + \text{vapour } f_1$  occurs.

If the pressure decreases still more, a diagram occurs which we shall call figure 2a. We obtain this figure 2a when we leave the point  $f$  in fig. 2 out of account. The two saturationcurves and curve  $de$  then go no more through one point; nor the two vapoursaturationcurves and curve  $d_1e_1$ . Only one solution now exists, nl.  $u$ , saturated with  $F + F'$ ; the other is metastable and replaced by the vapour  $f_1$ , which may be in equilibrium with the complex  $F + F'$ . The fourphaseequilibrium occurring in fig. 2 has vanished of course also in fig. 2a.

We shall now contemplate the diagram, occurring at the minimum-melting point of the complex  $F + F'$ , one of the many possible diagrams is drawn in fig. 3, wherein also are indicated the metastable parts of the two saturationcurves and of the liquid- and vapour-curve of the heterogeneous region.

Fig. 3 can be imagined to have arisen from fig. 2 in the following way. We change the temperature and the pressure in such a way, that we retain a diagram as fig. 2; the fourphase equilibrium  $F + F' + \text{liquid } f + \text{vapour } f_1$  therefore remains, although  $f$  and  $f_1$  change of course their composition. A similar change of pressure and temperature is always possible when we change these in accordance with the  $P, T$ -curve of the fourphase equilibrium  $F + F' + L + G$ . We take this change now in such

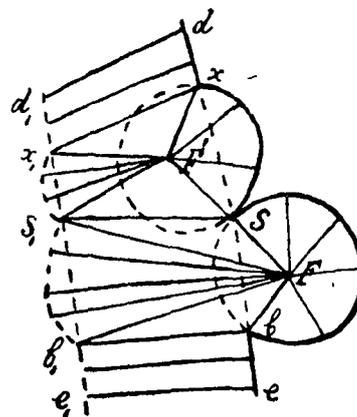


Fig. 3.

direction that the liquidcurve  $ed$  of the heterogeneous region, and therefore also the point  $f$  in fig. 2 shifts towards the line  $FF'$ . At a definite temperature and pressure the points  $u$  and  $f$  coincide then on the line  $FF'$  and fig. 3 may arise; herein however  $f$  is replaced by  $S$  and  $f_1$  by  $S_1$ . Therefore the fourphaseequilibrium  $F + F' + \text{liquid } S + \text{vapour } S_1$  occurs, wherein the liquid  $S$  is represented by a point on the line  $FF'$ . The pressure and temperature to which fig. 3 applies, agree therefore with the minimum meltingpoint of the complex  $F + F'$ .

From the situation of  $S$  with respect to  $F$  and  $F'$  it follows that in fig. 3 a congruent melting of the complex  $F + F'$  is assumed. With an incongruent melting either  $F$  or  $F'$  should be situated between the two other points.

Because the point  $S$  is situated on the line  $FF'$ , the two saturationcurves must touch each other in  $S$ . We now imagine in  $S$  the common tangent of the two saturationcurves and also the tangent to curve  $ed$  to be drawn. For the sake of simplicity we shall call the first the tangent  $S$  and the second the tangent  $de$ .

Now, as is known, the tangent  $S$  and the line  $FF'$  are conjugated diameters of the indicatrix in  $S$ ; the same applies to the tangent  $ed$  and the line  $SS_1$ . Because the indicatrix in  $S$  is an ellipse, on the turning of a diameter its conjugated one moves in the same direction; the lines  $SS_1$ ,  $FF'$  and the two tangents must therefore be situated with respect to each other as in fig. 3. The point  $S_1$  must therefore in fig. 3 be situated on the same side of the tangent  $S$  as the point  $F'$ , when however  $F'$  is situated within the liquid region and  $F$  outside that region, then  $S_1$  is situated on the same side of tangent  $S$  as the point  $F$ . Also in the case, that the points  $F$  and  $F'$  are situated both at the same time either within or outside the liquidregion, the situation of  $S_1$ , with respect to the tangent  $S$  is easy to indicate.

Besides the cases treated above, there are still numberless others which the reader can easily deduce for himself. For that reason we shall only still contemplate some points more in detail.

We take at a definite  $P$  and  $T$  the two solid phases  $F$  and  $F'$ ; perpendicular to the concentration diagram we draw the  $\xi$  of these substances; we shall call these points ( $F$ ) and ( $F'$ ).

When the point ( $F$ ) is situated below the liquid- and the vapour leaf of the  $\xi$  surface, then the compound  $F$  occurs in solid state. We can then construct two cones, which have both their apexes in ( $F$ ) and of which the one touches the liquidleaf and the other the vapourleaf

of the  $\zeta$  surface. As well a saturation- as a vapoursaturationcurve of the compound  $F$  exists therefore. When we contemplate the two curves with respect to each other, then either one completely or a part of both is metastable.

When the point ( $F$ ) is situated below the liquid- but above the vapourleaf of the  $\zeta$  surface, the compound  $F$  only exists in vapour-form. Then not a vapoursaturationcurve exists, but a metastable saturationcurve of  $F$ , therefore a series of metastable solutions, saturated with  $F$ .

When the point ( $F$ ) is situated below the vapour-, but above the liquidleaf of the  $\zeta$  surface, the compound  $F$  exists only in liquid state. Then not a saturation-, but a metastable vapoursaturation curve of  $F$  exists, therefore a series of metastable vapours in equilibrium with  $F$ .

When the point ( $F$ ) is situated above both the leaves of the  $\zeta$  surface, then the compound  $F$  occurs in liquid or in vapour-state, according as below the point ( $F$ ) the liquid- or the vapourleaf is situated the lowest. Then neither a saturation- nor a vapoursaturationcurve of  $F$  exists.

The four above mentioned cases apply of course also to the compound  $F'$ .

We now take a pressure and a temperature at which  $F$  and  $F'$  are both solid. The points ( $F$ ) and ( $F'$ ) are then situated below both the leaves of the  $\zeta$  surface and each of the compounds has then a saturation- and a vapoursaturationcurve.

We distinguish now four cases :

1. the line ( $F$ )( $F'$ ) intersects both the leaves of the  $\zeta$  surface.

We cannot construct through the line ( $F$ )( $F'$ ) a plane of contact on one of the leaves of the  $\zeta$  surface; the two saturationcurves, therefore, do not intersect each other, nor the two vapoursaturationcurves. The two saturationcurves may now be situated completely outside each other, or the one may surround the other; the same applies to both the vapoursaturationcurves. Therefore neither a liquid nor a vapour exists in equilibrium with  $F + F'$ .

2. The line ( $F$ )( $F'$ ) intersects the liquidsurface, but is situated below the vapourleaf of the  $\zeta$  surface.

Because we cannot construct through the line ( $F$ )( $F'$ ) a plane of contact on the liquidleaf, the two saturationcurves do not intersect each other, so that the one is situated outside the other, or the one surrounds the other.

We can (however) quite well construct two planes of contact on the vapourleaf through the line ( $F$ )( $F'$ ). The two vapoursaturationcurves, therefore, intersect each other in two points.

There exists therefore no liquid saturated with  $F + F'$ . Two vapours exist however, each of which may be in equilibrium with  $F + F'$ .

3. The line  $(F)(F')$  intersects the vapourleaf, but is situated below the liquidleaf of the  $\zeta$  surface.

It is evident, that now the two saturationcurves intersect each other in two points, while the two vapoursaturationcurves are situated outside each other or the one surrounds the other. Therefore two solutions exist, saturated with  $F + F'$ , but not a vapour which can be in equilibrium with  $F + F'$ .

The equilibria existing in the three cases treated above may become completely or partly metastable, by the occurrence of the heterogeneous region  $LG$ . Also it is evident, that in the previous cases not yet a fourphaseequilibrium  $F + F' + L + G$  can exist.

4. the line  $(F)(F')$  is situated below the two leaves of the  $\zeta$  surface.

We can now construct through the line  $(F)(F')$  two planes of contact on each of the two leaves of the  $\zeta$  surface. The two saturationcurves therefore, intersect each other in two points, situated on both sides of the line  $FF'$ . The same applies to the two vapoursaturationcurves. Therefore two solutions exist, saturated with  $F + F'$  and two vapours, saturated with  $F + F'$ .

In fig. 1,  $z$  and  $u$  are the points of intersection of the two saturationcurves; the points of intersection of the two vapoursaturationcurves  $a_1$ ,  $b_1$  and  $x_1$ ,  $y_1$  have not been drawn; we shall call these  $z_1$  and  $u_1$ ; we imagine  $z_1$  on the same side of the line  $FF'$  as the point  $z$ , and  $u_1$  on the same side as  $u$ . Under this pressure and at the temperature to which fig. 1 applies, the systems  $F + F' + \text{liquid } z$ ,  $F + F' + \text{liquid } u$ ,  $F + F' + \text{vapour } z_1$ , and  $F + F' + \text{vapour } u_1$  occur. Of these four threephaseequilibria of fig. 1, only the two first however are stable.

Now let us contemplate a point of intersection of two saturationcurves and the point of intersection of the two vapoursaturationcurves situated on the same side of the line  $FF'$  (therefore in fig. 1 the points  $z$  and  $z_1$ , or  $u$  and  $u_1$ ). If we imagine that through the line  $(F)(F')$  the two planes of contact on both the leaves of the  $\zeta$  surface are constructed, then the one point of contact is usually always situated above the other surface. Because the projections of the two points of contact of these surfaces represent the above mentioned points of intersection, only one of both these points of intersection will represent a stable phase.

Therefore, if we have a stable solution saturated with  $F + F'$ , then the vapour saturated with  $F + F'$ , being situated on the same

side of the line  $FF'$ , is metastable. Reversally, if we have a stable vapour saturated with  $F + F'$ , then the liquid saturated with  $F + F'$ , situated on the same side of the line  $FF'$  is metastable. Only in the case that a fourphase equilibrium  $F + F' + L + G$  occurs, this liquid and vapour are stable at the same time.

Let us now consider the occurrence of this system  $F + F' + L + G$ . For the occurrence of this fourphaseequilibrium it is not sufficient that the two threephaseequilibria  $F + F' + L$  and  $F + F' + G$  exist. In addition it is also necessary for this, that the liquid  $L$  of the one, and the vapour  $G$  of the other threephase system shall be in equilibrium with each other. The liquid curve  $ed$  of the heterogeneous region  $LG$  then must go through the point of intersection of the two saturationcurves and also the vapourcurve  $e_1d_1$  of the heterogeneous region must go through the point of intersection of the two vapoursaturationcurves. Because this is not the case in fig. 1, no fourphaseequilibrium can occur, at the temperature and under the pressure to which fig. 1 applies. In fig. 2 however, this is indeed the case. Therein curve  $ed$  goes through the point of intersection  $f$  of the saturationcurves and also curve  $e_1d_1$  goes through the point of intersection  $f_1$  of the vapoursaturationcurves. At the temperature and under the pressure, to which this figure applies, therefore the system  $F + F' + \text{liquid } f + \text{vapour } f_1$  can occur. This is also the case in fig. 3 wherein the fourphase equilibrium  $F + F' + \text{liquid } S + \text{vapour } S_1$  occurs.

Now we shall consider more in detail yet two points, nl. the situation with respect to each other of the four points  $F, F', f$  and  $f_1$  and also that of the three curves going through the points  $f$  and  $f_1$ .

In the previous communications the first point has already been treated here and there. We have seen there that the four points can be situated with respect to each other in seven different ways, so that between the four phases of the system  $F + F' + L + G$  one of the seven fourphasereactions:  $F + F' + L \rightleftharpoons G$ ,  $F + F' + G \rightleftharpoons L$ ,  $F + L \rightleftharpoons F' + G$ ,  $F' + L \rightleftharpoons F + G$ ,  $F + F' \rightleftharpoons L + G$ ,  $F \rightleftharpoons F' + L + G$  and  $F' \rightleftharpoons F + L + G$  occurs.

In the particular case that three of the four points are situated by chance on a straight line, (fig. 3) a threephasereaction occurs.

Let us contemplate now the three curves, going through the points  $f$  and  $f_1$ . With the aid of the indicatrix theorem, we can deduce the rule<sup>1)</sup>:

When two equilibriumcurves ( $P$  and  $T$  constant) intersect each

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von H. W. BAKHUIS ROOZEBOOM. III<sup>o</sup> 116.

other, their metastable prolongations are situated in the vicinity of the point of intersection, both within or both outside the corresponding threephaseangle.

Whether the two curves themselves with respect to the other phases are already metastable or not, does of course not effect the validity of this rule.

When two equilibriumcurves intersect each other in a point  $X$ , the phase  $X$ , (liquid, gas, mixed crystal) may be in equilibrium with two other phases which we shall call  $M$  and  $N$  (liquid, gas, mixed crystal etc.). The lines  $XM$  and  $XN$  form four angles; we shall now call the angle  $XMN$  therefore, the angle being one of the angles of the three-phaseangle, and its opposite angle, the threephaseangle of the point  $X$ .

We can express now the abovementioned rule also in this way:

When two equilibriumcurves ( $P$  and  $T$  constant) intersect each other, both curves are situated in the vicinity of the point of intersection, either within or outside the threephaseangle of the point of intersection.

In the figures 1, 2, and 3 we see, that the position of the curves in the vicinity of their points of intersection is in agreement with this rule.

Let us take for instance the point of intersection  $x$  in fig. 1 or 2. In this point  $x$  the curves  $dx$  and  $ux$  intersect each other and therefore the equilibrium  $F' + \text{liquid } x + \text{vapour } x_1$  occurs. The threephaseangle of the point  $x$  therefore is  $\angle x_1 x F'$  and its opposite angle. The curves  $dx$  and  $ux$  are drawn in fig. 1 and 2 within this angle, in fig. 3 (herein  $ux$  is replaced by  $Su$ ) outside this angle.

Let us now take a point of intersection of three curves as for instance the point  $f$  in fig. 2. Taking these curves two and two, we have three pairs of curves; the abovementioned rule is applicable to each of these pairs.

If we contemplate the pair of curves  $dfe$  and  $uxf$ , the equilibrium  $F' + \text{liquid } f + \text{vapour } f_1$  occurs in  $f$ . The threephaseangle of the point  $f$  is therefore  $\angle f_1 f F'$  and its opposite angle. The curves  $dfe$  and  $uxf$  are both drawn within this angle.

If we contemplate the pair of curves  $dfe$  and  $ubf$ , then in  $f$  occurs the equilibrium  $F + \text{liquid } f + \text{vapour } f_1$ ; the threephaseangle of the point  $f$  is therefore  $\angle f_1 f F$  and its opposite angle. The curves  $dfe$  and  $ubf$  are both drawn within this angle.

If we contemplate the pair of curves  $uxf$  and  $ubf$ , then in  $f$  occurs the equilibrium  $F + F' + \text{liquid } f$ , the threephaseangle of

the point  $f$  is now  $FfF'$  and its opposite angle. The curves  $uaf$  and  $ubf$  are both drawn within this angle.

Similar contemplations apply also to the three curves which intersect each other in the point  $f_1$ .

A relation exists also between the position of the curves in the point  $f$  and in the point  $f_1$ . This however we shall not discuss any further here.

In all our previous considerations we have always contemplated saturationcurves under their own vapourpressure and boiling pointcurves of a simple form, nl. curves existing only of a single branch. Under definite circumstances however also curves of a more composite form may occur. Here we shall briefly treat such a boilingpointcurve.

We take a ternary mixture, wherein the system  $L-G$  has a ternary point of minimum pressure, therefore also a ternary point of maximum temperature.

We suppose now that at a definite  $P$  and  $T$  the relations of fig. 1 (III) occur. Herein we find a closed region  $L-G$  and within the liquid region the saturation line of the compound  $F$ . We keep the pressure constant and raise the temperature; the liquid-region then becomes smaller or in other words:

The liquid curve of the region  $L-G$  contracts. Further we assume that heat is required for dissolving  $F$ , so that the saturationcurve of  $F$  contracts also.

If the saturationcurve of  $F$  contracts more rapidly than the liquid curve of the region  $L-G$ , then no points of intersection arise and therefore under the assumed pressure also no boilingpointcurve of  $F$  exists.

When the liquidcurve of the region  $L-G$  contracts more rapidly than the saturationcurve of  $F$ , at a definite temperature  $T_m$  contact takes place. We imagine in fig. 1 (III) that the curves are shifted in such a way, that anywhere on the left side of  $F$  a point of contact  $m$  arises. If the temperature rises still more, now two points of intersection arise, which move away from each other and shift towards the right. Now different cases may occur of which we have already treated some in communication (III). We assume that on a further increase of  $T$  the two points of intersection coincide anywhere on the right side of  $F$  in a point  $M$ .

We may now obtain a diagram as fig. 4. While at the temperature  $T_m$  the saturationcurve of  $F$  is surrounded by the liquidcurve of the region  $L-G$ , at the temperature  $T_M$  (fig. 4) it is just the

reverse. In fig. 4 the point  $F$  is situated within the region  $L-G$ ; of course it may also be situated in the liquid- or gasregion.

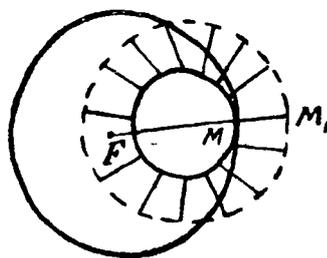


Fig. 4.

Further in fig. 4 the vapourcurve of the region  $L-G$  intersects the saturation curve of  $F$ ; however, it may also surround this curve so that the saturationcurve is situated completely within the region  $L-G$ . We shall confine ourselves

in the following to the case drawn in fig. 4.

When on further increase of  $T$  the liquid curve of the region  $L-G$  contracts now still more rapidly than the saturationcurve of  $F$ , no new points of intersection make their appearance. We have then obtained a boilingpointcurve of a simple form with a minimum boilingpoint in  $m$  and a maximum boilingpoint in  $M$ . It surrounds the point  $F$  and is itself surrounded by its corresponding vapourcurve.

We will assume however that the saturationcurve of  $F$  and the liquidcurve of the region  $L-G$  move in the point  $M$  of fig. 4 with the same rapidity (further we shall see under what conditions such a case is possible). While at a temperature somewhat lower than  $T_M$  the saturationcurve of  $F$  moves in the vicinity of  $M$  more slowly than the liquid curve of the region  $L-G$ , at a temperature somewhat higher than  $T_M$  this is just the reverse.

Consequently on increase of  $T$  above  $T_M$  in the vicinity of the point  $M$ , two points of intersection occur (again), which shift towards the left on further increase of  $T$  and finally coincide in a point  $Q$ . At this temperature  $T_Q$  the saturationcurve of  $F$  and the liquid curve of the region  $L-G$  touch one another again therefore in a point  $Q$ . However the two curves are situated now completely outside each other. The liquidregion therefore is now situated completely outside the saturationcurve of  $F$  and not as at the temperature  $T_M$  (fig. 4) within this

curve. On further increase of  $T$  points of intersection occur no more.

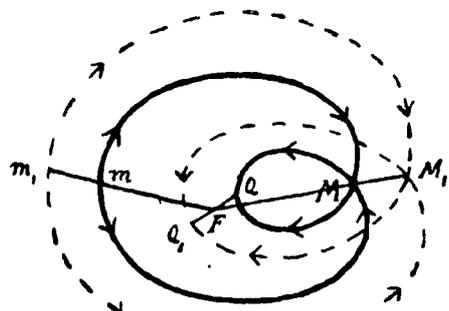


Fig. 5.

The boilingpointcurve will now have a form as curve  $mMQ$  in fig. 5: it shows a double point in  $M$ . The temperature increases in the direction of the arrows, it is a minimum in  $m$ , a maximum in

*Q*. The corresponding vapour-curve  $m_1M_1Q_1$  is dotted. In fig 5 the part  $M_1Q_1M_1$  is drawn circumphased. Of course it may be also expahsed.

If we determine the boilingpointcurve of  $F$  under a pressure somewhat different from that, to which fig 5 applies, the boilingpointcurve will suffer also a small change of form. The double point  $M$  disappears and either two branches separated from each other occur, of which the one surrounds the other, or one single curve is formed which is very concave and which has two parts which are curved sharply towards each other. The same applies to the corresponding vapour-curve. When in a system boilingpointcurves as deduced above occur, some of our previous deductions must be changed to a certain extent and they must be completed, this however is left to the reader.

Now we may still determine under what conditions the liquidcurve of the region  $L-G$  and the saturationcurve of  $F$  will move with the same rapidity in the point  $M$  of fig. 4.

To the saturationcurve of  $F$  applies:

$$[(\alpha-x)r + (\beta-y)s] dx + [(\alpha-x)s + (\beta-y)t] dy = BdT \quad (1)$$

To the liquidcurve of the region  $L-G$ :

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = -Ddt \quad (2)$$

(For the significance of  $B$  and  $D$  see communication (II)).

We now take any point  $M$  of the saturationcurve of  $F$ . We call  $l$  the length of the line  $FM$ . The saturationcurve of the temperature  $T + dT$  will intersect the line  $FM$  in a point  $M'$  in the vicinity of  $M$ . We put  $MM' = dl$  and we take  $dl$  positive in the direction from  $M$  towards  $F$ . We then have:

$$\frac{dx}{\alpha-x} = \frac{dy}{\beta-y} = \frac{dl}{l} \quad \dots \quad (3)$$

If we substitute these values of  $dx$  and  $dy$  in (1), it follows that:

$$dl = \frac{BldT}{(\alpha-x)^2 r + 2(\alpha-x)(\beta-y)s + (\beta-y)^2 t} \quad \dots \quad (4)$$

or:

$$dl = \frac{B}{lK \cos^2 \varphi} dt \quad \dots \quad (5)$$

wherein:

$$K = r + 2 \frac{\beta-y}{\alpha-x} s + \left( \frac{\beta-y}{\alpha-x} \right)^2 t \quad \text{and} \quad (\alpha-x)^2 = l^2 \cos^2 \varphi.$$

Therefore  $\varphi$  is the angle which the line  $FM$  forms with the X-axis. We now take any point  $M$  of the liquidcurve of the region  $L-G$ .

We put  $l_1$  the length of the conjugationline  $MM_1$  which joins the liquid  $M$  with its corresponding vapour  $M_1$ . The liquidline of the temperature  $T + dT$  will now intersect this conjugationline in a point  $M'$  in the vicinity of  $M$ . We represent  $MM'$  by  $dl_1$ ; we take  $dl_1$  positive in the direction from  $M$  towards  $M_1$ . We then find from (2)

$$dl_1 = - \frac{D}{l_1 K_1 \cos^2 \varphi_1} dT \dots \dots \dots (6)$$

wherein :

$$K_1 = r + 2 \frac{y_1 - y}{x_1 - x} s + \left( \frac{y_1 - y}{x_1 - x} \right)^2 t \text{ and } (x_1 - x)^2 = l_1^2 \cos^2 \varphi_1.$$

$\varphi_1$  therefore is the angle which forms the conjugationline  $MM_1$  with the  $X$ -axis.

We now suppose 1<sup>st</sup> that the saturationcurve of  $F$  and the liquidcurve of the region  $L-G$  go through a same point  $M$ ;

2<sup>d</sup> that the two curves touch each other in that point.

From 1<sup>st</sup> it follows that  $r$ ,  $s$  and  $t$  have the same value in  $K$  and  $K_1$  and that  $B$  and  $D$  apply to the same liquid.

From 2<sup>nd</sup> it follows, as is easily deduced, from the equations of the two curves, ( $P$  and  $T$  constant) that:

$$\frac{\beta - y}{\alpha - x} = \frac{y_1 - y}{x_1 - x}$$

and therefore also  $\varphi = \varphi_1$ . The meaning of this is that the lines  $FM$  and  $MM_1$  coincide. This follows as we saw already before, also immediately from the indicatrix theorem. From this now it follows that we may substitute  $l$ ,  $k$  and  $\varphi$  in (6) for  $l_1$ ,  $k_1$  and  $\varphi_1$ . We then obtain:

$$dl_1 = - \frac{D}{lK \cos^2 \varphi} dT \dots \dots \dots (7)$$

Now  $D$  is positive; if we assume further that heat is to be supplied for dissolving solid  $F$ , then  $B$  is also positive. From this it follows that  $dl$  and  $dl_1$  always have an opposite sign. In order that the liquidcurve of the region  $L-G$  and the saturationcurve of  $F$  may move in the same direction, when  $T$  is changed, the point  $M$  must therefore be situated between the points  $F$  and  $M_1$ . This is then also in agreement with fig. 4.

From (5) and (7) it follows, that the two curves will move with the same rapidity as

$$\frac{B}{l} = \frac{D}{l_1} \dots \dots \dots (8)$$

We may find this condition also in the following way. The boilingpointcurve of  $F$  is fixed by :

$$[(\alpha-x)r + (\beta-y)s] dx + [(\alpha-x)s + (\beta-y)t] dy = B dT \quad (9)$$

$$[(x_1-x)r + (y_1-y)s] dx + [(x_1-x)s + (y_1-y)t] dy = -D dT \quad (10)$$

From this follows

$$(Pr + Qs) dx + (Ps + Qt) dy = 0 \quad (11)$$

wherein

$$P = (\alpha-x)D + (x_1-x)B \text{ and } Q = (\beta-y)D + (y_1-y)B.$$

In order that the point of the curve under consideration may be an isolated or a double point, the coefficient of  $dx$  and  $dy$  must be  $= 0$ . Therefore  $P = 0$  and  $Q = 0$  or

$$(\alpha-x)D + (x_1-x)B = 0 \text{ and } (\beta-y)D + (y_1-y)B = 0 \quad (12)$$

If  $B$  and  $D$  are not  $= 0$ , then

$$\frac{\beta-y}{\alpha-x} = \frac{y_1-y}{x_1-x}$$

follows, which we have also found for this. This means, that the considered point, its corresponding vapour and the point  $F$  are situated on a straight line. Further it follows that the liquidcurve of the region  $L-G$  and the saturationcurve of  $F$  touch each other in the contemplated point. If we substitute for  $B$  and  $D$  their values in (12), then we find :

$$(\beta-x)H_1 + (x-x_1)\eta + (x_1-\alpha)H = 0 \quad (13)$$

or

$$(\beta-y)H_1 + (y-y_1)\eta + (y_1-\beta)H = 0 \quad (14)$$

The first part of (13) and (14) represents the change of entropy when a reaction takes place between the three phases  $F$ ,  $L$ , and  $G$ . From this it follows therefore, that the contemplated point of the boilingpointcurve will be an isolated or a double point, when an isentropic reaction takes place between the three phases  $F$ ,  $L$  and  $G$ ; in other words, when no heat must be supplied or removed. In (8) the same is expressed in quite an other form as in (13) and (14). In order to examine whether the contemplated point is an isolated or a double point, we must calculate terms of higher order, namely  $A dx^2 + B dx dy + C dy^2$ .

Because the fixing of  $A$ ,  $B$ , and  $C$  gives cause for extensive calculations, we will leave that aside.

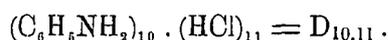
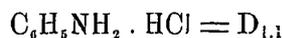
*To be continued.*

**Chemistry.** — “Concerning combinations of aniline with hydrochloric acid”. By J. C. THONUS. (Communicated by Prof. F. A. H. SCHREINEMAKERS).

As I am engaged in the investigation of the equilibria between water, aniline and an acid, I wish to state briefly the results, which I have found at  $0^\circ$  in the system Water-Aniline-Hydrochloric acid. In the literature is described :

1. the aniline hydrochloride, to which is given the formula  $C_6H_5 \cdot NH_2 \cdot HCl$ .
2.  $C_6H_5 \cdot NH_2 \cdot (HCl)_3$ , obtained by VON KORCZYNSKI at  $-75^\circ$ <sup>1)</sup>.

The compounds, which I have found at  $0^\circ$ , are the following :



From my research I cannot deduce with certainty that  $D_{1,1}$  exists at  $0^\circ$  (at  $25^\circ$  and  $35^\circ$  I have however, been able to determine the existence of  $D_{1,1}$  with certainty).

Fig. I, which has been very much schematized for the sake of clearness, represents the equilibria, which exist at  $0^\circ$  in the system Water-Aniline-Hydrochloric acid; the angular points W = water, Z = hydrochloric acid, An = Aniline represent the three components. The isotherm at  $0^\circ$  exists, as far as it has been determined out of the following saturationcurves :

*ab* is the saturationcurve of  $D_{6,1}$ .

*bc* represents solutions, in equilibrium, either with  $D_{1,1}$ , or with  $D_{10,11}$ .

*cd* is the saturation curve of the hydrate  $D_{5,3,1}$ .

*de* is the saturation curve of  $D_{10,11}$ .

. If *bc* represents solutions, saturated with  $D_{10,11}$ , then  $D_{10,11}$  makes its appearance twice, the saturation curve of  $D_{5,3,1}$  cutting out a part in the middle.

A second possibility is, that *bc* is the saturation curve of  $D_{1,1}$ .

Lastly, although *bc* is only a small curve, yet it may consist of two curves, viz. the saturation curve of  $D_1$ , and that of  $D_{10,11}$ . In this instance the isotherm would consist of five saturation curves, in which only four different solid substances make their appearance.

<sup>1)</sup> Berichte 43. 1820 (1910).

= In order to elucidate the relations, existing on the curve  $bc$ , I analysed four solutions of this curve with their corresponding solid phases; as the conjugation-lines liquid-solid make a very sharp angle with the side aniline-hydrochloric acid, no conclusion with respect to  $D_{1,1}$  and  $D_{10,11}$  could be arrived at.

Theoretically two saturation curves should meet each other in an angle; sometimes, however, as also in this instance, the saturation lines form practically one single continuous curve.

In the binary system Water-Aniline the solution separates into two liquid layers. On adding hydrochloric acid the two layers approach each other in composition and a binodal curve results, as is indicated schematically in Fig. I. The extreme points of it are situated on the side Water-Aniline, its plait-point within the triangle. From the figure can be seen, that, in agreement with the theory<sup>1)</sup>, the saturation curve in the vicinity of the plait-point is bent in the same direction as the binodal curve.

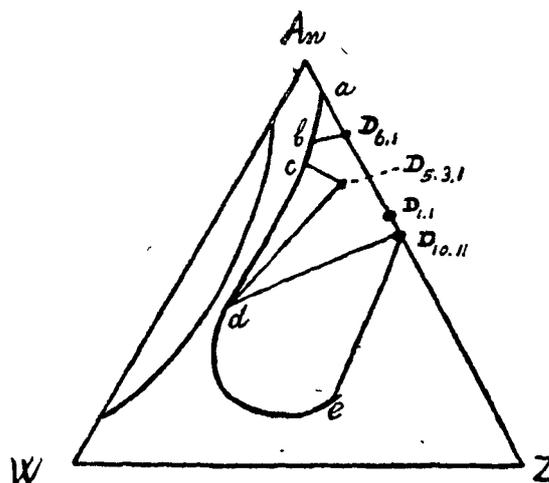
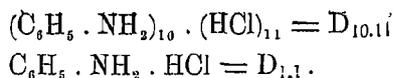


Fig. 1.

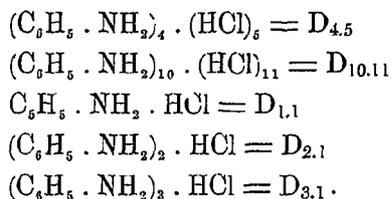
As the two curves do not intersect, a two-layer-system, which is saturated with a solid substance, will not exist at  $0^\circ$ .

The researches are continued at different other temperatures amongst others at  $25^\circ$  and  $35^\circ$ . At  $25^\circ$  neither the hydrate  $D_{5,3,1}$ , nor the double salt  $D_{6,1}$  exists. On the other hand other combinations at these temperatures have, been proved to exist. As far as I have determined, there exist at  $25^\circ$  amongst others:

<sup>1)</sup> F. A. H. SCHREINEMAKERS, Die heterogenen Gleichgewichte von BAKHUIS ROOZEBOOM III<sup>2</sup> 118.



At 35°:



The continuation of this work will have to solve the question, whether mixed-crystals may also perhaps make their appearance in this system.

*Leiden, Inorganic-chemical Laboratory.*

**Chemistry.** — “Concerning combinations of urea with acids.” By  
D. F. DU TOIT. (Communicated by Prof. F. A. H. SCHREINEMAKERS).

In all textbooks of organic chemistry it is usually stated as well-known facts:

1. that one molecule of urea forms an additive product with one molecule of a monobasic acid,
2. that urea can easily be demonstrated by making use of the small solubility of its nitrate,  $\text{CON}_2\text{H}_4 \cdot \text{HNO}_3$ , or of its oxalate,  $2 \cdot \text{CON}_2\text{H}_4 \cdot (\text{COOH})_2$  in the solutions of the corresponding acids.

Consequently it appeared interesting to find out how urea would behave with respect to other acids (mono- as well as poly-basic), what the real solubility of the two above-mentioned salts is, and whether urea is not capable of forming additive products with more than one molecule of an acid. For this purpose certain isotherms were determined in the ternary systems relative to this purpose, and with the help of the “rests-method” the compositions of the solid phases were deduced.

We will consider the solid substances only, which are in equilibrium with the solutions.

#### Urea-Oxalic acid-Water.

This system was determined at 20° and at 30°. In addition to urea and  $(\text{COOH})_2 \cdot 2 \text{H}_2\text{O}$ , the compound  $(\text{CON}_2\text{H}_4)_2 \cdot (\text{COOH})_2$  was found.

The compound  $\text{CON}_2\text{H}_4 \cdot (\text{COOH})_2 \cdot \text{H}_2\text{O}^1$ , of which the preparation is rather peculiar, was not found at this temperature.

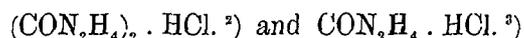
Urea-Acetic acid-Water.

At 16°, 30° and 32° was found in addition to urea the compound  $\text{CON}_2\text{H}_4 \cdot (\text{CH}_3 \cdot \text{COOH})_2$ .

This compound, which melts at about 35°, is very soluble in water, and is not dissociated by water.

Urea-Hydrochloric acid-Water.

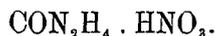
At 20° were found, in addition to urea the two salts



Both salts are soluble in water without dissociation.

Urea-Nitric acid-Water.

At 20° the solid phases urea and the salt

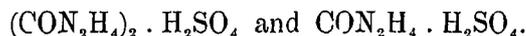


were found.

The solubility of this nitrate is very small and decreases as the amount of  $\text{HNO}_3$  in the solution increases, until at about 70% nitric acid a minimum is reached. In nitric acid solutions of about 74% the nitrate is completely decomposed.

Urea-Sulphuric acid-Water.

At 20° the solid phases urea and the two salts



were found.

The compound which HANTZSCH<sup>4)</sup> has obtained in all probability, viz.  $\text{CON}_2\text{H}_4 \cdot (\text{H}_2\text{SO}_4)_2$  was not found at this temperature.

These researches are continued at other temperatures as well as with other acids.

Leiden, *Inorganic chemical laboratory.*

<sup>1)</sup> LIUBAWIN A. Spl. 8, 83.

<sup>2)</sup> DESSAIGNES. J. 1854, 677.

<sup>3)</sup> ERDMANN. J. pr. Ch. 25, 506 (1842).

<sup>4)</sup> HANTZSCH. Z. für ph. Ch. 61, 280, 299 (1908).

**Chemistry.** — “The occurrence of an upper critical point of mixing at the coexistence of two mixed crystal phases.” By Prof. A. SMITS and C. A. LOBRY DE BRUYN. (Communicated by Prof. J. D. VAN DER WAALS).

1. When examining the system KCl — NaCl KURNAKOW and ZEMCZUZYNI<sup>1)</sup> found that as Fig. 1 shows, a continuous melting-point line occurs here with a temperature minimum at  $\pm 664^\circ$ , and that after the solidification a transformation still makes its appearance in different mixtures.

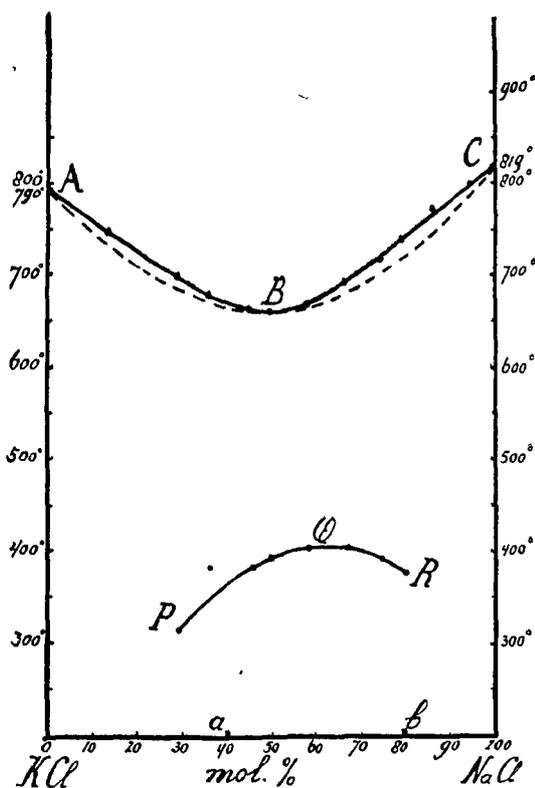


Fig. 1.

The existence of these transformations (which is chiefly of interest here) has appeared in two ways. In the first place from the curves of cooling and in the second place from the fact that, as was first found by OSTWALD<sup>2)</sup> and BEKETOFF<sup>3)</sup>, and afterwards confirmed by KURNAKOW and ZEMCZUZYNI, the heat of solution of a mixture

<sup>1)</sup> Z. f. anorg. Chem. 52, 186, (1907).

<sup>2)</sup> Journ. prakt. chem. 25, 8 (1882).

<sup>3)</sup> Z. f. anorg. chem. 40, 855 (1904).

which has *suddenly* been cooled from a temperature above  $407^{\circ}$  to  $0^{\circ}$ , differs considerably from that of a mixture that has been allowed to cool down *slowly*. In case of rapid cooling the heat of solution appeared namely to be much smaller negative, which points to an exothermal process, which failed to appear in case of rapid cooling. After continued heating at  $85^{\circ}$ — $150^{\circ}$  the negative value of the heat of solution rose, and after a few days it had acquired the value of the mechanical mixture.

It was on the ground of these phenomena that K. and Z. concluded that the isomorphous mixtures are decomposed at  $300^{\circ}$ — $407^{\circ}$ , so that solid solutions are formed, which already at  $100^{\circ}$ — $150^{\circ}$  consist almost exclusively of the components.

This conclusion is also optically confirmed, for as OSTWALD already observed, the suddenly cooled mass gives the impression of white enamel, whereas the salts taken separately yield a perfectly transparent solid substance when the melt is cooled. On slow cooling it is now clearly observable that the enamellar substance is converted to a transparent mass.

Though in these experimental data clear indications are to be found for the probable explanation of the observed phenomena, and this explanation is easy to test, KURNAKOW and ZEMCZUZYNI have evidently not realized this, for they conclude: "Weitere Untersuchungen müssen zeigen, ob die Zersetzung der festen Lösungen von Erscheinungen des Polymorphismus oder von anderen Ursachen abhängt." As however these "weitere Untersuchungen" seem not to have been undertaken by K. and Z., and as the question under discussion is an exceedingly important one, which can be answered in a simple way, we undertook the following investigation.

2 OSTWALD's experiments and those of KURNAKOW and ZEMCZUZYNI about the heat of solution show that the stable state of equilibrium at the ordinary temperature is most probably an equilibrium of two mixed crystal phases, one of which consists practically of *KCl*, and the other of *NaCl*.

If this be true, we meet here with the interesting case that at higher temperature these coexisting mixed crystal phases approach each other more and more in concentration, and become perfectly identical at  $407^{\circ}$ , or in other words they exhibit an upper critical mixing-point.

The top of the line *PQR* in Fig. 1 lying at about 66.6 mol. % *NaCl*, the possibility of the occurrence of a compound might, however, also be thought of. It should be noted, however, that not a single

fact pleads in favour of this supposition, but that on the contrary the observed phenomena make this supposition highly improbable. Nevertheless it is here of some importance to consider also this case, in which the curve  $PQR$  then would indicate in what way the temperature of the transformation homogeneous mixed crystals  $\rightarrow$  mixed crystal phase + compound varies with the concentration.

To arrive at perfect certainty about the interpretation of the phenomenon, the ternary system  $H_2O - NaCl - KCl$  was studied at  $25^\circ$  and atmospheric pressure, for so far as this was necessary with a view to the question under investigation.

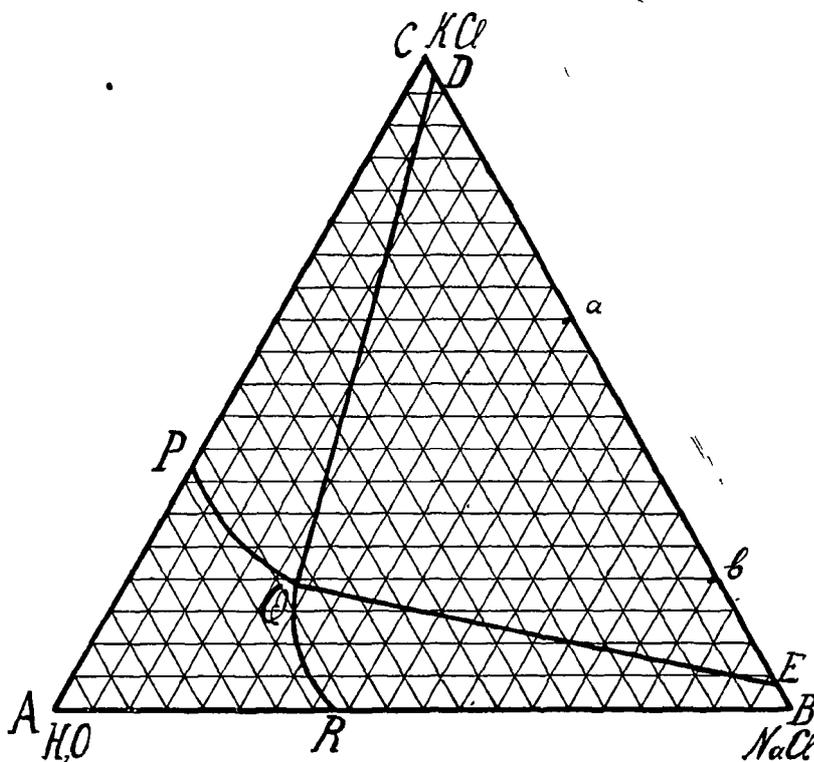


Fig. 2.

If no compound is found, and if  $D$  and  $E$  in Fig. 2 are the mixed crystal phases coexisting at  $25^\circ$ , we shall have to do with two solubility-isotherms  $PQ$  and  $QR$ , so that  $Q$  is the solution that coexists with the two solid phases  $D$  and  $E$ . If we start from two concentrations  $a$  and  $b$ , on the lefthand and the righthand of the top  $Q$ , (see Fig. 1), it is clear that these two mixtures, which are homogeneous at temperatures above  $407^\circ$ , will consist of the two-phase complex  $D + E$  at  $25^\circ$ , but in different ratio.



put in a vessel of Jena glass, which had been placed in a nitrate bath of  $\pm 360^\circ$ . The nitrate bath was then allowed to cool very slowly, in which the range of temperature between  $370^\circ$ — $340^\circ$  was passed through in about 3 hours; the further cooling proceeded more rapidly. The obtained solid substance was then ground to powder, and then shaken in a thermostat with a little water at  $25^\circ$  for 2 hours, after which in the usual way a certain quantity of saturated solution was twice pipetted off.

We determined of each quantity obtained in this way:

1. the total weight.
2. the weight of the sum  $\text{NaCl} + \text{KCl}$  (by careful evaporation, followed by heating to the temperature of melting).
3. the weight of  $\text{KCl}$  (according to SCHLÖSING-WENSE'S method).

At the same time for a comparison the solubility of the same mixtures *a* and *b* was determined at the same temperature, but when they had not been heated previously.

1	Mixture <i>a</i>		Mixture <i>b</i>	
	60% KCl	40% NaCl	20% KCl	80% NaCl
	Melted and slowly cooled down 2	Mixed mechanically at room temperature 3	Melted and slowly cooled down 4	Mixed mechanically at room temperature 5
KCl + NaCl (in gr. to 100 gr. solution)	31.59	31.61	31.63	31.56
	31.63	31.57	31.61	31.57
Weight KCl	11.01	11.00	11.04	11.01
	11.00	10.98	11.00	10.97
Weight NaCl	20.58	20.61	20.59	20.55
	20.63	20.59	20.61	20.60
Weight H <sub>2</sub> O	68.41	68.39	68.37	68.44
	68.37	68.43	68.39	68.43

The weight of the *NaCl* has been calculated from the difference in weight between *KCl + NaCl* and *KCl*; the weight of the *water* has been calculated from the total weight of the solution, diminished by the weight of the  $\text{NaCl} + \text{KCl}$ .

The two mixtures *a* and *b* had the following concentration :

$$\begin{array}{l}
 a \left\{ \begin{array}{ll} 4,476 \text{ gr. KCl} & 60 \text{ mol. } \% \text{ KCl} \\ 2,340 \text{ gr. NaCl} & 40 \text{ mol. } \% \text{ NaCl} \end{array} \right. \text{ or} \\
 b \left\{ \begin{array}{ll} 1,492 \text{ gr. KCl} & 20 \text{ mol. } \% \text{ KCl} \\ 4,680 \text{ gr. NaCl} & 80 \text{ mol. } \% \text{ NaCl.} \end{array} \right. \text{ or}
 \end{array}$$

The result of the investigation is given in the preceding table, p. 561 in which all the quantities are calculated for 100 gr. of the mixture. It appears with the greatest clearness from the good agreement between the values in the columns 2, 3, 4, and 5 that in the two cases the coexisting liquid has the same concentration for the examined threephase equilibrium, from which follows that we have really to do here with the phenomenon of unmixing in the solid state, which, as is indicated in the *T,X*-figure, occurs over an ever diminishing region of concentration at higher temperature, terminating finally in an *upper critical mixing-point*.

Towards lower temperature the unmixing always increases so that

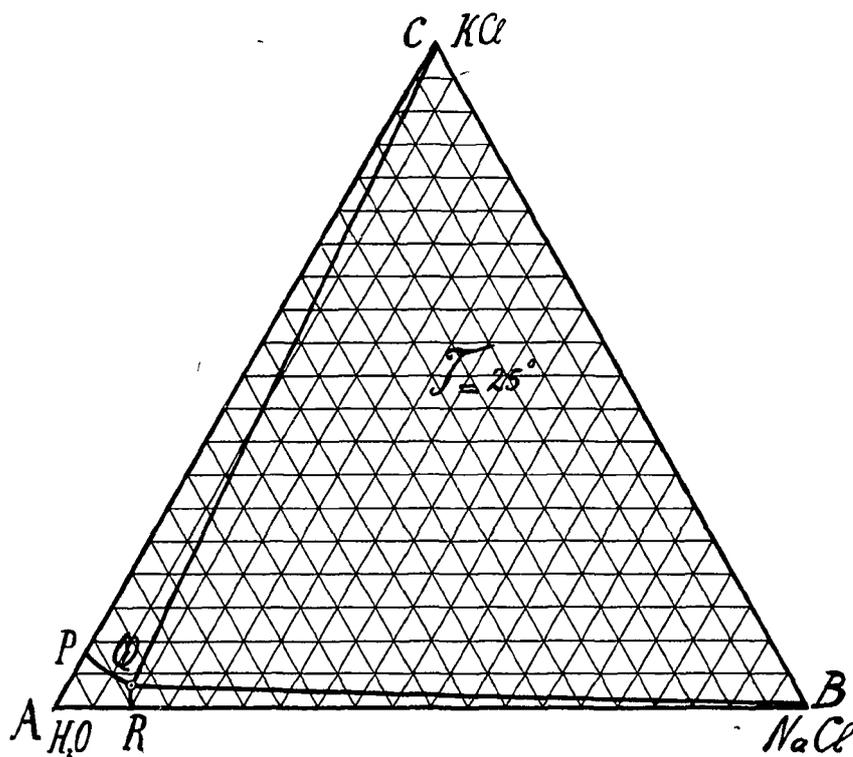


Fig. 4.

according to KRICKMEYER's investigations <sup>1)</sup>, only one of the two salts could be demonstrated in each of the coexisting solid phases at 25°.

The real situation of the isotherms at the temperature of 25° has been given in Fig. 4. According to this investigation the point *Q* lies at :

8,20 mol. % NaCl  
 3,43 „ „ KCl  
 88,37 „ „ H<sub>2</sub>O

whereas VAN 'T HOFF and MEIJERHOFFER <sup>2)</sup> found

7,9 mol. % NaCl  
 3,5 „ „ KCl  
 88,6 „ „ H<sub>2</sub>O.

The situation of the points *P* and *R* has not been determined anew, but was derived from the literature <sup>3)</sup>.

*P* denoting the solubility of KCl at 25°, lies at 7,96 mol % KCl  
 and 92,04 „ „ H<sub>2</sub>O

*R* denoting the solubility of NaCl at 25°, lies at 9,96 „ „ NaCl  
 and 90,04 „ „ H<sub>2</sub>O.

4. What is remarkable about this is that these solubility-isotherms *PQ* and *RQ* must be connected continuously by means of a ridge with a partially metastable, partially unstable part, and that at the temperature of the upper critical mixing point this continuity enters the stable region.

In this connection it may be pointed out that by this investigation it has been proved for the first time that  $\zeta$ -lines exist for solid mixtures, which must actually have a shape as is schematically given in Fig. 5. This line points to an interrupted series of mixed crystals, though the  $\zeta$ -line is continuous. This continuity, however, lies here in the unstable region, and enters the stable region for the first time at the upper critical mixing point.

In Fig. 6 the *P, T*-projection of the system KCl—NaCl is schematically represented to show that here a plaitpoint curve for the solid substance ( $S_1 = S_2$ ) must exist, which will probably run to infinite pressure.

In conclusion it may be stated that the phenomenon of the appearance of an upper critical mixing point in the solid state discussed here probably occurs for a number of other systems, as

<sup>1)</sup> Z. f. phys. Chem. **21**, 53, (1896).

<sup>2)</sup> Ber. Kgl. Pr. Akad. Wiss. Berlin 590 (1898).

<sup>3)</sup> ANDREAÈ J. pr. Chem. **29**, 456 (1839).

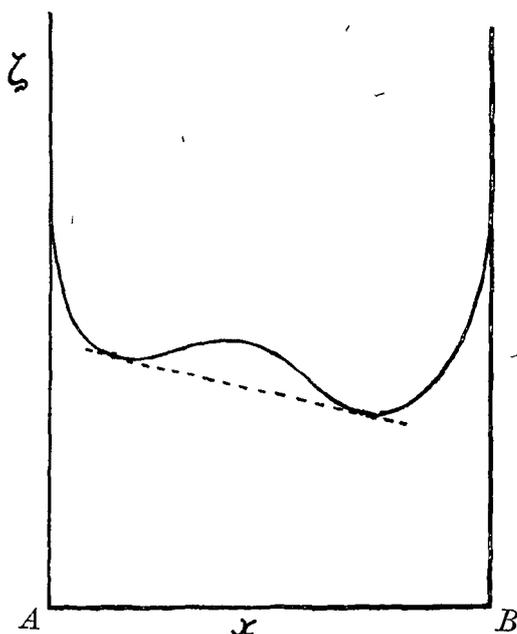


Fig. 5.

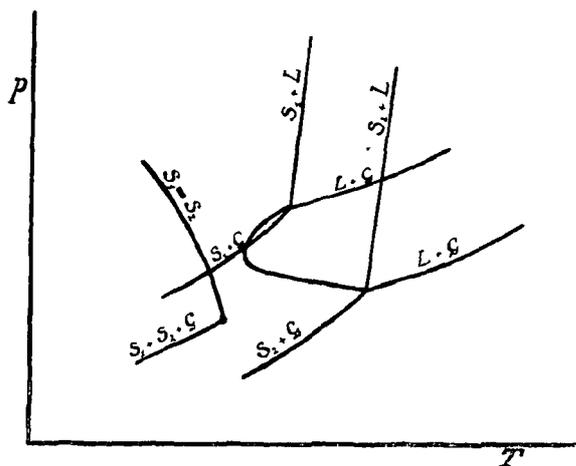


Fig. 6.

e.g. for  $\text{LiCl—NaCl}$ <sup>1)</sup>  $\text{CaCl}_2\text{—MnCl}_2$ <sup>2)</sup>,  $\text{CaCl}_2\text{—SrCl}_2$ <sup>3)</sup>  $\text{CaSiO}_3\text{—CaS}$ <sup>4)</sup>  $\text{KBO}_2\text{—NaBO}_2$ <sup>5)</sup>,  $\text{Fe—Ni}$ <sup>6)</sup>.

Amsterdam, 23 Nov. 1913.

Anorg. Chem. Laboratory  
of the University.

<sup>1)</sup> ZEMCZUZYNI and RAMBACH, Z. f. anorg. Chem. **65**, 403 (1910).

<sup>2)</sup> SANDONNINI. Rend. Linc **20**, 11, 456 (1911).

<sup>3)</sup>

<sup>4)</sup> LEBEDEW. Z. f. anorg. Chem. **77**, 301 (1911).

<sup>5)</sup> VAN KLOOSTER. Z. f. anorg. Chem. **69**, 122 (19,0)

<sup>6)</sup> GUERTLER and TAMMANN. Z. f. anorg. Chem. **44**, 205 (1905).

**Chemistry.** — "*The allotropy of zinc.*" I. By Prof. ERNST COHEN and W. D. HELDERMAN.

As long as half a century ago various investigators tried to solve the problem whether zinc might be capable of existing in different allotropic modifications.<sup>1)</sup> As late as 1890 LE CHATELIER<sup>2)</sup> proved that this metal does really show a transitionpoint in the neighbourhood of 350°. MÖNKEMEYER<sup>3)</sup> found this point at 321°, BENEDICKS<sup>4)</sup> at 330° (melting point of pure zinc 419°.4) whilst the measurements of MAX WERNER<sup>5)</sup> (who found 300°), published some weeks ago, agree sufficiently with those of LE CHATELIER. We shall discuss in a subsequent paper the differences which exist amongst the results of the investigators mentioned above. Whilst BENEDICKS mentions a second transitionpoint (at 170°), MAX WERNER was unable to find this point. The question whether it really exists or not may be left open for the moment.

As long ago as 1806 CHARLES HOBSON and CHARLES SYLVESTER<sup>6)</sup> stated that the mechanical properties of zinc are very different in different ranges of temperature. It may be pointed out here (as also stated by ourselves) that zinc which is hard at ordinary temperatures, becomes extremely brittle after having been melted and chilled.

Most of those who have studied this metal, point out that the values which are given in the literature for its density differ amongst themselves very considerably.

This fact has formed the starting point for the researches of KAHLBAUM and his collaborators<sup>7)</sup> (following a way indicated by SPRING) on the influence of very high pressures on the density of metals in general. We shall discuss this question in a special paper; here it may be pointed out that years ago BOLLEY<sup>8)</sup> as well as RAMMELSBERG<sup>9)</sup> carried out some experiments in order to find out

<sup>1)</sup> The earlier literature on this subject will be given in our paper in the *Zeitschrift für physik. Chemie*.

<sup>2)</sup> C. R. **111**, 414, 454 (1890). Contribution à l'étude des alliages, Paris 1901, p. 416.

<sup>3)</sup> *Zeitschr. f. anorg. Chemie*, **43**, 182 (1905).

<sup>4)</sup> *Arkiv för Matematik, Astronomi och Fysik*, **6** (1910), quotation from a separate copy *Metallurgie*, **7**, 531 (1910).

<sup>5)</sup> *Zeitschr. f. anorg. Chem.* **83**, 275 (1913).

<sup>6)</sup> NICHOLSON'S *Journal of Natural Philosophy*, **11**, 304 (1806). Translation in GEHLEN'S *Neues allgemeines Journal der Chemie*, **6**, 728 (1806).

<sup>7)</sup> *Zeitschr. f. anorg. Chemie* **29**, 177 (1902).

<sup>8)</sup> *LIEBIG'S Annalen*, **95**, 294 (1855).

<sup>9)</sup> *Monatsberichte der königl. preussischen Akad. der Wiss. zu Berlin*, 1880, pag. 225.

if its previous history (chilling, slowly cooling etc.) had any influence on the density of zinc. These investigations are not exact enough to yield a definite conclusion. RAMMELSBERG, summing up his measurements, says: "Nach dem Gesagten handelt es sich hier nicht um molekulare Modifikationen. Wir finden nur, dass der schnelle Uebergang aus dem flüssigen in den festen Zustand die Sprödigkeit des Metalls erhöht..." It will be proved here that this conclusion does not agree with the facts.

We thought it necessary to carry out fresh experiments on this subject. Considering the results of our investigations on tin, bismuth<sup>1)</sup> and cadmium<sup>2)</sup>, and in view of the existence of a transitionpoint at 350° it might be expected that the metal, which has been called "zinc" until now, might be a *metastable* system, containing two or more allotropic modifications of this metal.

The following experiments prove that such is really the case. We melted one kilo of the metal (Zink-"KAHLBAUM"; we were not able to detect any impurity in 100 grams of the material). It was then poured out into a cylinder made of asbestos-paper, which was placed in a glass beaker. The beaker was filled up with solid carbon-dioxyde and alcohol. In this way the melted metal was chilled very quickly. The cylinder of zinc formed in this way, was turned into small pieces on a lathe; the outer layer was not used in the following experiments. The metal was washed with ether; after this we carefully determined its density  $\left(d \frac{25^{\circ}.0}{4^{\circ}}\right)$ , using a pycnometer containing 25 cc. The material was divided into two parts ( $Zn_I$  and  $Zn_{II}$ ), which were manipulated separately.

In this way we found (21 hours after having chilled the metal)

$$d \frac{25^{\circ}.0}{4^{\circ}} Zn_I 7.130 \quad Zn_{II} 7.129.$$

We then brought the samples (weighing each 35 grams) into a Jena glass flask, into which was poured so much of a solution of zincsulphate, (saturated at 15°) that the metal was covered by the solution. The whole was then heated at 100° for a long time.

At different intervals of time we took the metal out of the flasks washed it with dilute hydrochloric acid and water (until the reactions for  $SO_4$  and  $Cl$  had disappeared), alcohol and ether. It was then dried in vacuo, using sulphuric acid as a drying agent. After these operations the density of the two samples was determined again, using the whole mass (35 grams) in the pycnometer.

<sup>1)</sup> Zeitschr. für physik Chemie **85**, 419 (1913).

<sup>2)</sup> Proceedings **16**, 485 (1913).

In this way we found:

$$\text{Density } d \cdot \frac{25^{\circ}.0}{4^{\circ}}$$

	Specimen Zn <sub>I</sub>	Specimen Zn <sub>II</sub>
After 24 hours	7.124	7.128
„ 72 „	7.114	7.121
„ 192 „	7.116	7.112
„ 336 „	7.102	7.109

In comparing these values with the original one, it will be seen that the density has decreased at least 24 units of the third decimal place and that this decrease was a continuous one during the whole experiment.

Now there exists full agreement between these results and that of KAHLBAUM and his collaborators, described in the paper mentioned above. In the distillation of zinc in a porcelain tube in vacuo they determined the place where the metal was deposited in the inner side of the tube by photographing it by means of RÖNTGEN-rays. In this way they found (the photo is reproduced in their paper), that the zinc was deposited at a small distance from the hottest part of the tube. Consequently the metal has been able to remain during the cooling in the condition which corresponded to its temperature. In full agreement with this manner of cooling the density of the metal was found to be very low  $\left(d \cdot \frac{20^{\circ}}{4^{\circ}} 6.922\right)$ . This value probably lies very near to the density of pure  $\alpha$ -zinc.

Our experiments prove that we have to consider "zinc" as a *metastable* system. The modification formed at high temperatures, only very slowly changes into that which is the stable one at 100° (at ordinary temperature). In this way we find (as in the case of tin, bismuth and cadmium), that our "zinc world" is in a *metastable* condition.

As there exists a great difference between the specific volume of the modifications of zinc, all objects made from this metal will disintegrate in the long run.

In conclusion the following facts may be pointed out:

Quite recently M. U. SCHOOP invented a method of covering any object with a layer of metal. In order to do so (the operation is called "schopieren") the metal (in the form of a wire) is mechanically moved through an oxy-hydrogen flame. A strong current of nitrogen "atomizes" the metal which immediately covers the object which is held before the burner. Evidently this device forms an

ideal method for producing chilled metal. If any object has been covered in this way with "zinc", this layer is in a *metastable* condition after cooling to ordinary temperature:

In consequence such a layer will disintegrate in the long run. That the metal made in this way is not in the ordinary condition is proved by experience. NEUBURGER <sup>1)</sup> says about it (in the case of tin):

"... ebenso erleiden diese unter Umständen auch eine teilweise Veränderung ihrer physikalischen Eigenschaften, die in einer Vergrößerung der Härte besteht. ... Während gegossenes Zinn nach der BRINELLSCHEN Kugeldruckprobe einen Härtegrad von 9.5 aufweist, zeigt gespritztes einen solchen von 14.2".

We hope to be able to report shortly on the metastability of these "atomized" metals.

VAN 'T HOFF—*Laboratory.*

*Utrecht, November 1913.*

**Physics.** — "*A rapid Thermopile.*" By Dr. W. J. H. MOLL. (Communicated by Prof. W. H. JULIUS.)

Among the many instruments, which have been devised for the quantitative investigation of visible and invisible radiation, the thermopile occupies the foremost place in order of both priority and merit. Though for special researches and under particular circumstances the bolometer and the radiometer may be deemed more suitable, the thermopile has never ceased to find its application, for the most delicate measurement as well as for the simple demonstrative experiment.

It is particularly of late years, that it has once again attracted the attention of a number of investigators, and that numerous improvements in its construction have been tried. All of these had the same purpose, namely to increase the *sensitiveness* of the instrument.

Another property, however, is by no means of less importance, viz. the *rapidity* with which, after the radiation has been admitted or intercepted, thermal equilibrium is reached in the pile. The greater this rapidity, the better is the instrument adapted to the investigation of all sorts of radiation-phenomena of short duration and of rapid variability, and also to those researches which require a long series of successive readings, and which with a slow instrument

<sup>1)</sup> Die Naturwissenschaften, 1, 465 (1913).

become extremely wearisome. But besides all this, great rapidity of the thermopile implies, as is easily conceivable, great stability of the zero, and its indications will therefore be the more certain, the more quickly they are arrived at.

The common thermopile, as is generally known, is a rather slow instrument.

In the original form, devised by MELLONI, it consists of a number of metal bars, joined so as to form a bundle, at the terminals of which the two sets of junctions are found. The great heat-capacity of such a system causes the rise in temperature of the exposed junctions to continue a long time, and thus a considerable delay occurs before equilibrium of temperature is reached.

The thermopile of RUBENS is built up from metal wires, arranged zig-zag wise in the same plane. A slit is adjusted so as to admit the radiation only to the "odd" junctions. The much smaller heat-capacity of this pile is to the advantage of both its rapidity and its sensitiveness. The rapidity, nevertheless, is still comparatively small; in the case of a specimen which I examined the thermo-electric current took 6 seconds to reach 99 % of its definitive value.

The improvements, which in recent years the thermopile has undergone, relate to small details of construction only, viz. the number, the dimensions, and the material of the wires. It is true, that sometimes the sensitiveness was thus improved, but invariably at the cost of the rapidity.

The rapidity of a thermopile is determined by the rapidity with which a difference in temperature of the junctions comes to an equilibrium; a process in which not only the heat-capacity of the junctions plays a rôle, but also, and chiefly, the heat-exchange by conduction, radiation, and convection.

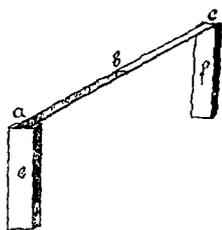
Heat-exchange also takes place while the instrument is being exposed to the radiation, and will thus have a directly prejudicial effect on the sensitiveness. If therefore this exchange be furthered in order to increase the rapidity, we shall have to expect a diminution of the sensitiveness, unless we arrange so as to compensate for it in some other way.

Now, for various applications of the thermopile (in particular, when it is employed not for spectral work, but for the measurement of "total radiation") the narrowness of the exposed surface is of no advantage. A wider surface, which receives a greater part of the radiation, would appear more suitable for the work in hand.

In the following lines a thermopile will be briefly described,

which has been constructed according to a wholly different principle. In its construction the two conditions — a prompt heat-exchange and a wide surface exposed to radiation. — are satisfied, and consequently a high degree of both rapidity and sensitiveness has been attained.

The thermopile is built up of a great number of metal strips. Each of these consists partly (*ab*) of constantan, and partly (*bc*) of copper, and is soldered at both ends on two copper bars (*e* and *f*).



This constantan-copper strip can be exposed to the radiation throughout its entire length. Then, on account of the great difference in heat-capacity of the two junctions *a* and *b*, *b* will attain a higher temperature than *a*; the equilibrium of temperature being attained in a very short time, in consequence chiefly of the

good heat-conduction between the junctions.

As copper and constantan differ considerably in heat-conductivity, the two metals which form the strip are taken of different thickness (and length), so as to have the temperature highest at *b*, while the strip is exposed to radiation.

Elements, as described, may be readily combined to form a pile. Thus I built a *surface thermopile* of 80 elements, which, being arranged in three rows (of 24, 32, and 24 elements respectively), practically fill a circular surface of 2 cm. in diameter. The total resistance is about 9 ohms. The sensitiveness and the rapidity of this thermopile may be inferred from the following data. The radiation from a standard candle at a distance of 1 metre produces an electromotive force of 18 microvolts, the current reaching 99% of its definitive value within  $1\frac{1}{2}$  seconds.

The heat-capacity of the bars *e* and *f* is still further increased by clamping them (with the insertion of a thin sheet of mica) to a heavy piece of copper, this piece of copper occupying the space between the bars as far as just below the strip *abc*. When the pile has been exposed for some time, and therefore has absorbed heat, the temperature of this metal mass will certainly have risen somewhat, but both the junctions will undergo its influence practically to the same degree. The thermopile therefore displays an uncommonly great zero-stability.

Similar elements may also be combined so as to form a thermopile for spectral investigation, but, since in this case the exposed surface must be narrow, such an instrument will be less sensitive. I have

compared a *linear thermopile* of this kind, consisting of 30 elements, with a RUBENS pile. Their resistance is the same (3—5 ohms), and in the case of equal surface ( $20 \times 1$  mm.) my thermopile exhibits a sensitiveness some 20% smaller. This disadvantage, however, is amply compensated for by its rapidity, which is 4 times as great<sup>1)</sup>.

Thermopiles of this construction are manufactured by Messrs. KIPP & SONS of Delft.

**Physiology.** — "*Experiments on the atonical muscle.*" II. By Prof. J. W. LANGELAAN. (Communicated by Prof. H. ZWAARDMAKER.

(This communication will not be published in these Proceedings).

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<sup>1)</sup> A rapid and sensitive galvanometer of low resistance, adapted for use in combination with these thermopiles, has been described in the proceedings of the meeting of June 28, 1913, p. 149.

(December 27, 1913).

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