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**Chemistry.** — “*On an Indirect Analysis of Gas-Hydrates by a Thermodynamic Method and its Application to the Hydrate of Sulphuretted Hydrogen*”. II. By Prof. F. E. C. SCHEFFER and G. MEYER <sup>1)</sup>. (Communicated by Prof. BÖESEKEN.)

(Communicated in the meeting of March 29, 1919).

7. *Determination of the Three-Phase Lines  $SS_B G$  and  $SL_2 G$ .*

A number of apparatus of the shape of fig. 3 was supplied with small quantities of water, which were introduced through *C* and conveyed to the widened part *A* by tilting the apparatus. These quantities of water were chosen so that the vessel *A* was filled with water for about a fifth part. Every apparatus was then in succession connected with a sulphuretted hydrogen apparatus in which the gas could be developed by the addition of drops of diluted sulphuric acid to a solution of acid sodium sulphide. The latter was obtained by saturating a solution of sodium hydroxide made free from carbonic acid with barite with sulphuretted hydrogen.

Before the preparation of the gas the wall of *B* and *C*, which was still damp with water, was dried by being heated at an air-pressure of 2 cm. of mercury, the bulb *A* being placed in carbonic acid<sup>2)</sup> and alcohol. Between the filling-apparatus and the apparatus *C* a *T*-piece was inserted for this purpose, which made connection with a waterjet pump possible. Then bulb *A* was filled for about two thirds with dry liquid sulphuretted hydrogen (the gas was led through a *U*-tube with  $P_2O_5$  to prevent liquid from being carried along), after which the tube was fused to at *C*, and the cooling mixture was removed.

When the temperature was raised to room-temperature, the ice melted, and two layers were observed separated by a crust of sulphuretted hydrogen hydrate. In order to convert the mass as much as possible to hydrate, bulb *A* was carefully heated by immersion in a waterbath of over  $30^\circ$  (the quadruple point  $SL_1 L_2 G$  lies at  $29.5^\circ$  <sup>2)</sup>), till the hard crust had disappeared. Then the apparatus

<sup>1)</sup> First communication, These Proc. 21. 1204. (1919).

<sup>2)</sup> These Proc. 13. 843. 1911). Table.

being continually shaken was cooled down to the ordinary temperature to make the action of the two layers as complete as possible. If any liquid sulphuretted hydrogen had been distilled over, it was always poured back into *A* by tilting of the apparatus. When in this way the cooling down to room-temperature had been achieved, the apparatus was left for a few days to promote the action.

To make vapour pressure determinations bulb *A* was cooled in liquid air, the apparatus was opened at *C*, and connected to the tube *D* of the apparatus represented by fig. 4 by means of india

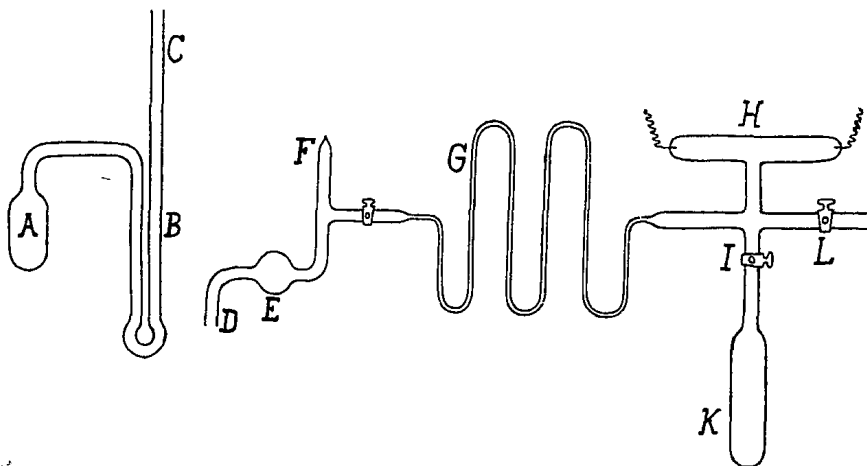


Fig. 3.

Fig. 4.

rubber. By exhaustion through tap *L* with a waterjet airpump the sulphuretted hydrogen-air mixture was partially removed from *B* and *C* (fig. 3); the rest of the gas was absorbed by the cooled cocoanut carbon, *K* by opening of *I* (after *L* had been shut). When the gaseous sulphuretted hydrogen had entirely disappeared from the apparatus, air was admitted, and the apparatus of fig. 3 was fused to that of fig. 4 at *D*. Then the apparatus was again evacuated, the liquid air round *A* was replaced by carbonic acid and alcohol, and the sulphuretted hydrogen was sucked off through *L*. After the liquid sulphuretted hydrogen had been removed from *A* by boiling, the apparatus remained in connection with the waterjet pump for a few hours more in order to remove the sulphuretted hydrogen absorbed in the solid substance as completely as possible. Then bulb *A* was again placed in liquid air, the apparatus was completely evacuated by the aid of the cocoanut carbon, air was admitted, tube *F* was temporarily opened to convey mercury into *E*, and the whole apparatus was exhausted again.

The mercury in *E* was freed from air by heating in vacuum. After the mercury had been cooled, *A* was again placed in carbonic

acid and alcohol, and evacuated with the waterjet pump, afterwards with the carbon.

When after the evacuation with the cocoanut carbon tap *I* was closed, a gas pressure again appeared in the apparatus after a short time (GEISSLER tube *H*), and this was continually repeated. We shall discuss the cause of this phenomenon later on. When the gas that had generated in the apparatus, had been removed a few times, so that it might be assumed that the apparatus did not contain any more air, the mercury was transferred from *E* into *B* by tilting of the lefthand part of the apparatus (the glass spring *G* made this movement possible). The tap near *G* was now closed, and the apparatus was cut through between this tap and the glass spring *G*.

The lefthand part was connected by means of a rubber tube to a manometer one meter long, for the higher pressures three meters long. By a sucking pump, a tap that allowed contact with the outer air, and a tap that was connected with a cycle pump, the pressure of the air between *B* and the manometers could be regulated at will in the measurements. Hence tube *B* acts as a cut-off valve in the determinations, the difference of level in the manometer corrected for the difference of position in *B* yields the value of the three-phase pressure. In order to make it possible to determine the difference of level in *B* a glass scale graduated in millimeters was attached to the tube *B* by the aid of cork disks and copper wire. The determinations being carried out exclusively at temperatures below room temperature, only bulb *A* was placed in a bath of alcohol, which could be cooled down to definite temperatures by addition of solid carbonic acid; a stirrer ensured uniform temperature in the alcohol bath. The cut-off valve *B* remained continually in contact with the outer air.

During the slow heating of the alcohol bath it now appeared that already at low temperatures a rapid rise of pressure appeared, which could not possibly be attributed to decomposition of the hydrate. When the pressure had reached a definite value, the change with the temperature had greatly diminished again. This fact pointed to this that in spite of the exhaustion with the cocoanut carbon the hydrate had absorbed appreciable quantities of sulphuretted hydrogen, which were liberated already at temperatures of about  $-50^{\circ}$  C.

The exhaustion with the cocoanut carbon had, accordingly, not been sufficient to remove the absorbed quantity of sulphuretted hydrogen; prolonged evacuation is, however, undesirable, because as will appear later, the hydrate still possesses an appreciable tension of dissociation at  $-80^{\circ}$  C., and decomposition must, accordingly

take place in vacuum. Hence the appearance of this gas-absorption, and the pressure of dissociation which is not negligible at  $-80^{\circ}\text{C}$ . are the cause that the compound cannot be prepared in pure state in the way described above. These two phenomena have, however, no disturbing influence on the determination of the three-phase pressures, at least when the gas adsorption does not attain to too large amounts.

It is namely clear from the described phenomena that the gas-adsorption is no phenomenon of equilibrium; at higher temperatures, where the equilibria set in more rapidly, this adsorption soon stops, and the liberated sulphuretted hydrogen cannot influence the three-phase pressure (the three-phase equilibria are monovariant). Nor can a partial decomposition of the hydrate have any influence on the pressure of equilibrium.

Nevertheless a difficulty presents itself in these determinations. When the compound had absorbed no gas, a gas pressure could only appear on heating through decomposition of the compound into ice and gas; the observation of a gas pressure would then be a sufficient criterion that a three-phase pressure existed. In consequence of the said adsorption it is, however, possible that with increased temperature through liberation of gas a gas pressure occurs without any decomposition of the compound taking place. As the transformation of part of the compound into ice and gas cannot be directly observed, the possibility exists that pressures of two-phase equilibria compound-gas are measured instead of three-phase equilibria. It now appeared in the determinations that at lower temperatures no corresponding values were found for the pressure (the two-phase coexistences are divariant); at higher temperature the correspondence became, however, very good. This can, evidently, be accounted for in this way that the solid substance had absorbed different quantities of sulphuretted hydrogen, which were liberated on increase of temperature. When this released quantity of gas yields a pressure higher than the three-phase pressure, the decomposition of the compound cannot begin. Not until through increase of temperature the three-phase pressure rises so much that this becomes greater than the pressure caused by the liberated adsorbed gas, three-phase pressures occur. On account of the different adsorbed quantities this takes place for the different mixtures at different temperatures. In none of the experiments did the adsorption prove to be so great that the determinations of the three-phase pressures were rendered impossible. As was natural only the values in the neighbourhood of the quadruple point, where the correspondence was good, were used for the calculations. (See §§ 8 and 9).

8. *The Three-Phase Line Hydrate-Ice-Gas.*

In the tables 1—3 the results have been recorded of three sets of observations. In the first and second columns of every table the temperatures and the corresponding three-phase pressures (in cm.) are given, the last have been reduced to mercury of 0° C. The third column contains the tensions corrected for the vapour tension of ice, the fourth and the fifth contain the differences in the BRIGG logarithms of the pressure and in the reciprocal absolute temperatures of the successive observations. The sixth column gives the value of  $\frac{Q_1}{2.303 R}$  calculated according to § 5; as in § 5 the calculation was made with Neperian, in tables 1—3 with ordinary logarithms, the modulus 2 303 occurs here in the denominator. The last column records the mean values of the last mentioned expression. The first value of  $P$  in table 3 is too high; it probably refers to the equilibrium hydrate-gas (cf. § 7). It is easy to see that the too small

TABLE 1.

$t$	$P$	$P(\text{corr})$	$10^2 \Delta \log P$	$10^5 \Delta T^{-1}$	$\frac{Q_1}{2.303 R}$	<i>mean</i>
—25.85	22.4	22.35				
—19.75	30.2	30.1	12.929	9.74	1327	
—15.8	36.2	36.1	7.894	6.07	1300	
—11.85	43.3	43.15	7.747	5.88	1318	
— 7.95	51.5	51.25	7.471	5.63	1327	1327
— 4.95	58.6	58.3	5.598	4.23	1323	
— 2.4	65.5	65.1	4.791	3.51	1365	

TABLE 2.

$t$	$P$	$P(\text{corr})$	$10^2 \Delta \log P$	$10^5 \Delta T^{-1}$	$\frac{Q_1}{2.303 R}$	<i>mean</i>
—21.1	28.0	27.95				
—16.8	34.35	34.25	8.828	6.66	1326	
—11.85	43.05	42.9	9.780	7.40	1322	
— 5.75	56.5	56.2	11.728	8.74	1342	1344
— 3.0	63.6	63.25	5.132	3.81	1347	
— 1.25	68.65	68.25	3.304	2.39	1382	

TABLE 3.

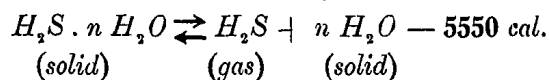
$t$	$P$	$P(\text{corr})$	$10^2 \Delta \log P$	$10^5 \Delta T^{-1}$	$\frac{Q_1}{2.303 R}$	<i>mean</i>
-24.6	[24.9]	24.85	10 160	9.27	[1096]	1329
-18.75	31.5	31.4	11.955	8.91	1342	
-12.85	41.5	41.35	11.309	8.53	1326	
- 6.95	53.9	53.65	9.063	6.87	1319	
- 2.0	66.5	66.1				

value of  $Q_1$  is in accordance with this supposition; the region where compound coexists by the side of gas, lies namely on the side of higher pressure with respect to the three-phase line.

When we take the mean value from the three tables, it appears that the value for  $\frac{Q_1}{2.303 R}$  amounts to 1333, from which follows the value 6090 for  $Q_1$ .

The external work in the transformation amounts to  $RT$ , because one gramme-molecule of gas is formed in the conversion; at the quadruplepoint ( $t = -0.4^\circ$ , see § 9) this work is 541 cal.

The change of energy amounts, therefore, to 5550 cal. The transformation is given by:



### 9. The Three-Phase Line Hydrate-Aqueous Liquid-Gas.

In the tables 4—6 the results are recorded, which were obtained with the same samples as those in § 8. In the fifth column  $a$  represents the number of volumes  $H_2S$  of one atmosphere, (corrected for  $0^\circ$ ), which dissolves in one volume of water.<sup>1)</sup> It follows from this by a simple calculation on assumption of HENRY'S law that in one gramme-molecule of water  $1.057 \cdot 10^{-5} aP$  gramme-molecules of sulphuretted hydrogen dissolve; this amount is indicated by  $q$ .

In the tables  $b$  gives the absolute value of  $\frac{(1+r-s) \Delta \log P}{\Delta T^{-1}}$   $2.303 R$  (see equation 13),  $r$  and  $s$  have been calculated according to  $10a$  and  $b$ , in which the value 6 was substituted for  $n$ .

The found values of  $E_2$  can now serve for the calculation of that value at the quadruplepoint.

<sup>1)</sup> LANDOLT-BÖRNSTEIN-ROTH. Tables p. 601. Determinations by WINKLER.

TABLE 4.

$t$	$P$	$P_{H_2O}$	$P_{H_2S}$	$a$	$10^3q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3r$ ( $n=6$ )	$10^2s$ ( $n=6$ )	$rQ_v$	$sQ_0$	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	$b$	$E_2$	$E_2(t=-0.4)$	mean
0.85	83.5	0.5	83.0	4.497	3.945	60	5.86	2.37	63	108	0.9822						
1.9	93.1	0.55	92.55	4.347	4.253	59	5.75	2.55	62	116	0.9803	1.39	4.726	15250	14750	14660	14110
2.9	102.4	0.55	101.85	4.210	4.532	54	5.25	2.72	56	124	0.9781	1.32	4.135	14020	13530	13380	
3.9	113.5	0.6	112.9	4.076	4.864	53	5.15	2.92	55	133	0.9760	1.31	4.470	15240	14760	14560	
4.85	125.3	0.65	124.65	3.954	5.210	52	5.04	3.13	54	143	0.9737	1.23	4.295	15560	15090	14840	
6.85	151.25	0.75	150.5	3.710	5.902	50	4.82	3.54	52	161	0.9694	2.58	8.175	14070	13620	13290	
8.85	183.9	0.85	183.05	3.485	6.743	46	4.41	4.05	47	185	0.9639	2.53	8.488	14820	14390	13950	

TABLE 5.

$t$	$P$	$P_{H_2O}$	$P_{H_2S}$	$a$	$10^3q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3r$ ( $n=6$ )	$10^2s$ ( $n=6$ )	$rQ_v$	$sQ_0$	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	$b$	$E_2$	$E_2(t=-0.4)$	mean
-0.05	74.0	0.45	73.55	4.628	3.598	61	5.97	2.16	64	98	0.9844	1.34	4.722	15840	15340	[15290]	14330 (resp. 14570)
+0.95	82.5	0.5	82.0	4.482	3.885	61	5.96	2.33	64	106	0.9827	2.58	8.701	15120	14630	14510	
2.9	100.8	0.55	100.25	4.210	4.461	55	5.35	2.68	57	122	0.9786	2.61	8.680	14840	14370	14140	
4.9	123.1	0.65	122.45	3.948	5.110	53	5.14	3.07	55	140	0.9744	2.57	8.757	15140	14680	14350	
6.9	150.6	0.75	149.85	3.704	5.867	50	4.82	3.52	52	161	0.9696						

TABLE 6.

$t$	$P$	$P_{H_2O}$	$P_{H_2S}$	$a$	$10^3q$	$10^4 \frac{P_{H_2O}}{P_{H_2S}}$	$10^3r$ ( $n=6$ )	$10^2s$ ( $n=6$ )	$rQ_v$	$sQ_0$	$1+r-s$	$10^5 \Delta T^{-1}$	$10^2 \Delta \log P$	$b$	$E_2$	$E_2(t=-0.4)$	mean
0.97	82.5	0.5	82.0	4.479	3.882	61	5.96	2.33	64	106	0.9827	2.68	8.959	14990	14500	14370	14370
3.00	101.4	0.55	100.85	4.196	4.473	55	5.35	2.68	57	122	0.9786	2.65	8.913	15010	14540	14310	
5.03	124.5	0.65	123.85	3.931	5.146	52	5.04	3.09	54	141	0.9741	2.59	8.867	15210	14760	14420	
7.05	152.7	0.75	151.95	3.686	5.920	49	4.73	3.55	51	162	0.9692						



The situation of the quadruple point could be found by graphically determining the point of intersection of the two three-phase lines  $SS_BG$  and  $SL_2G$ . In this way by the aid of the data recorded in the tables 1—6 we find  $t = -0.6 \pm 0.2$ ; the corresponding pressure amounts to about 70 cm. of mercury. The quadruple point temperature can, however, be calculated more accurately as follows.

Under the circumstances of the quadruple point the liquid  $L_2$  is a diluted solution of sulphuretted hydrogen in water. When  $a$  again represents the number of volumes  $H_2S$  of one atmosphere (corrected for  $0^\circ$ ), which dissolves in one volume of water, the number of gramme-molecules  $H_2S$  that dissolves in 100 grammes of water, is  $5.87 \cdot 10^{-5} aP$ . If  $H_2S$  were a non-electrolyte, the lowering of the freezing-point would accordingly amount to  $5.87 \cdot 10^{-5} aP \cdot 18.5^\circ$ . When in this we introduce for  $a$  and  $P$  the solubility at  $t = -0.6^\circ$  (4.709) and the quadruple point pressure found graphically (70), we find a lowering of the freezing point of  $0.4^\circ$ ; the quadruple point temperature amounts, therefore, to  $-0.4^\circ$  C. When for  $a$  the solubility at  $-0.4^\circ$  is chosen, this brings no change in the calculation.

Nor does the fact that sulphuretted hydrogen in water is partially electrolytically dissociated bring a change in the above calculation. The dissociation constant of  $H_2S$  amounts (first stage) to about  $10^{-7}$ . The dilution under the circumstances of the four-phase equilibrium amounts to 5.2, the degree of dissociation in consequence of this to about  $7 \cdot 10^{-4}$ , and consequently the latter has no appreciable influence on the situation of the quadruple point.

In order to find the value of  $E_2$  at this temperature, the specific heats of the reacting substances must be known. As the molecular specific heat of the hydrate ( $n = 6$ ) would amount to 61.6 according to the law of KOPP<sup>1)</sup>, and as the specific heat of six molecules of water and one mol. of sulphuretted hydrogen is  $108 + 6.3 = 114.3$ , the algebraic sum is about 53. The correction required for the calculation of  $E_2$  at the quadruple point is, therefore,  $53(t + 0.4)$ . The mean of the values thus found is recorded in the last column of the tables 4—6.

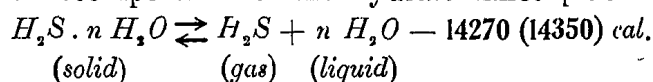
The values of the last column but one in tables 4 and 5 still present appreciable deviations. This is owing to the small differences of temperature between the successive observations. In order to determine these differences more accurately the ANSCHÜTZ-thermometer (division into  $\frac{1}{5}$  degree), which was used in the other determinations, was replaced by a BECKMANN-thermometer (division

<sup>1)</sup> NERNST. Theoretische Chemie. Gesetz VON DULONG und PETIT.

into  $1/100$  degree) in the experiments of table 6. Consequently the agreement of the values in the last column but one of table 6 is much better, the mean values of the three tables are in good concordance.

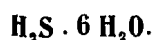
When we now determine the mean of the values from the last columns of tables 4—6, the first value of table 5, which is evidently too high (probably because the transformation in the quadruple point had not yet entirely taken place), being eliminated, the value 14270 for  $E_2$  is found; when the value in question is taken into account, the mean amounts to 14350 cal.

Hence the decomposition of the hydrate takes place according to:



An objection that may be adduced against the above calculations, is the choice of  $n = 6$  in the determination of  $r$  and  $s$  from equation 10  $a$  and  $b$ , and in the calculation of the algebraic sum of the specific heats. We shall come back to this in § 11.

10. From the values  $E_1 = 5550$  cal. (§ 8) and  $E_2 = 14270$  (14350) cal. (§ 9) follows according to equation 1:  $n Q = 8720$  (8800) cal., and as  $Q = 1440$  cal., the value 6.06 (6.11) follows for  $n$ . Hence the conclusion from these calculations is, that the hydrate has the formula:



11. As was stated in § 9,  $n = 6$  was already taken in the calculation. A choice of  $n$  was necessary to render it possible to calculate  $r$  and  $s$  (equation 10  $a$  and  $b$ ), and find the algebraic sum of the specific heats. We shall, therefore, still have to show that  $n = 6$  is the only value that satisfies the observations. It might, namely, also be possible that with the choice  $n = 5$  the result of § 10 was also appreciably changed, and would correspond to the choice  $n = 5$ . This is, however, not the case. The following considerations may make this clear.

If  $n = 5$ , the molecular specific heat of the hydrate would amount to 53.0, and as the specific heat of five molecules of water and one mol. of sulphuretted hydrogen is  $90 + 6.3 = 96.3$ , the algebraic sum would be about 43.

When on assumption  $n = 5$  we calculate the values of  $r$  and  $s$ , and by the aid of this the other values, it appears that this does not give any change in the result, and that, therefore, the assumption  $n = 5$  is erroneous. We have carried out this calculation for the data of table 4; the results are recorded in table 4a. The mean

value of the last column becomes 100 cal. higher than the corresponding value of table 4. A difference of one molecule of water

TABLE 4a.

$t$	$10^3 r$ ( $n=5$ )	$10^2 s$ ( $n=5$ )	$rQ_v$	$sQ_0$	$1+r-s$	$b$	$\bar{E}_2$	$E_2(t=-0.4)$	<i>mean.</i>
0.85	5.88	1.97	63	90	0.9862				
1.9	5.78	2.13	62	97	0.9845	15310	14800	14720	
2.9	5.28	2.27	57	104	0.9826	14080	13570	13450	
3.9	5.17	2.43	56	111	0.9809	15310	14810	14650	
4.85	5.06	2.61	54	119	0.9790	15640	15150	14940	14210
6.85	4.85	2.95	52	135	0.9754	14150	13670	13400	
8.85	4.44	3.37	47	154	0.9707	14920	14460	14110	

in the composition of the hydrate would require a difference of 1440 cal., and besides the difference lies in the wrong direction. Accordingly the value  $n = 5$  does not correspond to the observations.

It will be clear from the tables 4—6 that it is permissible to neglect the values spoken about in § 6 in the expressions  $10a$  and  $b$ .

12. When we now compare the results of this indirect analysis with the determinations carried out before by a direct way, it appears that at the quadruple point the composition of the compound is given by  $H_2S \cdot 6H_2O$ , that, however, at  $-80^\circ$ , when the compound is formed of water and an excess of sulphuretted hydrogen, a quantum of gas is persistently retained by the solid substance, which does not even escape at a pressure of 2 cm (waterjet pump) in some hours. When the compound is heated, this gas is, however, quickly liberated, and this latter causes two-phase equilibria to be measured in vapour pressure determinations at low temperatures (Cf. § 7).

The analyses executed before can be explained by this gas-adsorption. The quantity of sulphuretted hydrogen retained was not inconsiderable. When we bear in mind that the composition of the solid substance varied between  $H_2S \cdot 5.1H_2O$  and  $H_2S \cdot 5.5H_2O$ , it appears that per molecule  $H_2S \cdot 6H_2O$  resp. 0.18 and 0.09 mol.  $H_2S$  have remained adsorbed. That these quantities have not rendered the above three-phase determinations impossible is owing to this that during the filling of the apparatus, it was repeatedly evacuated cooled with liquid air, hence at lower pressure, that therefore the sulphuretted hydrogen could more easily escape, and the time of evacuation was chosen long.

In the direct analysis exhaustion with liquid air is not permissible,

because the pressure then falls below the three-phase tension  $SS_BG$ , in other words the hydrate can be decomposed. From the determinations of the tables 1—3 the three-phase pressure hydrate-ice-gas at  $-80^\circ$  can be calculated by extrapolation. When we assume the heat of transformation to be independent of the temperature — it has already been proved in § 5 that the influence of the temperature is small — the following equation is found for the three-phase line  $SS_BG$  by the aid of the tables 1—3:

$$\log P = -\frac{1333}{T} + 6,7393.$$

When in this we substitute  $t = -80^\circ \text{C.}$ , the pressure appears to amount to 7 mm. In the carbonic acid-alcohol mixture the three-phase tension may certainly not be neglected. In the filling of the apparatus in the evacuation with cocoanut carbon we have, therefore, to do both with slowly decreasing adsorption, and with decomposition of the hydrate. It appears from the above-described observations that the time of evacuation can easily be chosen so that neither has a disturbing influence in the determination of the equilibrium pressures.

Decomposition of the hydrate should, however, be avoided in the direct analysis. The pressure of the waterjet pump lies sufficiently high above the three-phase pressure, that decomposition may be left out of account; under these circumstances the adsorption can, however, not be abolished in a few hours. Improvement in the direct analysis method is only possible by choosing the time of evacuation longer. We have still performed three direct analyses in the way described above (cf. § 1 loc. cit.), in which the time during which the hydrate remained connected with the waterjet pump, was carried up to 5 (one determination) resp. 7 (two determinations) hours. Notwithstanding this these determinations yielded for the water content 5.39, 5.46, and 5.61  $\text{H}_2\text{O}$ . Only the last value falls somewhat outside the limits 5.1 to 5.5 of the determinations performed before (see § 1). Accordingly the value 6 is far from being reached here either.

The gas-adsorption discussed here is, therefore, the cause that the sulphuretted hydrogen hydrate has not yet been prepared by a direct way in pure state, and that it cannot be analysed either, but that an indirect method which can be applied here at temperatures where this adsorption is no longer active, yields the right composition for this substance. At these temperatures direct analysis is, however, impossible on account of the great tension of dissociation.

*Delft—Amsterdam, March 22, 1919.*