the liquid mixtures in a bath of solid carbon-dioxyde and alcohol.

When the solid compound had once been obtained in this way, the different points of the stable melting-point line were determined by seeding the undercooled mixtures with solid hydrate, and by determining the temperature, in which the last trace of solid substance vanishes by slow heating.

Instead of the metastable three-phase equilibrium between two liquid layers and solid phenol discussed just now, we now likewise get such a three-phase equilibrium in stable state, but now between two liquid layers and solid hydrate. For this stable three-phase equilibrium indicated by the points ldb the temperature 12,2° was found.

If we now go to lower temperature, we get the continuation of the melting-point line of the compound which lies very much to the side of the component, water, and ends in the entectec point for *ice, liquid* and *solid hydrate*, the temperature of which appeared to lie at — 1.0°.

In conclusion we may still mention that to get perfect certainty that the top of the melting-point line of the hydrate really lies in the stable region it must be examined if there exists a euteclic point of *solid hydrate, liquid,* and *solid phenol,* which in this case must lie below the highest melting-point observed on the melting-point line of the hydrate. This question was settled beyond all doubt by the following procedure: we started from a mixture lying in concentration between y and h; this mixture was entirely melted, then undercooled by cooling to $\pm 15°$, and then seeded with a conglomerate of the solid compound and the solid phenol. Then the temperature rose to 15°.8 and remained constant there for a considerable time, from which follows that the top of the melting-point line of the hydrate really still lies just in the stable region, as has been indicated in the T-x-figure.

Anorg. Chem. Laboratory of the University.
Amsterdam, June 1911.

Chemistry. — *"On the system hydrogensulphide-water."* By Dr.
F. E. C. Scheffer. (Communicated by Prof. A. F. Holleman.)

1. In a previous communication[1]) I already mentioned the principal part of the results of my investigation on the system hydrogen sulphide-water in the neighbourhood of the quadruple point hydrate-two liquid layers-gas. From the determination of the P-T-projection of the four three-phase lines the behaviour of the said system could

[1]) These Proc. Jan. 1911.

already be examined in main lines. By the aid of these determina-
tions I have already schematically given the shape of the P-x-section
through the spacial figure for about 20°, which is reproduced in
figure 1. From the slight differences in pressure between the tension-
line of the liquid hydrogensulphide on -one side (a in Fig. 1), and
the two three-phase lines SL_1G (b) and L_1L_2G (c) on the other side
it was already very probable that the concentrations of L_1 for the
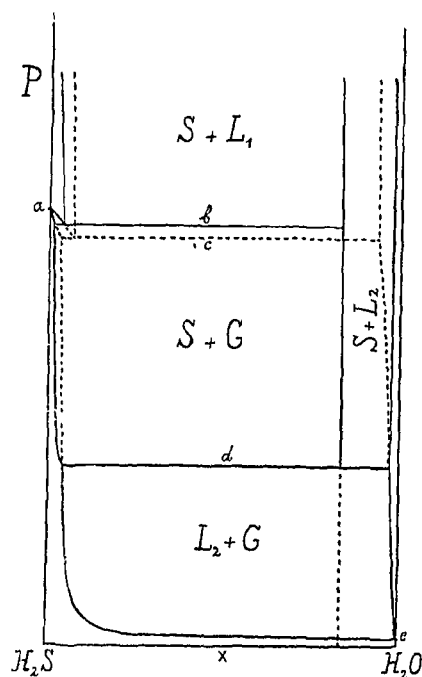two mentioned three-phase pressures would lie near the hydrogen

Fig. 1.

sulphide side, while the gas phases corresponding to them - must
contain still less water than L_1. With regard to the situation of
G and L_2 on the three-phase line SL_2G (d) we may derive from
the relative volatility of the two components that G lies on the
side of the first component; the situation of L_2, however, cannot
be found from the determinations of vapour tension. 1 had already
drawn L_2 in the P-x-section on the side of water, as some preli-
minary experiments had already proved that the liquid coexisting
with hydrate on SL_2G (d) contains only little hydrogensulphide.

To obtain further certainty I have determined the situation of the
liquid branches on the three-phase lines SL_1G (b) and SL_2G (d) by

the aid of sealed tubes. A tube provided with a capillary was weighed first empty, then with water. After condensation of hydrogen sulphide the tube was sealed at the constriction, and the weight of the condensed gas was easily found by weighing of the tube with the melted off part. Then the tube was slowly heated in a water-bath, and the temperature was determined at which the last crystals disappeared. It will be clear that this observed temperature will be on the liquid branch of the three-phase line only when the vapour phase disappears at the same moment as the solid substance. This can, of course, not be carried out in practice; it is, however, possible to choose the quantity of vapour small, and then the observed temperature differs in general only very little from the real one. This latter precaution, which will have little, if any, influence for the determination of the liquid points on SL_1G, must, however, be carefully observed for the determination of the discussed points on SL_2G. We can easily see this in the following way. If the last crystals disappear, the observed temperature agrees entirely with the liquid point of the mixture, the quantity of vapour being neglected. If we now are on SL_1G, the vapour consists for the greater part of hydrogensulphide, the substance which is present in the mixture in great excess; so a neglect of the vapour space is undoubtedly justified, when it is small. For the line SL_2G, however, the situation is just the reverse; the vapour which remains at the observed vanishing point of the solid substance, consists for the main part of hydrogensulphide, the substance which is present in a small quantity, and with appreciable vapour space the errors can reach here a high value. Accordingly in the first place the vapour space should be chosen small; to enhance the accuracy, however, I have determined the vapour space by calibration with water at the end of the determination. The quantity of hydrogensulphide in the vapour could then be roughly calculated by the aid of the three-phase pressures from the preceding communication, and the law of BOYLE, which though probably not holding strictly here, can yet be used in the determination of the correction which is already small. Moreover it appeared that after the said correction the points determined with great gas volume, agreed satisfactorily with the observations with small gas volume. The observed liquid points have been collected in the following table:

SL_1G.		SL_2G.	
x (in mol. % H_2O)	Temp. of L_1.	x (in mol. % H_2O)	Temp. of L_2.
0,4	< 0	99,5	5,3
0,5	6	99,25	11,4
0,8	17	99,1	13,7
1,2	26	98,8	17,2
1,6*	29,5*	98,2	22,9
		98,1	23,3
		98,1**	23,8**
		97,5	26,3
		97,3**	26,9**
		96,9	28,5
		96,3*	29,4*

The observations marked with a * refer to the four-phase equilibrium; those with ** have been made in the presence of a great quantity of vapour.

In the determination of the first series we met with more difficulties than in the determination of the second. Whereas the disappearance of the last crystals is easy to ascertain in solutions rich in water, this is attended with difficulties in those rich in hydrogensulphide, as the crystals of the hydrate were hardly to be seen as long as they were covered by liquid hydrogensulphide. Only by making the liquid continually flow from one side of the tube to the other we could succeed in ascertaining whether the last crystals had disappeared.

The determinations of SL_2G can still be supplemented as follows. When we bear in mind that the pressure on SL_2G reaches one atmosphere at 0,35° according to the determinations of DE FORCRAND and VILLARD [1]), and so that at this temperature the intersection with the isobar section of one atmosphere through the $L—G$ surface, takes place, for which sufficient data are to be found in the literature, it will be clear that we may add to the table for SL_2G the concentration of the solution of H_2S in H_2O, which has a pressure of one atmosphere at 0,35°. From FAUSER's [2]) determinations of solubility, we derive that 4,64 volumes of H_2S dissolve in one volume of water at 0,35°, from which follows $x = 99,63$. The value found thus: $x = 99,63$, $t = 0,35$ appears to be in harmony with the other values.

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[1]) DE FORCRAND and VILLARD. C. r. 106 851 (1888).

[2]) LANDOLT—BÖRNSTEIN. Tables 1905. p. 602.

So we can derive from the table that L_1 contains about 1,3 mol. $^o/_o$ H_2O and L_2 3,4 mol. $^o/_o$ H_2S at the quadruple point. So it appears really that non-miscibility extends almost over the full width of the figures of concentration.

2. In the preceding communication uncertainty continued to prevail about the constitution of the hydrate. The first analysis of the hydrate found by WÖHLER in 1840 was made by DE FORCRAND. In reference to these analyses, which first led to the formula $H_2S\,15\,aq$ [1]), afterwards to $H_2S\,12\,aq$ [2]), DE FORCRAND remarks that it is difficult to obtain this compound in dry state; generally in the formation of the compound a quantity of water remains excluded from the action of the gas owing to its being enveloped by a layer of solid substance. To this difficulty, which presents itself in a perfectly analogous way for other gas-hydrates, it is owing that the most divergent formulae have been proposed for the concentration of the hydrates, which possess the smaller ratio of water as the investigations were repeated with greater care. Thus in an analysis carried out later on by DE FORCRAND and VILLARD the concentration $H_2S\,7\,aq$ appeared to be the most probable one [3]), but of this analysis the two investigators state that also in this case the ratio of water is probably still too high. VILLARD [4]) comes to this conclusion on account of the great analogy between this hydrate and the numerous other hydrates examined by him, for which his extensive investigation has made the general formula $M\,.\,6\,H_2O$ probable. Besides in virtue of this analogy VILLARD thinks he has to ascribe the analogous formula $H_2S\,.\,6\,H_2O$ to the hydrate of H_2S, also on account of the possibility of seeding a mixture of N_2O and H_2O with the hydrate of H_2S, so that $N_2O\,.\,6\,H_2O$ is deposited. VILLARD has, however, not made any direct determinations to prove this constitution.

DE FORCRAND arrives at the same conclusion by another way. From some regularities found empirically between caloric quantities and the temperature, in which the line SL_2G reaches the pressure of one atmosphere, DE FORCRAND finds a means to calculate the concentration of the hydrates. This calculation, which I shall not discuss any further here, has yielded the value $H_2S\,.\,5,69\,aq$ for the hydrate of hydrogen sulphide [5]), which led DE FORCRAND to conclude to the formula $H_2S\,.\,6\,aq$.

1) DE FORCRAND. C. r. 94 967 (1882).

2) DE FORCRAND. Ann. chim. phys. (5). 28. 5 (1883).

3) DE FORCRAND and VILLARD. C. r. 106. 1402 (1888).

4) VILLARD. Ann. chim. phys. (7) 11 289 (1897).

5) DE FORCRAND. C. r. 135. 959 (1902).

Though in this way the two investigators concur in considering the formula $H_2S \cdot 6\,aq$ the most probable, neither reasoning seems to me to be conclusive for the given composition. In the first place VILLARD's arguments can at most make the said formula probable, while we cannot attach absolute certainty to DE FORCRAND's calculation in my opinion already for the reason that an analogous calculation applied to the hydrate of SO_2 yielded the value $SO_2 \cdot 8\,H_2O$, whereas the analysis of BAKHUIS ROOZEBOOM already made $7\,H_2O$ probable, and VILLARD's later determinations, which were carried out with great care have proved with certainty in my opinion that the content of water cannot be higher than 6 molecules.

For this reason a renewed analysis seemed desirable to me. I have carried it out in a way which the spacial figure naturally suggests, and which was already applied before for the determination of the composition of gas hydrates by different investigators, among others a single time by BAKHUIS ROOZEBOOM and repeatedly by VILLARD. In the spacial figures of the gas hydrates in general a large region is found where the solid hydrate occurs by the side of a gas phase, which practically consists entirely of the most volatile component. So when we first realise the state on SL_1G, and then evaporate the liquid phase L_1, we shall retain the pure hydrate by the side of gas.

The determinations were made in wide tubes provided with stems with two capillary constrictions; after the tube had been weighed empty and with a certain quantity of water an excess of H_2S was condensed, and the tube was fused to at the upper constriction. By first heating the mass to the quadruple point and then cooling it shaking it violently the mass was converted into hydrate [1]. After the state SL_1G obtained in this way had been preserved for some days, the tube was cooled in carbonic acid and alcohol, and opened; then we either evacuated the hydrogensulphide at $-80°$ by means of the water-jet circulation pump, or removed it by boiling about $-13°$ (ice and salt). In both cases we are in the S-G-region, as will be clear from the P-T-projection of the preceding paper. Three weighings, the last after the tube has been sealed at the lower constriction, yield the data required for the calculation.

I have carried out some thirty analyses of this kind; the values obtained thus oscillate round 5,3 mol. water; almost all lie between $5,3 \pm 0,2$ mol. water (28 observations) so that I think I may conclude that the formula $H_2S \cdot 5\,H_2O$ is the most probable. I think I am justified in this because the found oscillations can only be accounted

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[1] In some analyses this was promoted by glass rods or small glass spheres, which, however, had no influence on the result.

for by incomplete combination of the two components, so that a
small quantity of water escapes further action of the gas by being
enveloped in solid hydrate. A further proof of this is furnished by
the fact that some preliminary experiments, in which little care was
devoted to the complete formation of the hydrate by shaking, yielded
far more oscillating values, which were all higher than those men-
tioned above. So it is beyond doubt that the values found can only
indicate a too great content of water.

So the hydrate $H_2S . 5 H_2O$ differs from the many hydrates
$M . 6 H_2O$ examined by VILLARD.

3. When in conclusion we survey the results of the investigation,
it appears that the system $H_2S—H_2O$ presents great analogy to the
system $SO_2—H_2O$, one of the gashydrate systems investigated by
BAKHUIS ROOZEBOOM. The solubility of the hydrate of SO_2 under the
three-phase pressure in the condensed gas is only small, like that
of the hydrate of H_2S, because in both cases the pressure of the
line SL_1G lies only little lower than the vapour tension line of the
liquid, most volatile component. The other systems examined by
BAKHUIS ROOZEBOOM deviate more or less from this system, either in
consequence of the fact that the concentration of L_1 on SL_1G lies
much less on one side, or because this line shows higher pressure
than the two components, so that the L-G-surface presents a maxi-
mum in the isothermal sections.

Anorg. Chem. Laboratory of the University of Amsterdam.

Physics. — "*On the inconsistency of my heat theorem and VAN DER
WAALS' equation at very low temperatures.*" By Prof. W.
NERNST of Berlin. (Communicated by Prof. H. A. LORENTZ).

(Communicated at the meeting of May 27, 1911.)

Messrs. KOHNSTAMM and ORNSTEIN[1]) have published a criticism on
my theorem of heat[2]) in these Proceedings, which is based on clearly
mistaken premises, and which therefore calls for a refutation.

Everybody who has studied Thermodynamics, knows the form,
in which HELMHOLTZ and others have expressed the second theorem
of heat:

$$A — U = T \frac{dA}{dT}. \qquad \qquad (1)$$

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[1]) These Proc. of 24 Dec. 1910.

[2]) NERNST, Theoret. Chem. VI Aufl. S. 699 (1909); cf. also the literature
mentioned in my paper, Journ. de Chim. Phys. 8 228 (1910).