it was supposed that this substance would always behave in a unary way. Experiment has fully confirmed this conjecture. Whether mercury was suddenly cooled by water in vacuo from $\pm$ 300°, and then by solid carbonic acid and alcohol, or whether it was rapidly heated from 80 , the point of solidification, resp. melting-point always remained the same, and the substance perfectly behaved as a unary one, from which we may therefore draw the conclusion that when the substance is complex the internal transformations must proceed with extraordinarily great rapidity, or what is more probable that mercury really consists of one kind of molecules.

The third substance examined by us, for which in view of its transition points, the same was expected as for the phosphorus, was tin.

Though the investigation made bears as yet still a preliminary character, we may yet communicate that tin of particularly great purity can solidify entirely as a unary substance, but that it betrays its complex character when the experiment is made very rapidly, just as phosphorus does. In a following communication we hope briefly to communicate the result of the final investigation.

Amsterdam, December 23$^{\text{rd}}$ 1910.

Anorg. Chem. Lab. of the University.

Chemistry. *"On the determination of threephase pressures in the system hydrogen sulphide + water."* By Dr. F. E. C. Scheffer. (Communicated by Prof. A. F. Holleman).

1. In the investigation of the systems in which hydrogen sulphide is one of the components, the difficulty presents itself that a chemical action can affect the mercury that shuts off the mixture, when it is not sufficiently purified from admixtures. This action will chiefly be due to the presence of slight quantities of air. By excluding the presence of air (and water), as completely as was possible in the methods used, I succeeded before in determining the situation of the three-phase curves in the system hydrogen sulphide + ammoniac. The methods used in the investigation, had to be adapted to high pressures, as it was my principal aim to determine the points of intersection of the critical line and the three-phase curves, the critical end-points. In this I have at the same time found an opportunity to determine the shape of the spacial figure of the mentioned system at lower temperature; the observations at these low tempe-

ratures and the low three-phase pressures corresponding with them though perfectly sufficient qualitatively, could of course lay claim to but little accuracy, particularly because the pressures were read on a metal manometer, which indicated up to 250 atmospheres, and which can give only rough values below about 20 atmospheres, and because the slow setting in of equilibrium can cause a great relative error at these low pressures.

I have now tried to find an improved method for the investigation at pressures below 20 atmospheres, which could yield more accurate results. I intend to give here a description of this method and to demonstrate its efficiency not by the aid of the system hydrogen sulphide + ammoniac, as this would only involve a repetition of former observations, which would not open new vistas [1]), but apply this method to another system with hydrogen sulphide as component, namely the system hydrogen sulphide + water. As will appear from the following description, mercury is not affected by moist hydrogen sulphide, at least below 30°, when presence of air is carefully excluded.

2. *Preparation of the mixtures.*

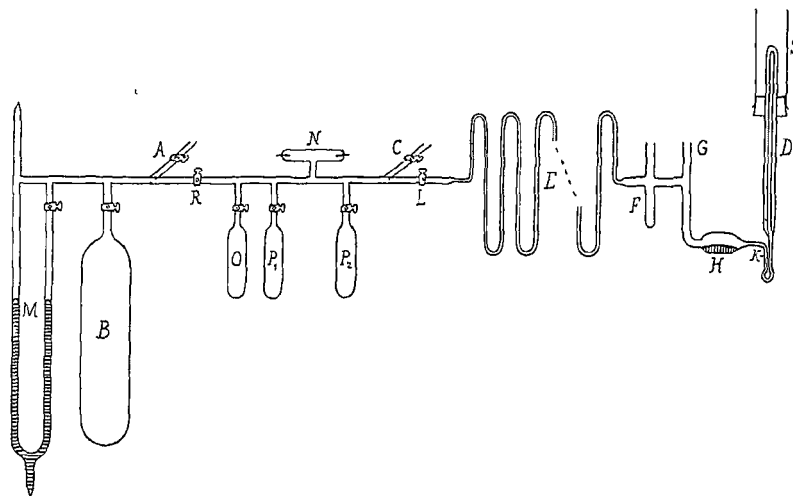For the preparation of a hydrogen sulphide + water mixture the

Fig. 1.

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[1]) These observations will shortly appear in the Zeitschrift für physikalische Chemie. It may only be remarked here that action of hydrogen sulphide on mercury was no longer observed, and that e.g. reduction of the volume under three-phase pressure to half its size, gave an increase of pressure, which generally amounted to less, but in one case to slightly more than 0,1 atmosphere; these deviations are about as great as the errors of observation.

apparatus was used, represented in figure 1. The hydrogen sulphide was prepared from a solution of natrium sulphide, which was free from carbonic acid and diluted sulphuric acid; the former solution was obtained by saturating natron, which had been freed from its carbonic acid by the addition of barium hydroxide, with hydrogen sulphide. The gas prepared in this way was dried by phosphoric anhydride, and led into the exhausted vessel B through the cock A (fig. 1); it was then freed from air by condensation in O by means of the two vessels P_1 and P_2, which were filled with carbon. of cocoa-nut; O, P_1, and P_2 had been placed in liquid air for this purpose. If now there were no discharges at all in the GEISSLER tube N, the hydrogen sulphide was again conveyed from O into the reservoir B by evaporation. Then the gas which had remained in the tubes of the apparatus between M and L could be sucked off by means of a water-jet-pump, when the cock C was opened.

The Cailletet tube, which was made of common glass for this experiment, where the pressures did not exceed 25 atmospheres, and which could have a comparatively large bore (5 mm.), was sealed to a glass spring E, and thus connected with the apparatus.

Now a quantity of mercury freed from air by boiling which was sufficient to fill the entire test-tube D, was brought into the reservoir H through G. After G had been sealed, F was provided with a little distilled water, and the upper end of this tube was also sealed. Now the water in F was frozen, and the test-tube was evacuated by means of the water-jet-pump (cock C) and carbon (F_1 and P_2). After the cock L had been closed, the water could now be distilled over from F to the upper end of the test-tube, which had been cooled with liquid air (vessel S).

A quantity of hydrogen sulphide was admitted from B into the apparatus between M and L with open vessel O; by means of the manometer M, whose rightside leg had been evacuated, this quantity could be roughly estimated. This gas too was solidified in the upper end of the test-tube when L was opened.

When I had then convinced myself that no air was present in the test-tube (discharge in N), the Cailletet tube was tilted, in consequence of which the mercury flowed from H into the U-shaped lower end of the test-tube, and was forced up to the top of the test-tube by the air in consequence of the opening of the cocks C and L. Now the Cailletet tube was separated from the apparatus at K, and placed in the pressure cylinder which was filled with mercury purified and freed from air by boiling.

When we work in this way the presence of air is practically

54

excluded and the mixture is only in contact with a small quantity of pure mercury; so contact with not entirely air-free mercury and rubber joints are entirely avoided in this way.

3. *Determination of pressure and temperature.* A cylindric vessel conically narrowed at the lower end was fastened to the Cailletet-tube by means of a cork, and filled with water. The heating took place electrically; the temperature was regulated by means of an incandescent lamp resistance, and read on an Anschützthermometer, which had been compared with a normal thermometer. The stirring took place in the waterbath by means of lead plates, which moved vertically up and down, in the test tube by means of a KUENEN stirrer; the electromagnetic coil required for this was vertically moved round the heating-vessel.

For the determination of the pressure I used two air-manometers, one of which indicated a minimum pressure of about 3, the other of about 8 atmospheres. The errors of the method remain in this way below $0°.1$ and 0.1 atmosphere (errors of the manometer and difference of position between the mercury in the test tube resp. manometer and in the pressure cylinder); the errors which can be made in the determination of the three phase curves, may be generally estimated at about 0.1 atmosphere, as appears from the concordance of the results. I shall, however, return to this, when discussing the·results.

4. *Results.* In fig. 2 the P-T-projection of the spacial figure is represented. In the first place we see drawn in it the vapour-pressure curve of hydrogen sulphide, which had been determined before by many observers. Just as in my previous determinations concerning the system hydrogen sulphide + ammoniac I arrived again at the result that the values given by REGNAULT, are too high; in the range of temperature investigated by me the deviations vary between 0.8 and more than one atmosphere. The only value which was determined by OLSZEWSKI in the range examined by me, presents a deviation of less than 0.1 atmosphere from mine, and has been denoted by O in the graphical representation; REGNAULT's deviating values I have omitted in the figure for the sake of clearness.

The hydrogen sulphide showed a variation of pressure of less than 0.1 atmosphere on isothermal compression to a fourth of the total volume, while also the pressure at which the last quantity of vapour disappeared differed less than 0.1 atmosphere from that at the greatest possible volume.

Immediately below this line two three phase curves appear in the P-T-projection, one of which indicates the coexistence of the hydrogen sulphide hydrate by the side of vapour and a liquid rich

in hydrogen sulphide, and the second the equilibria between two liquid layers and vapour. The former three-phase curve (SL_1G) gives
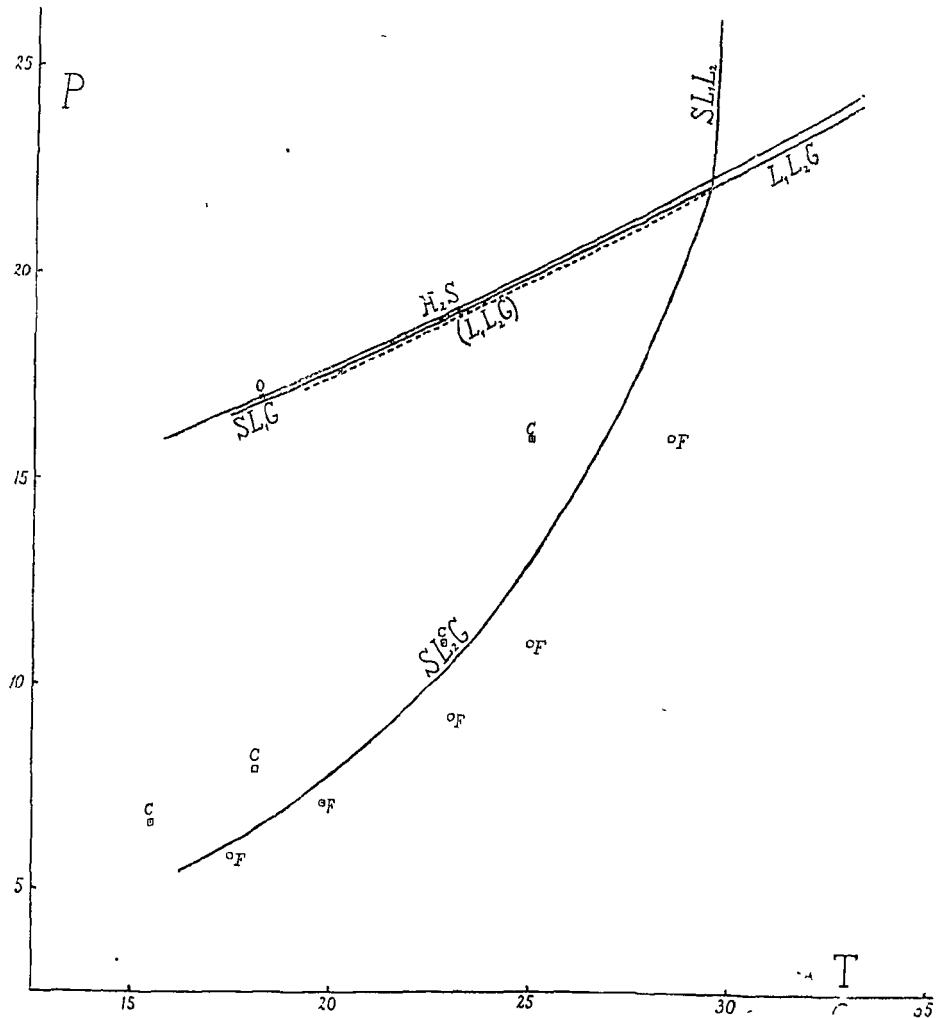

Fig. 2.

stable states all over its course; the other (L_1L_2G) metastable states below 29.5°, above this stable equilibria. The isothermal differences of pressure between these two three-phase curves and the above-mentioned boiling-point curve of hydrogen sulphide, are very slight, and are near the errors of observation, as regards their order of magnitude. Still I think I am justified in concluding with certainty from the great number of observations given in the table that the pressures are greater on the three-phase curve SL_1G than on L_1L_2G, and that the boiling-point line of hydrogen sulphide lies higher than either.

Also looked upon from a theoretical point of view this order

seems the most probable one; for if the liquid-vapour surface of the hydrogen sulphide continually descends to the side of the water, the three-phase pressures will lie below the maximum tension of liquid hydrogen sulphide at a certain temperature, and (below 29.5°) the metastable $L_1 L_2 G$ curve will have to lie lower than the stable $SL_1 G$-curve. We can see this, among others, already from this that for the coexistence $L_1 L_2 G$, the liquid L_1, being metastable, must be super-saturate with respect to the hydrate, and so richer in water than the liquid L_1 on the three-phase curve $SL_1 G$.

LG (H_2S)			L_1L_2G		SL_1G		SL_2G		
T	P	P	T	P	T	P	T	P	P
15		16.38 R							
15.8	15.9+		19.4	17.3	17.4	16.6	15.5		6.6 C
15.9	16.0—; 16.0+		19.8	17.4	18.4	17.0—	16.3	5.3—	
16.0	16.0		20.6	17.8—	18.7	17.05	17.5		5.8 F
16.2	16.1		20.8	17.9—	19.0	17.2	17.9	6.3—	
17.0+	16.5-		21.2	18.0; 18.0	19.9	17.6—	18.1	,	7.9 C
17.6	16.7		21.4	18.15; 18.2	20.9	18.0—	19.7	7.6	
17.8	16.8—; 16.8—		22.8	18.85	21.2	18.1+	19.8		7.1 F
18.2	.	16.95 O	23.0	18.95	21.8	18.4+	21.0	8.6+	
19.0	17 3—		23.65	19.3—	22.9	18.9+	22.8		11.0 C
20		18.62 R	24.6	19.7+	23.65	19.3	23.0		9.2 F
20.4	17.9+		24.8	19.85; 19.8—	23.8	19.35	23.3	10.7	
21.2	18.25		25.1	20.0—	24.1	19.5+	24.8+	12.9	
22 0	18.65		25.4	20.0—	26.0	20.5	25.0		11F; 16C
23.6	19.4+		25 6	20.1—	26.6	20.7—	25.6	14.0—	
24.9	20.0+; 20.4—		25.8	20.2; 20.3—	27.2	21 0+	27.4	17.1	
25		21.07 R	26.1	20.6	27.3+	21.05	28.5	19.5+	16 F
25.4+	20 3—		26.9	20.75	28.2	21.5+	29.2	21.3+	
25.8	20.5—		27.5	21.0+	28.8	21.8			
26.1	20.6+		28.0	21.3—	29.4	22.1			
26.2	20.7—		28.2	21.4					
27.5	21.3		28.4	21.5+					
29.6	22.35		29.1	21.75					
30		23.73 R	29.2	21.9—					
30.6	22.9		30.3	22.45					
31.6	23.4+		31.0	22.9—					
31.6+	23.45		31.2	22.9+					
33.4	24.45		32 0	23.4					
			32.7	23.8+					
			33.2	24.0+					

SL_1L_2

T	P
29.8	32

Quadruple point.
T 29.5 ; P 22.1 +

R = REGNAULT
O = OLSZEWSKI
C = CAILLETET and BORDET
F = DE FORCRAND

The possibility that on the liquid-vapour plane a line of maximum pressure occurs, cannot be excluded beforehand, of course, more especially because in this system a compound occurs, and moreover, one of the components (H_2O) is certainly abnormal. It seems even still possible here, that immediately on the hydrogen sulphide side such a line of maximum pressure occurs; then it must lie, however, at concentrations which are smaller than the gas and liquid concentrations on both the three-phase curves. This, however, does not seem probable for the present, and so I have not taken it into consideration in the P-x-section (fig. 3).

The two three-phase curves SL_2G and L_1L_2G intersect in the quadruple point (29.5°; 22.1 atm.); the two other three-phase curves which pass through this point, where resp. solid hydrate occurs by the side of two liquid layers (SL_1L_2) and by the side of vapour and liquid rich in water SL_1G, have also been represented in the graphical representation.

The preceding table gives a survey of the observations of the discussed lines of equilibrium.

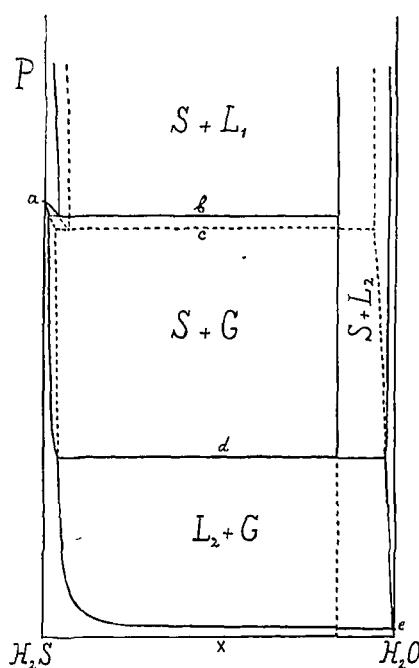5. By the aid of the above data, a P-x-section has been given schematically in fig. 3, which has been drawn through the spacial figure for about 20°. In this we have assumed, as was mentioned above, that the liquid-vapour surface descends continually from the first to the second component; the point a, the maximum tension of liquid hydrogen sulphide lies higher than the stable three-phase curve $S L_1 G (b)$ and the metastable $L_1 L_2 G (c)$ [1]. The other equilibrium curves and the regions given in the figure do not call for a further explanation. I will only draw attention to the fact that the hydrate in this section can no longer occur stable below the three-phase curve $S L_1 G (d)$; for with isothermal increase of volume the transformation $S \rightarrow L + G$ occurs on this three-phase curve, in other words, the

Fig. 3.

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[1] All the metastable lines of equilibrium have been indicated by dotted lines.

hydrate evaporates and melts. Then it will be clear at the same time that the earlier observations of DE FORCRAND [1]) and of CAILLETET and BORDET [2]) refer to this three-phase curve, as they have determined pressures which were necessary for the formation of hydrate; then it becomes also clear that this pressure as DE FORCRAND points out, is independent of the concentration of the mixture, which is, indeed required for this three-phase equilibrium by the phase rule.[3]) I have indicated their observations by the figures C and F both in the table under $S L_2 G$ and in the P-T-projection of fig. 2. My observations appear to lie between them. The pretty large deviations between the three lines must, in my opinion be ascribed to this, that the formation of the hydrate in case of compression, and the melting in case of expansion takes place slowly; in the first case we find too low, in the second too high pressure. I have made my observations of these three-phase equilibria by slowly heating at constant pressure, and by determining the temperature at which the trans-formation $S \rightarrow L + G$ occurred. This method of working appeared to yield more accurate results than that in which the transformations were observed for isothermal change of volume.

Whereas the equilibria on the other three phase curves establish themselves spontaneously at constant temperature, and the deviations rarely exceed 0.1 atmosphere, I think I shall have to estimate the accuracy of the observations on the lines SL_2G and SL_1L_2 at 0.1 to 0.2° [4]).

In the P-x-section the gasphase G and the liquid phase L_1 lie on the three-phase-curves on the hydrogen sulphide side; now it appeared from some preliminary experiments that the liquid phase L_2 lies near the water side, in other words that the region of non-miscibility extends over almost the full width of the figure.

Finally a few remarks may be made on the composition of the hydrate. It is not to be derived with certainty from the literature on the subject. DE FORCRAND, who has made numerous analyses of hydrate, considered successively $H_2S.15H_2O$, $H_2S.12H_2O$, and $H_2S.7H_2O$ the most probable formula. He justly ascribes the very bad agree-ment of the analysis results to the fact that the hydrate easily

[1]) DE FORCRAND. C.r. 94, 967 (1882); DE FORCRAND and VILLARD C r. 106, 849 (1888).

[2]) CAILLETET and BORDET. C.r. 95, 58 (1882).

[3]) DE FORCRAND. C.r. 94, 967 (1882).

[4]) Also the observation of $SL_1 L_2$ took place by the determination of the tem-perature at which the transformation $S \rightarrow L_1 + L_2$ is found with slow heating at constant pressure.

retains water. When we further bear in mind that the hydrate is only constant below 0.35° under atmospheric pressure, and that, accordingly, formation of the hydrate at atmospheric pressure without formation of ice will only be possible between 0° and 0.35°, it will be clear that we must here have recourse to special methods of analysis. I shall have to postpone a description of a method suitable for this purpose to a following communication; it may only be mentioned here that even the formula $H_2S.6H_2O$ derived later by DE FORCRAND on theoretical grounds probably still contains too great a quantity of water.

(February 23, 1911).