

Citation:

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coexisting liquid will diminish to a still greater degree, so that $\ln \left(\frac{\theta_S}{\theta_L} \right)$ will become smaller negative or greater positive. It is evident that the two equations, if they are correct, must give the same result, as is really the case here.

Hence we have come to the conclusion in this way that a metal with the most simple constitution can exhibit the phenomenon of anodic polarisation, resp. passivity as well and in virtue of the same circumstance as a more complicated metal. The said phenomena will present themselves for every metal when the removal of metal ions and electrons from the metal takes place more rapidly than their formation in the metal¹⁾. It is clear that a passivity brought about by chemical action, might be explained in exactly the same way when we consider that ions and electrons react chemically more quickly than uncharged atoms. We have not mentioned cathodic polarisation here, but it is clear that this phenomenon is to be expected here too, and can then be explained according to the same principle. In a following communication the cases will be treated represented by the equations (2) and (3).

The views given here are new, as far as we have been able to ascertain. In our subsequent study of the literature we have only in one place come across statements which suggest that the writer had views tending in the same direction in which the problem is treated here, but the thoughts were not elaborated. We allude here to a paper by HABER and ZAWADSKY²⁾; this paper ends with an "Anhang", and in this the statements above referred to are found.

(To be continued).

Anorganic Chemical Laboratory of
the University.

Amsterdam, February 24, 1916.

Chemistry. — "On the allotropy of the ammonium halides". II³⁾.

By Dr. F. E. C. SCHEFFER. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of Feb. 26, 1916).

10. *The transformation heat of ammonium chloride at the transition point.*

I have determined the difference of energy of the two modifica-

¹⁾ From this must ensue that the superficial electric conductivity of a metal must be smaller in the passive state than in the active state.

²⁾ Zeitschr. f. physik. Chem. **78**, 228 (1911).

³⁾ First communication. These Proc. XVIII p. 446.

tions of the ammoniumchloride by a series of calorimetric experiments, in which Mr. G. MEYER assisted me; I gladly express my indebtedness to him here.

A number of glass tubes was filled with ammoniumchloride and fused to; the quantity of glass and ammoniumchloride was determined by weighing. The tubes were successively heated to 156° (boiling point of bromo benzene), 177° (ortho-dichloro benzene), 194° (dimethyl aniline), and 212° (nitrobenzene), and quickly conveyed to the calorimeter. The two first-mentioned temperatures lie below, the two others above the transition point. When we conveyed it to the calorimeter the glass broke sufficiently through the sudden cooling to bring about a very rapid dissolving of the ammoniumchloride. Hence in these experiments the heat of solution was always included in the measurement, and in order to avoid corrections for the heat of dilution we have always chosen the quantity of water in the calorimeter so that the obtained solution contained one gramme molecule of NH_4Cl to 320 gramme molecules of water. In consequence of the rapid solution the temperature had generally established itself already after 1 or 2 minutes, and the time, over which corrections have to be applied for radiation, was, therefore, only small, which enhances the accuracy of the determinations. The specific heat of the glass was determined by separate experiments by heating up to 156° , resp. 212° , and on the assumption that the true specific heat changes linearly with the temperature between 156° and 212° , the mean specific heat between room temperature and a temperature lying between the two said temperatures could then be found by linear interpolation. In every experiment with the tubes of ammoniumchloride the heat which the glass alone yielded, was therefore known; if we subtract this heat from the found amount, we keep, in the experiments of 156° and 177° , the heat which $\alpha\text{-NH}_4\text{Cl}$ yields when it is cooled down from the said temperatures to that which the calorimeter possesses after the experiment, and then dissolved isothermically. From these values the mean specific heat of ammoniumchloride between 156° and 177° can, therefore, be calculated, and by extrapolation to the transition point ($184^{\circ}.5$) it is also to be found what heat $\alpha\text{-NH}_4\text{Cl}$ would yield when it was cooled down from the transition point.

The experiments in which heating above the transition point took place, yield, after correction for the heat of the glass, the heat which β -ammonium chloride gives off when it is cooled down to the transition point, transforms isothermically to the α -form, and this then falls to the calorimeter temperature and goes into solution isothermically.

From these experiments the mean specific heat of the β -form can therefore be calculated, and besides extrapolation to the transition point yields the heat which is liberated when ammoniumchloride is transformed at the transition temperature and then cooled. The difference between the two values found by extrapolation yields the required heat of transformation at the transition point.

TABLE 5.

No.	Temperature boiling jacket	Temperature calorimeter	Heat	Heat of the glass	Heat NH_4Cl	Weight NH_4Cl	Heat per gramme NH_4Cl
1	157.7	13.5	127.7	187.8	- 60.1	3.600	-16.69
2	158.25	13.55	115.0	171.7	- 56.7	3.487	-16.26
3	158.9	14.5	116.7	174.3	- 57.6	3.603	-15.99
4	159.25	15.75	115.9	171.0	- 55.1	3.456	-15.94
5	157.95	16.7	105.6	169.2	- 63.6	3.879	-16.40
6	158.7	16.0	111.3	166.6	- 55.3	3.556	-15.55
7	178.35	17.6	170.4	194.7	- 24.3	3.771	- 6.44
8	179.1	15.45	187.3	206.9	- 19.6	3.186	- 6.15
9	179.25	15.35	203.8	227.5	- 23.7	3.471	- 6.83
10	179.55	15.5	191.0	212.8	- 21.8	3.620	- 6.02
11	195.2	16.1	321.8	250.5	+ 71.3	3.742	+19.05
12	195.5	15.7	327.6	256.6	+ 71.0	3.714	+19.12
13	195.5	15.75	297.9	231.7	+ 66.2	3.424	+19.33
14	211.45	16.35	382.5	280.0	+102.5	4.080	+25.12
15	211.55	15.95	348.8	259.8	+ 89.0	3.742	+23.78
16	211.7	16.3	359.3	260.2	+ 99.1	3.931	+25.21

The tables 5 and 6 yield the results obtained; in table 6 the mean values have been recorded of the experiments, which have been carried out under nearly comparable circumstances. For the extrapolation to the transition point also the temperature of the calorimeter has been extrapolated.

It is clear that a correction can be avoided in this way which is difficult to determine experimentally. If namely in two experiments the temperature of heating is the same, but the temperature of the calorimeter different, a correction is to be applied for this difference.

TABLE 6.

No.	Temperature boiling jacket	Temperature calorimeter	Heat per Gramme NH ₄ Cl	Extrapolation to the transition point column		
				2	3	4
1, 2, 3	158.3	13.85	-16.31	184.5	16.55	- 3.75
7, 8, 9, 10	179.05	16.0	- 6.36			
4, 5, 6	158.6	16.15	-15.96	184.5	15.95	- 3.80
7, 8, 9, 10	179.05	16.0	- 6.36			
11, 12, 13	195.4	15.85	+19.17	184.5	15.6	+15.45
14, 15, 16	211.6	16.2	+24.70			
1-10				184.5	15.6	- 3.83

of temperature, multiplied by the difference in specific heat of the solution and of pure water. This is clear as follows: Let us call the temperature at which the tube is heated T_1 , the temperature of the calorimeter after the experiment T_c and T_c' , then the liberated heat in the two cases (after correction of the heat of the glass) is:

$$\int_{T_c}^{T_1} \gamma dT - Q_c \quad \text{resp.} \quad \int_{T_c'}^{T_1} \gamma dT - Q_c', \quad \text{in which } Q \text{ denotes the heat of solution.}$$

The difference, therefore, amounts to $\int_{T_c}^{T_c'} \gamma dT + Q_c - Q_c'$.

Bearing in mind that:

$$Q_c' - Q_c = (T_c - T_c')(\gamma + \gamma_{H_2O} - \gamma_{opt.}),$$

it is clear that in this correction the specific heat of the ammonium chloride disappears, and the difference in specific heat between the solution which contains 1 Gramme of NH₄Cl, and the water of this solution remains. This difference could not be determined except as the difference between two much larger values; it appears, however, from table 6 that this difference has hardly any influence on the transition heat. In the experiments 1, 2, and 3 the calorimeter temperature is on an average 13.85°, in 4, 5, and 6 however 16.15°; in the transition heat this difference yields only a value of 0.05 gramme calorie per gramme of ammonium chloride as appears from the last column of table 6. If therefore, the calorimeter had been

15.6° just as in the experiments 11—16 the heat would have been — 3.83 gramme calorie per gramme of ammonium chloride.

The heat of transition per gramme of NH_4Cl amounts therefore to $15.45 + 3.83 = 19.28$ gramme calories or **1.03 kilogram calorie per gramme molecule**.

In table 5 the differences in the last column are partly to be attributed to the said difference in specific heat between water and solution. It can be derived from the data of the literature that this difference for our solutions amounts to about 0.2 calorie per Gramme of NH_4Cl . The values of the last column of table 5 are not directly comparable either on account of the difference in temperature of heating. Through the mode of calculation followed these corrections have been eliminated, as has been said.

In table 7 the mean specific heats for the α - and β -modifications in the neighbourhood of the transition point have been recorded.

TABLE 7.

No.	Limits of the temperature	Heat per Gramme NH_4Cl	Temperat. difference	Heat difference	Mean specific heat
4, 5, 6	16.15—158.6	—15.96	} 20.45	9.60	0.469
7, 8, 9, 10	16.0 —179.05	— 6.36			
11, 12, 13	15.85—195.4	+19.17	} 16.2	5.53	0.341
14, 15, 16	16.2 —211.6	+24.70			

In these calculations the above correction for the difference in specific heat between solution and water has been put zero; this will give rise to a small error here, because the difference in calorimeter temperature is only small in the experiments of table 7. This table yields the conclusion that in the neighbourhood of the transition point the specific heat of the β -modification is smaller than that of the α -form. The difference of energy between the two modifications, which amounts to 1.03 kilogram calories at the transition point, will therefore become smaller at higher temperature.

11. *The vapour tension of dry ammonium chloride.*

The determinations of the transition point (§§ 5 and 6) and of the heat of transformation (§ 10) in connection with Prof. SMITH'S recent researches on the vapour pressure line of ammonium chloride and on the degree of dissociation of the saturate vapour¹⁾ open a

¹⁾ SMITH. Journ. Amer. Chem. Soc. **36**, 1363. (1914); **37**, 38 (1915).

possibility to a discussion of the remarkable results of JOHNSON (§ 2).

In his cited paper Prof. WEGSCHEIDER stated that he considered polymorphy as the most probable explanation for the evaporation phenomena. He expresses himself as follows:

“Es kann z. B. zwischen Zimmertemperatur und der Temperatur der Verdampfungsversuche ein Umwandlungspunkt liegen. Die bei Zimmertemperatur stabile Form könnte über 300° unbeständig sein, aber bei Abwesenheit von Feuchtigkeit erhalten bleiben. Wasserdampf wäre dann ein Katalysator, der nicht bloss die Dissociation der gasförmigen NH_4Cl -Moleküle, sondern auch die polymorphe Umwandlung der über 300° unbeständigen Form des festen Salmiaks sehr stark beschleunigt. Hieraus ergibt sich dann die Erscheinung, dass die unbeständige feste Form undissociierten Dampf gibt und die beständige Form dissociierten Dampf.”¹⁾

It has appeared from the experiments of § 5 and 6 that there really lies a transition point at 184.5° between room temperature

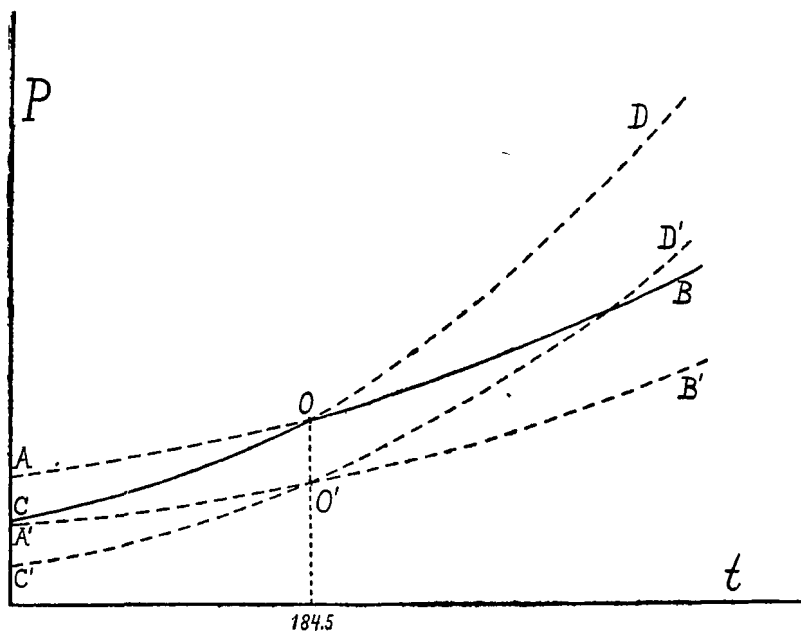


Fig. 3.

and the temperatures of JOHNSON'S experiments. WEGSCHEIDER'S explanation comes to this. In fig. 3 AB and CD represent the vapour tension lines of the β - and α -modifications of ammonium chloride in ordinary (somewhat humid) state; these lines intersect in the transition point O . The vapours are partly dissociated in NH_3 and HCl . If for both lines we draw the partial pressures of unsplit

¹⁾ WEGSCHEIDER. Zeitschr. f. physik. Chem. 65. 102. (1908).

NH_4Cl in the vapour, we get two lines $A'B'$ and $C'D'$, which would hold resp. for the evaporation without dissociation of β - and α - NH_4Cl . These lines intersect again at the transition temperature. If with WEGSCHEIDER we, therefore, assume that the α -form stable at the ordinary temperature could continue to exist above the transition point, we should find the line OD , if the homogeneous dissociation continued to exist; if, however, the dissociation in the vapour phase does not set in, the realizable states lie on $O'D'$. Accordingly the vapour tension values of JOHNSON'S experiments lie on $O'D'$, the vapour pressure determinations of ordinary (somewhat humid) NH_4Cl on OB . It is clear that the equality of the pressures in humid and in dry state over an appreciable range of temperature becomes a coincidence, and that strictly speaking equality of pressure could only occur in a point of intersection of OB and $O'D'$.

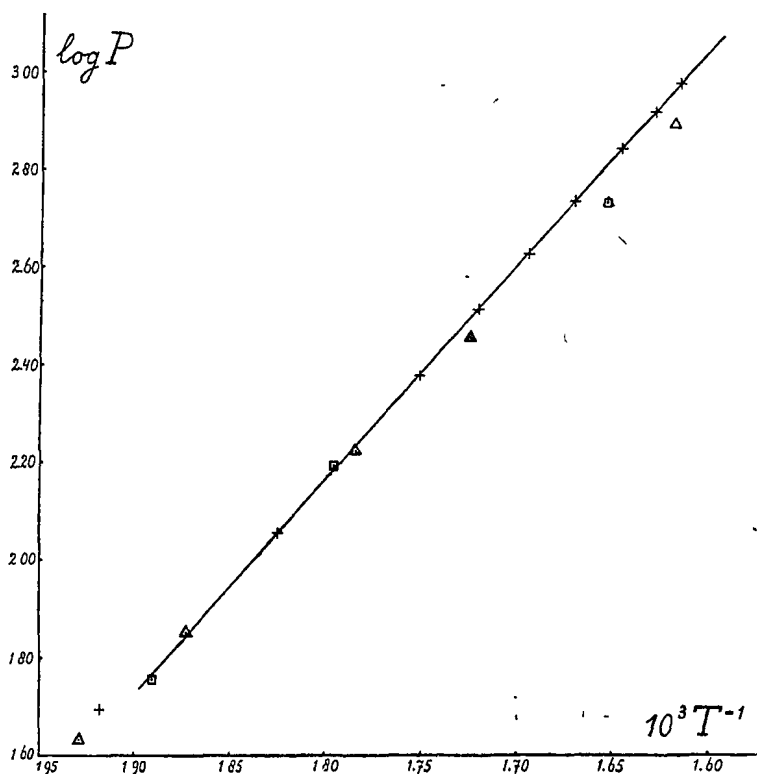


Fig. 4.

If we should wish to accept this explanation, we shall have to conclude from the results that the differences in vapour pressure over the examined temperature range are only small and lie within the errors of observation. It is, therefore, now the question whether the investigations mentioned allow of such an explanation.

In fig. 4 I have indicated the experimental results by drawing the logarithm of the vapour pressure as ordinate, the reciprocal value of the absolute temperature as abscissa. This way of representation has the advantage that the vapour pressure lines thus obtained are almost straight, and interpolations and extrapolations are more easily and more accurately executed graphically than with curves as in fig. 3. That the lines become almost straight with the indicated mode of representation, follows from:

$$\frac{d \log P}{d 1/T} = - T^2 \frac{d \log P}{dT} \text{ and } \frac{d \log P}{dT} = \frac{Q}{RT^2},$$

which latter equation holds for substances which evaporate without dissociation. Hence the slope of the lines amounts to $-\frac{Q}{R}$, and is therefore constant, when the heat of evaporation does not change with the temperature, which is often true in a first approximation¹⁾. If, namely, the change of Q with the temperature or in other words the difference in specific heat between solid and gas is not too great, the influence of the temperature is generally small in proportion to the great heat of evaporation. This even appears to be the case in the observations of somewhat humid NH_4Cl , which have been carried out by SMITH, and which are indicated by asterisks in fig. 4, though here a degree of dissociation varying with the temperature changes the simple equation $\frac{d \log P}{dT} = \frac{Q}{RT^2}$ into $\frac{d \log P}{dT} = \frac{Q}{(1+\alpha)RT^2}$, and the change of α with the temperature will therefore also cause a deviation from a straight line in fig. 4. The vapour tensions of somewhat humid NH_4Cl have also been measured by JOHNSON and are indicated by triangles in fig. 4. These two series of observations correspond therefore with the line OB of fig. 3. There appears to be a discrepancy between the observations of SMITH and JOHNSON, which for the greater part will no doubt have to be ascribed to inaccuracies in the temperature measurement. Besides the results of the remarkable experiment with dry ammonium chloride have been indicated by squares in fig. 4; they belong, therefore, to the line $O'D'$ of fig. 3.

When we compare figures 3 and 4, the given explanation seems already little probable; fig. 4, namely, sooner makes the impression that the observations of dry NH_4Cl coincide with those of humid NH_4Cl than that intersection of the vapour pressure lines would take

¹⁾ The common logarithm has been used in the figures and tables; the modulus has therefore been taken into account. ($R = 4.571$).

place. So the question remains whether two lines OB and $O'D'$ can be drawn so that they show a point of transition at $184,5^\circ$, that the heat of conversion of § 10 corresponds with the angle between the lines, and that the observed points depart from these lines within the errors of observation. As when we use the mode of representation of figs. 4 and 5 the slope of the lines is indicated by $-\frac{Q}{R}$, it is clear that the angle between the lines $O'B'$ and $O'D'$ of fig. 3, transferred to figs. 4 and 5, will be a direct measure for the difference in heat of evaporation, and will, therefore, have to amount to $-\frac{1,03}{R}$, the difference in heat of evaporation at the transition temperature being equal to the heat of transformation of 1,03 kilogram calories determined in § 10.

TABLE 8.

t	P	α	$\log p$	$10^3 \frac{1}{T}$
280	135.0	0.668	1.429	1.808
290	185.3	0.660	1.579	1.776
300	252.5	0.652	1.726	1.745
310	341.3	0.644	1.869	1.715
320	458.1	0.636	2.008	1.686
330	610.6	0.628	2.145	1.658

In table 8 the two first columns give the corresponding temperatures and pressures according to SMITH; they correspond therefore with the line OB of fig. 3 and with the asterisks of fig. 4. In the third column the degrees of decomposition are recorded of the saturate vapour, which SMITH has calculated from his observations as the most probable. The fourth column gives the value of $\log p$, in which p represents the partial pressure of the unsplit part in the vapour. It is clear that the relation

$$p = \frac{1-\alpha}{1+\alpha} P$$

holds between p and P .

These values of p refer, therefore, to the line $O'B'$ of fig. 3.

The last column gives the value for T^{-1} . In fig. 5 the calculated values of columns 4 and 5 of table 8 are graphically represented

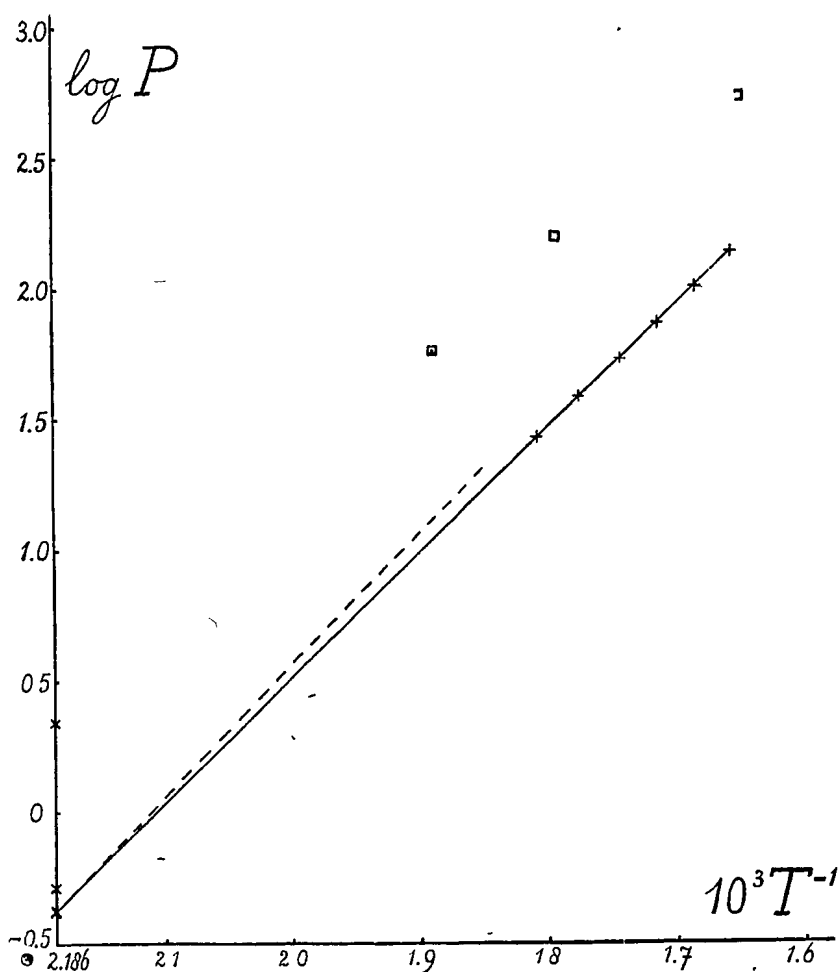


Fig. 5.

It appears that through the points found thus a straight line can be drawn of the equation :

$$\log p = -\frac{4770}{T} + 10.055.$$

If this line is extrapolated to the transition point ($t = 184.5$; $10^3 T^{-1} = 2.186$) we find $\log p = -0.371$. This value is also given in fig. 5. If the explanation given is correct, this point must be the point of intersection of the lines $O'B'$ and $O'D'$ fig. 3. Hence in fig. 5 the line $O'D'$ must therefore be drawn through this latter point, and the points which are found for evaporating dry ammonium chloride, and which are again indicated by squares in fig. 5. It appears from fig. 5 that this is impossible. If we draw straight lines through the point of transition and the three observations, the deviations of the two other observations become very large, as appears

TABLE 9.

<i>t</i>	<i>P</i> (observed)	<i>P</i> (calculated)			Error		
184.5	—	0.426	0.426	0.426	—	—	—
256	57	57	37	22	0	— 20	—35
284	156	274 ⁱ	156	80	+ 118	0	—76
332	540	2880	1340	540	+2340	+800	0

from table 9, in which the three observations with dry NH_4Cl have been given. But at the same time the heat of conversion is much too great. Then the angle between the lines thus traced and the line through the partial pressure (fig. 5) corresponds with **11.1**, **8.2**, and **4.8** kilogram calories, though it must be **1.03** kilogram calories. The line that corresponds with the last heat has been indicated dotted at the transition point in fig. 5. These calculations and fig. 5 will in my opinion make it sufficiently clear that the explanation which Prof. WEGSCHEIDER considered the most probable, is untenable; the only objection that can be made against the executed calculations is that experimental errors in the quantities used, and also the way of extrapolating may perhaps appreciably change the result. To obviate this objection I will add the following considerations.

12. *Possible errors in the calculations of § 11.*

To detect all possible sources of error in the calculations we should know in the first place the accuracy of the data used. The determinations of the vapour pressure carried out by Prof. SMITH, are without doubt very accurate; the observations lie very well on a curve with a regular course, as is also clear from figure 4. The errors in these observations (table 8, column 2) can have only little influence. Much more weight is to be attached to the errors of observation in the rate of dissociation (table 8, column 3). To examine the influence of this the values found for $\log K$ have been drawn as function of T^{-1} in fig. 6, and besides the curve has been given which SMITH considers the most probable. That the observed points deviate comparatively much from the curve, is easy to understand, when we consider that the experimental errors in α appear greatly enlarged in K . This is clear, as:

$$K = \frac{\alpha^2}{1 - \alpha^2} \frac{P}{RT}$$

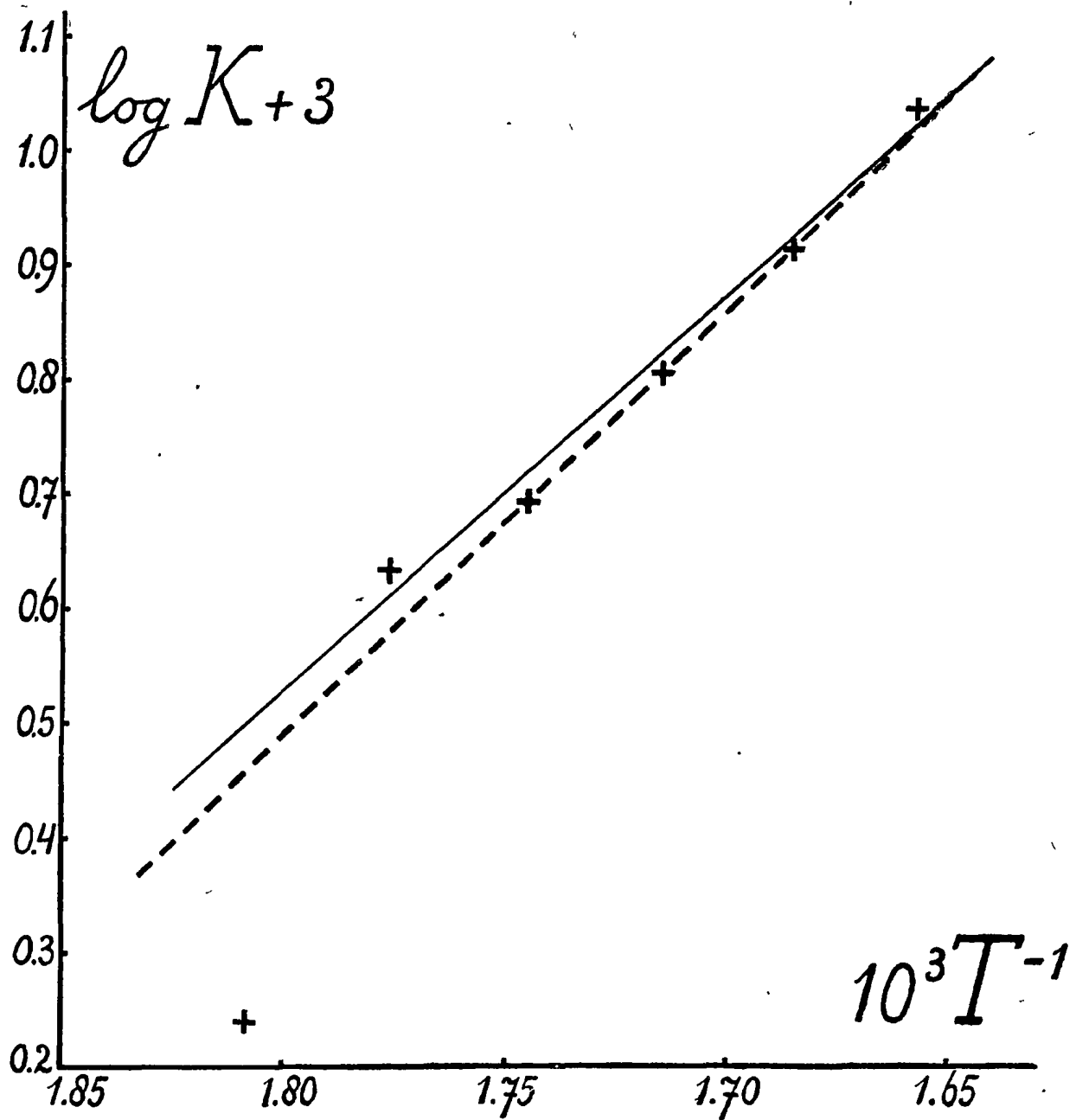


Fig. 6.

and as therefore the change in numerator and denominator caused by an error in α , changes the value of K in the same direction.

SMITH'S line has certainly been drawn somewhat arbitrarily through the observed points. In order to examine the influence of a change in this line on the calculations of § 11 I have indicated a second line in fig. 6 dotted, which has a steeper slope than that of SMITH.

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It is clear that a steeper course is favourable to the explanation given in § 11. If namely K decreases more quickly with the temperature, the rate of dissociation will become smaller at the transition point, and O' approaches more to O ; this favours the coinciding of OB and $O'D'$, (see fig. 3). The equation of the line dotted in fig. 6 is:

$$\log K = -\frac{3770}{T} + 4.274.$$

If from this we calculate the values for $\log K$ at the temperatures of table 8, and from this the ratio of dissociation we find the values recorded in table 10.

TABLE 10.

t	P	α	$\log p$	$10^3 \frac{1}{T}$
280	135.0	0.652	1.454	1.808
290	185.3	0.647	1.599	1.776
300	252.5	0.641	1.742	1.745
310	341.3	0.638	1.878	1.715
320	458.1	0.632	2.014	1.686
330	610.6	0.627	2.146	1.658

The curve $\log p = -\frac{4610}{T} + 9.790$, which satisfactorily represents the observations of the columns 4 and 5 of table 10, yields $\log p = -0.287$ for $t = 184.5^\circ$. This value is given in fig. 5. It is seen that the modification is much too small to make a satisfactory solution of this question possible.

A line of still greater slope in fig. 6 must be considered improbable in my opinion. It is true that the observation at the lowest temperature lies appreciably lower than the lines drawn, but then this is the least accurate, and must certainly be omitted when the most probable line is drawn. Besides the angle at the point of transition would become much too large, if we wished to take this observation into account. I have already demonstrated before that the line which represents $\log K$ as function of $\frac{1}{T}$ can present no perceptible departure from a straight line—I shall come back to this in a following paper—and besides the curvature if it were percep-

tible, would render the deviation of the lowest point still greater instead of smaller, because the specific heat of the products of dissociation NH_3 and HCl will certainly be greater than that of unsplit molecules of ammonium chloride; hence the heat of dissociation will increase at higher temperature; therefore the curve in fig. 4 will turn its *convex* side to the T^{-1} -axis. The points for $\log p$ in fig. 5 can therefore undergo but little modification.

There further remains an objection possible against the way of extrapolation. Decidedly the extrapolation can cause here pretty great inaccuracies, and the influence of this should therefore also be studied.

In the extrapolation a straight line has been drawn through the points of fig. 5, whereas in reality the line will be curved, though probably exceedingly little also here. The straight line

$$\log p = -\frac{a}{T} + b$$

supposes that the heat of evaporation ($4.571 a$) does not vary with the temperature. This is only the case when the specific heats of gas and solid are equal. The curvature is determined in the representation of fig. 5 by the difference in these specific heats, for:

$$\frac{d \log P}{d 1/T} = -\frac{Q}{R}$$

and

$$\frac{d^2 \log P}{d (1/T)^2} = +\frac{T^2}{R} \frac{dQ}{dT}$$

When we bear in mind that $\frac{dQ}{dT} = C_{gas} - C_{solid}$, in which C represent specific heats, it is clear that the curvature will be positive, if $C_{solid} < C_{gas}$. Now the specific heat of solid ammonium chloride at the point of transition is 0.34 or molecularly about 18 according to table 7; this value will increase with the temperature. The specific heat of HCl and NH_3 amounts about to 15 or 16 calories; the specific heat of gaseous NH_4Cl will be smaller, hence the curvature, if it is perceptible, will lower the point of transition in fig. 5 instead of raising it. The point drawn therefore gives indeed the highest value for $\log p$ at the transition point.

Now the question remains whether we can draw a curve through the points of the dry ammonium chloride (squares in fig. 5) with so great a curvature, that it attains the indicated value at the transition point. For this the curvature will have to be negative, hence in

virtue of the above $C_{\text{solid}} > C_{\text{gas}}$. We will take 15 for this difference, which will probably be high enough. The curve which corresponds to this has for equation

$$\log p = -\frac{a}{T} - \frac{15}{R} \log T + c.$$

In order to reach this purpose as well as possible, I shall draw the curve through the two most favourable observations (2nd and 3rd of table 9). We then find $a = 6390$, $c = + 34.415$. From this we find for the point of transition $\log p = + 0.344$ (see fig. 5). This is therefore the lowest value that can be reached, all allowances being made. From this calculation and fig. 5 we see clearly the slight influence of the term with the specific heats.

Even with the most favourable assumption of errors of observation and of the data that are little or not known, it appears impossible to explain JOHNSON'S experiments by the above assumption. I have ascertained by determination of curves of heating and cooling that between 180° and the temperatures of the experiments of evaporation there is no second transition point to be found.

13. If JOHNSON'S experiments are correct, the difference in thermodynamic potential of the solid NH_4Cl in humid and dry state is still to be explained. There is no explanation to be found in the phenomena of allotropy discussed in this paper.

Before the cited investigation by SMITH it was pretty generally accepted that ammonium chloride in gas form practically splits up entirely into NH_3 and HCl . If this were so, the partial tension of the unsplit part could only be very slight. If during the drying the homogeneous dissociation did not take place, we should have to find a vapour tension which is very small. Yet BAKER has carried out vapour density determinations with non-dissociated vapour at atmospheric pressure!

Now it has appeared in SMITH'S investigation that the dissociation is far from perfect; the partial tension has therefore a pretty great value. From the calculations of § 12 it appears that the value of the vapour tension of $\beta\text{-NH}_4\text{Cl}$ on the assumption that the homogeneous dissociation does not take place, is indicated by:

$$\log p = -\frac{4610}{T} + 9.790,$$

and the pressure of $\alpha\text{-NH}_4\text{Cl}$, the transition heat mentioned in § 10 being taken into account, by:

$$\log p = -\frac{4835}{T} + 10.281.$$

If from this the vapour pressure is calculated at 360°, we find 440 mm., so far below the atmospheric pressure.

BAKER's vapour density determinations are carried out in boiling mercury (360°) both according to VICTOR MEYER's method and according to DUMAS. That the substance would have had such a small pressure in the first determinations is, indeed, little probable. Professor BAKER informed me that the DUMAS-bulb entirely filled with water after the experiment; the absence of air proves that the vapour pressure was not smaller than one atmosphere. Accordingly I am of opinion that BAKER's experiments cannot be explained by the current theoretical considerations either.

So we have here two series of experiments, those of JOHNSON and those of BAKER, which are both still unexplained. It is desirable in my opinion that the vapour tension determinations of dry ammonium chloride are carefully repeated. It can then appear at the same time whether the vapour tension lines of dry and humid NH_4Cl coincide or intersect; the latter is in my opinion the more probable according to the theoretical views.

Petrography. — “*On the post-carboniferous age of granites of the highlands of Padang.*” By Dr. H. A. BROUWER. (Communicated by Prof. G. A. F. MOLENGRAAFF).

(Communicated in the meeting of March 27, 1915).

The occurrence of young granites in the East Indian Archipelago has first been stated by MOLENGRAAFF¹⁾ as a distinct contact-metamorphism was observed by him at the contact of granites with rocks of the mesozoic, probably jurassic Danau formation.

Of late, mesozoic granites have been stated by WICHMANN²⁾ to occur also in the Moluccas, (Taliabu, Sula-isles).

In Sumatra, till of late all the granites have been considered as precarbonic ones, but the researches of these later years by SCRIVENOR, TOBLER and VOLZ have proved or made probable the occurrence of mesozoic granites in Sumatra and in the neighbouring Malacca³⁾.

¹⁾ G. A. F. MOLENGRAAFF. Geologische verkenningstochten in Centraal-Borneo p. 458. Leiden 1900.

²⁾ C. E. A. WICHMANN. On some rocks of the island of Taliabu (Sula Islands). Proceedings Royal Acad. of Sciences. Amsterdam. Vol. XVII (1914), p. 226.

³⁾ J. B. SCRIVENOR. The Rocks of Pulau Ubin and Pulau Nanas (Singapore). Quart. Journ. Geolog. Soc. 66. 1900. p. 429. A. TOBLER. Voorloopige mededeeling over de Geologie van de Residentie Djambi. Jaarb. Mijnw. Ned. Indië over 1910, p. 18—19. W. VOLZ. Oberer Jura in West-Sumatra. Centralbl. f. Min. 1913, p. 757.