

*Citation:*

Postma, S. & A. Smits, The system ammonia-water, in:  
KNAW, Proceedings, 17 I, 1914, Amsterdam, 1914, pp. 182-191

Substituting these values in (40) we find:

$$2 (y_1 - \beta) RT \xi = a \pi^2 \dots \dots \dots (42)$$

wherein  $a$  has the same value as in (21) (XII).

From this it follows with the aid of the first relation (41) that:

$$2 (y_1 - \beta) RT \xi = \frac{a t^2}{\left(\mu - \frac{\partial V}{\partial y}\right)^2} \eta^2 \dots \dots \dots (43)$$

In the same way as in (XII) we find that we may write for this:

$$2 RT \xi = \frac{t^3 (y - \beta) (y_1 - y) \frac{d^2 l}{dP^2}}{(y_1 - \beta) \left(\mu - \frac{\partial V}{\partial y}\right)^2} \eta^2 \dots \dots \dots (44)$$

wherein  $\frac{d^2 l}{dP^2}$  is fixed by (24) (XII). From this it follows that the curve going in fig. 4 through the point  $H$  is parabolically curved in this point and touches the side  $BC$  in this point.

As in this point  $y - \beta < 0$ ,  $y_1 - y < 0$ ,  $y_1 - \beta < 0$  and  $\frac{d^2 l}{dP^2} > 0$ ,  $\xi$  is always negative. From this it follows that this parabola has only the point  $H$  in common with the triangle and is further situated completely outside the triangle. Consequently only the point  $H$  represents a liquid; its other points have no meaning.

(To be continued).

**Chemistry.** — “*The system Ammonia-water*”. By Prof. A. SMITS and S. POSTMA. (Communicated by Prof. J. D. v. D. WAALS).

(Communicated in the meeting of May 30, 1914).

After the preliminary communication <sup>1)</sup> on this subject the investigation of the system  $\text{NH}_3\text{-H}_2\text{O}$  has been continued in different directions, and it has now been completed.

The continued research was directed in the first place to the accurate determination of the meltingpoint lines, corresponding with the pressure of one atmosphere. These determinations, which were now carried out by means of a gauged resistance thermo-

<sup>1)</sup> These Proc. XII, p. 186.

meter<sup>1)</sup>, as is in use in this laboratory<sup>2)</sup>, gave the following result.  
(Method of procedure: supercooling a little and then seeding).

Concentration mixture	Initial point of solidification	Final point of solidification
100 mol. % NH <sub>3</sub>	- 77.6°	
94.7	- 80.9	
90.4	- 83.7	
86.5	- 87.2	
81.55	- 92.4	
	- 92.6	- 92.5°
78.45	- 88.7	- 92.5
73.5	- 82.2	- 92.6
71.1	- 80.3	
69.9	- 79.7	
66.7	- 78.8	
65.8	- 78.9	
64.6	- 79.2	
62.0	- 81.0	
61.3	- 81.7	- 86.0
60.7	- 82.3	- 86.0
60.3	- 82.9	- 86.0
59.0	- 85.2	- 85.8
57.0	- 84.1	- 85.8
53.0	- 80.2	
50.2	- 79.1	
50.1	- 79.0	
49.3	- 79.0	
43.9	- 83.0	
42.2	- 86.0	

<sup>1)</sup> Gauging points were: melting ice 0°, melting mercury - 38.85°. Boiling CO<sub>2</sub> + alcohol - 78.34° + 0.20 (B-76). Boiling point of oxygen - 182.8° + 0.36 (B-76).

<sup>2)</sup> Cf. DE LEEUW. Z f. phys. Chem. 77, 303 (1911).

Concentration mixture	Initial point of solidification	Final point of solidification
40.6	- 88.2	
39.8	- 90.7	
39.1	- 91.7	
35.75	- 97.1	
34.5		- 100.3
34.0	- 96.7	
32.6	- 89.2	
29.7	- 74.2	
28.7	- 68.8	
27.6	- 63.7	
26.55	- 59.4	
23.0	- 43.5	
20.2	- 34.9	
17.9	- 28.6	
4.46	- 4.8	
0.0	0.0	

This result is expressed in Fig. 1.

From this *T-X* fig. follows:

for the point of solidification of the compound  $2 \text{NH}_3 \cdot \text{H}_2\text{O}$ — $78^\circ.9$ .

„ „ „ „ „ „ „ „ „  $\text{NH}_2 \cdot \text{H}_2\text{O}$ — $79^\circ.0$ .

Further the eutectic point of  $\text{NH}_3 + 2 \text{NH}_3 \cdot \text{H}_2\text{O} + \text{L}$  appears to lie at  $81.4\%$   $\text{NH}_3$  and  $-92.5^\circ$ .

„ „ „ „ „ of  $2 \text{NH}_3 \cdot \text{H}_2\text{O} + \text{NH}_3 \cdot \text{H}_2\text{O} + \text{L}$  appears to lie at  $58.5\%$   $\text{NH}_3$  and  $-86.0^\circ$ .

„ „ „ „ „ of  $\text{NH}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} + \text{L}$  appears to lie at  $34.7\%$   $\text{NH}_3$  and  $-100.3^\circ$ .

Great difficulties were experienced in the case of the mixtures with less than  $50\%$   $\text{NH}_3$ , in consequence of the great viscosity of these mixtures at low temperature.

Shortly after our just mentioned preliminary communication a treatise on the same subject by RUPERT<sup>1)</sup> appeared in Journ. Am. Chem. Soc. **31** 866 (Aug. 1909).

<sup>1)</sup> Further communication Journ. Am. Chem. Soc. **32**. 748 (1910).

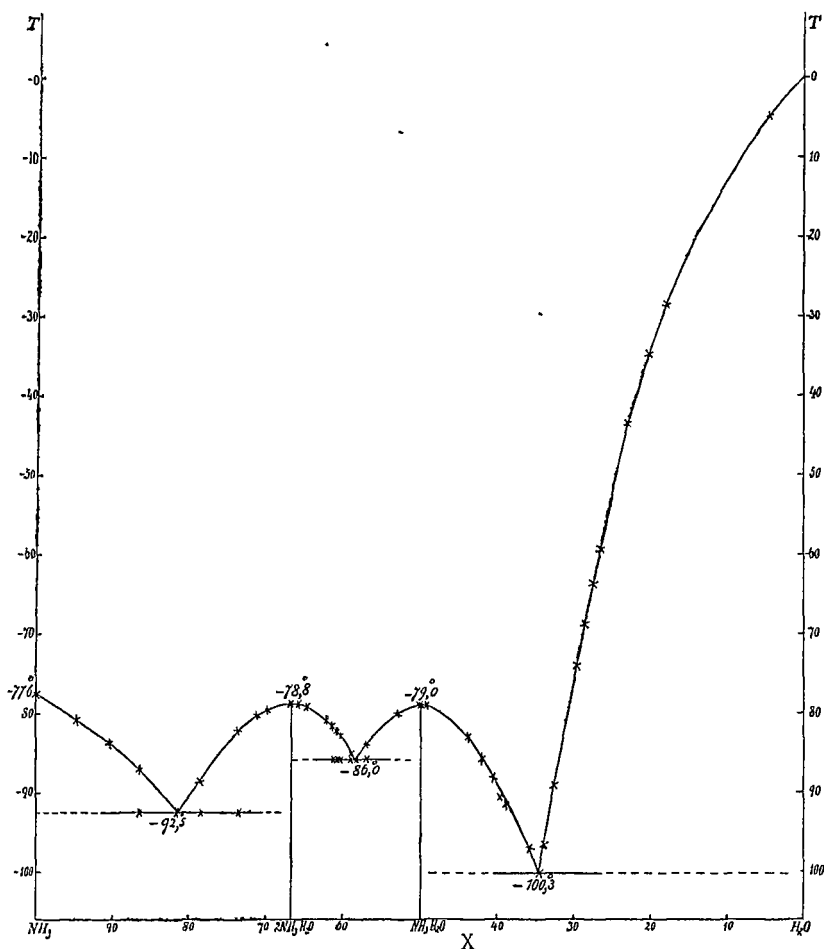


Fig. 1.

As point of solidification RUPERT determines the point at which the crystals brought into the liquid no longer grow or disappear. He measures the temperature accurate down to  $0^{\circ}.5$  with a verified toluol-thermometer. Below  $-100^{\circ}$  he uses a thermo-element, tested by comparison with the toluol thermometer and with the boiling point of liquid air. He himself considers the determinations with this thermo-element insufficient, which tallies with our results, as by extrapolation about  $-125^{\circ}$  may be derived from RUPERT's investigation for the temperature of the eutectic point  $\text{NH}_3 \cdot \text{H}_2\text{O} + \text{H}_2\text{O} + \text{L}$ , whereas this point lies certainly  $24^{\circ}$  higher according to Fig. 1.

Leaving the region of concentration 30—40% out of account, the agreement between RUPERT's results and ours is fairly satisfactory. If we compare the principal points, we get what follows:

Observer	NH <sub>3</sub>	2NH <sub>3</sub> .H <sub>2</sub> O	NH <sub>3</sub> .H <sub>2</sub> O
RUPERT.	- 78.°0	- 79.°0	- 79.°3
SMITS, POSTMA	- 77.°6	- 78.°8	- 79.°0

Observer	Eutecticum	Concentration	Temperature
RUPERT.	NH <sub>3</sub> + 2NH <sub>3</sub> .H <sub>2</sub> O + L	81.2 mol % NH <sub>3</sub>	- 94.°0
S. P.	" " "	81.5 " "	- 92.5°
RUPERT.	2NH <sub>3</sub> .H <sub>2</sub> O + NH <sub>3</sub> .H <sub>2</sub> O + L	57.9 " "	- 87.0
S. P.	" " "	58.5 " "	- 85.9°
"	NH <sub>3</sub> .H <sub>2</sub> O + H <sub>2</sub> O + L	not determined by RUPERT	
"	" " "	34.7 mol. % NH <sub>3</sub>	- 100.3°

It is at once apparent from the determination of the melting-point diagram that the two chemical compounds, one with 2 mol. of NH<sub>3</sub> to 1 mol. of H<sub>2</sub>O, and the other with 1 mol. of NH<sub>3</sub> to 1 mol. of H<sub>2</sub>O are already considerably dissociated in liquid state at the temperature of solidification.

#### *Boiling-point lines.*

After certainty had been obtained in the way described here about the existence of two solid compounds between NH<sub>3</sub> and H<sub>2</sub>O, it was of importance to examine whether the existence of these compounds in the liquid state would also follow from the boiling-point lines observed at different pressures. These determinations, which were carried out with an apparatus as was used by Dr. DE LEEUW<sup>1)</sup>, yielded the result that there was no indication to be perceived that could point to the existence of compounds in the liquid. Hence it followed from this that at the observed boiling temperature the dissociation was already too strong, and that the investigation has therefore to be continued at still lower pressures.

As the dynamic method is attended with all kinds of difficulties at low pressure, it was desirable to apply the static and not the dynamic method in the continuation of this investigation, and determine the vapour pressure line of different mixtures of definite concentration, from which the boiling-point lines and the *p-x*-lines

<sup>1)</sup> Z.f. phys. Chem. 77, 284 (1911).

might then be derived. This investigation, in which also the mixtures which had previously been investigated dynamically were verified, yielded the following result.

The following mixtures were examined.

88,0 mol. % $\text{NH}_3$	54,7 mol. % $\text{NH}_3$
84,1 " " "	51,5 " " "
77,8 " " "	39,7 " " "
74,6 " " "	35,9 " " "
69,5 " " "	32,7 " " "
66,3 " " "	25,6 " " "
62,7 " " "	

the results of which are expressed in fig. 2.

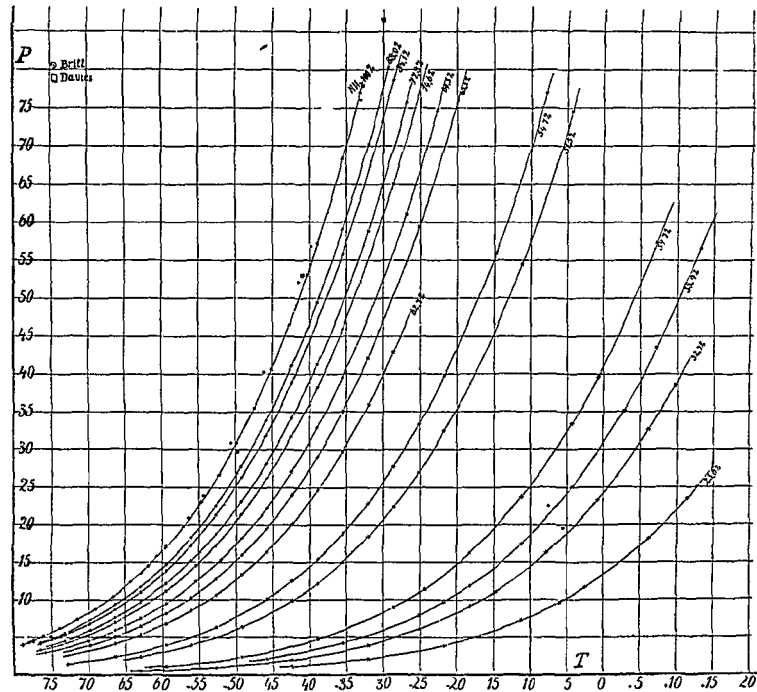


Fig. 2.

These vapour pressure lines enable us to read the corresponding boiling temperature for a definite pressure (see table I), hence to indicate the boiling-point lines, and that with an accuracy down to tenths of degrees, and it is also possible to indicate the vapour tension of different mixtures for a definite temperature (see table II), hence to find the  $(p_x)_T$ -lines with an accuracy of  $\pm 0,5$  m.m. Hg.

Fig. 3 contains the boiling-point curves, from which it appears

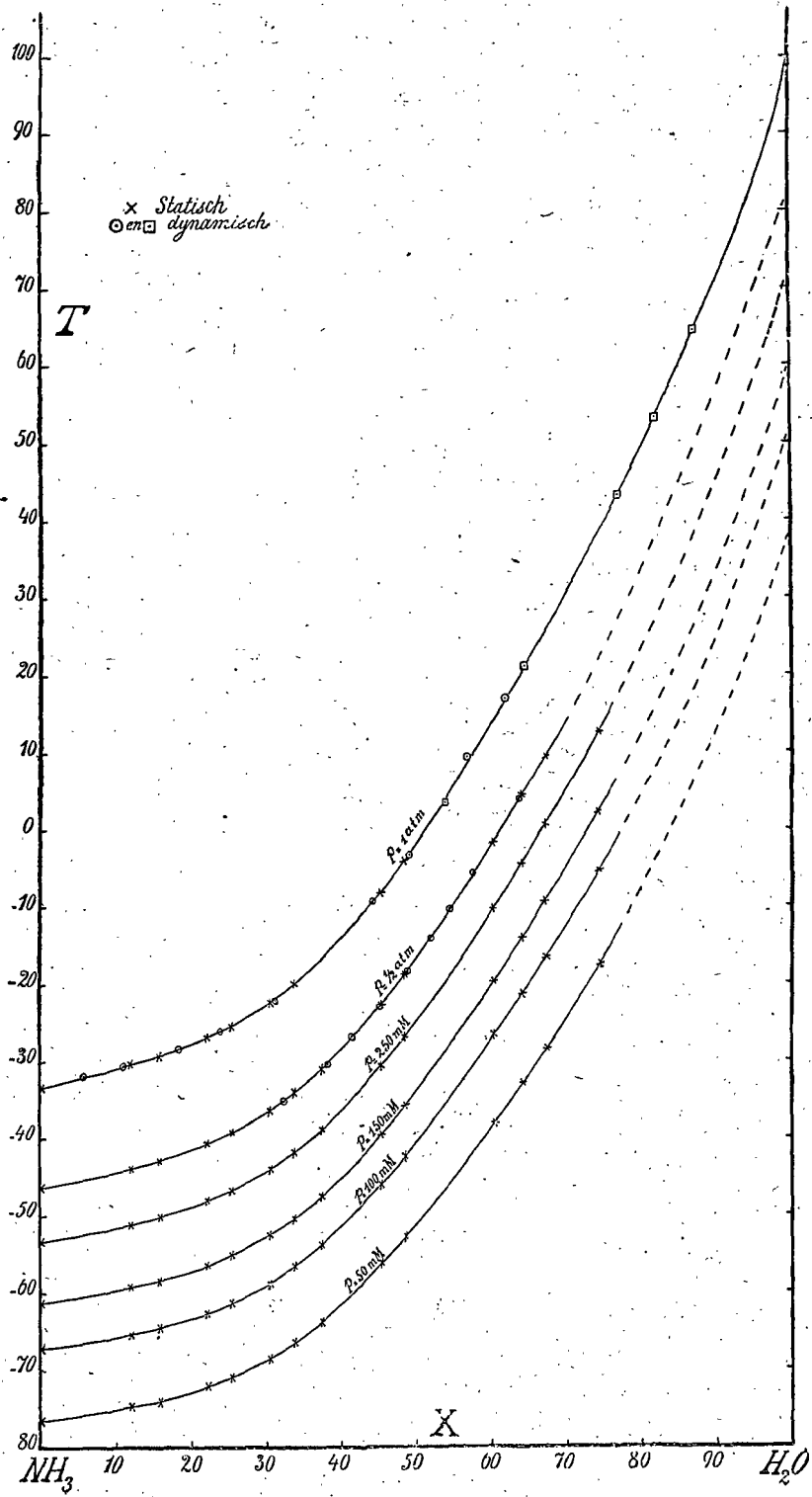


Fig. 3.



T A B L E I.  
T-X- or boiling-point lines for different pressures.

mol. % NH <sub>3</sub>	p = 50 mm.	p = 100 mm.	p = 150 mm.	p = 250 mm.	p = 380 mm.	p = 760 mm.
100	- 76.6	- 67.2	- 61.4	- 53.3 <sup>5</sup>	- 46.3	- 33.4
88.0	- 74.6	- 65.3	- 59.1 <sup>5</sup>	- 51.1	- 43.8	- 30.4
84.1	- 74.1	- 64.3 <sup>5</sup>	- 58.3	- 50.1	- 42.8	- 29.3
77.8	- 72.0	- 62.5	- 56.3	- 47.9	- 40.5	- 26.8
74.6	- 70.8 <sup>5</sup>	- 61.1	- 54.9	- 46.6	- 39.1	- 25.4
69.5	- 68.6	- 58.7	- 52.4	- 43.8	- 36.3	- 22.3
66.3	- 66.4	- 56.4	- 50.2	- 41.7	- 34.0	- 19.9
62.7	- 63.6	- 53.6	- 47.2 <sup>5</sup>	- 38.6	- 30.9	- 8.1
54.7	- 55.9 <sup>5</sup>	- 45.9 <sup>5</sup>	- 39.3	- 30.5	- 22.6	- 3.9
51.5	- 52.5	- 42.1	- 35.6	- 26.6	- 18.6	-
39.7	- 38.0	- 26.7	- 19.6 <sup>5</sup>	- 10.2	- 1.6	-
35.9	- 32.7	- 21.3	- 14.0	- 4.4	+ 4.4	-
32.7	- 28.3 <sup>5</sup>	- 16.6	- 9.2 <sup>5</sup>	+ 0.6 <sup>5</sup>	+ 9.4	-
25.6	- 17.2 <sup>5</sup>	- 5.3	+ 2.4	+ 12.7 <sup>5</sup>	-	-

T A B L E II.  
p-X-lines for different temperatures.

	t = -70°	t = -65°	t = -55°	t = -45°	t = -35°	t = -30°	t = -25°
mol. % NH <sub>3</sub>	p in cm.Hg.	p	p	p	p	p	p
100	8.2 <sup>5</sup>	11.7 <sup>5</sup>	22.6	40.9 <sup>5</sup>	69.9 <sup>5</sup>	-	-
88.0	7.2	10.2	19.6	35.5	60.6	77.4	-
84.1	6.7	9.6	18.5	33.4	57.3	73.6	-
77.8	5.8	8.4	16.2	29.5	50.5	65.0	-
74.6	5.3	7.7	14.9	27.4	47.2	61.0	77.4
69.5	4.5 <sup>5</sup>	6.5	12.7	23.3	40.7	52.5	66.8
66.3	3.8	5.5	11.0	20.5	36.0	46.9	59.7
62.7	3.1	4.5 <sup>5</sup>	9.2	17.2 <sup>5</sup>	30.5 <sup>5</sup>	39.9	-
54.7	1.7	2.5	5.4	10.6	19.4	25.7	33.5 <sup>5</sup>
51.5	± 1.3	1.9 <sup>5</sup>	4.2	8.3	15.5	20.7	27.1 <sup>5</sup>
39.7	-	0.8 <sup>5</sup>	1.4	3.0 <sup>5</sup>	6.1	8.3	11.0
35.9	-	-	± 1.1	2.1 <sup>5</sup>	4.3 <sup>5</sup>	5.9	7.9 <sup>5</sup>
32.7	-	0.4	0.8	1.6	3.1 <sup>5</sup>	4.5	6.1 <sup>5</sup>
25.6	-	-	-	0.9	1.6 <sup>5</sup>	2.3	3.1

that even that corresponding to a pressure of 50 m.m. Hg. does not reveal anything about the existence of compounds in the liquid phase; there is nothing to be detected here of a constriction at the place of the compounds, as was found by Dr. ATEN<sup>1)</sup> in his investiga-

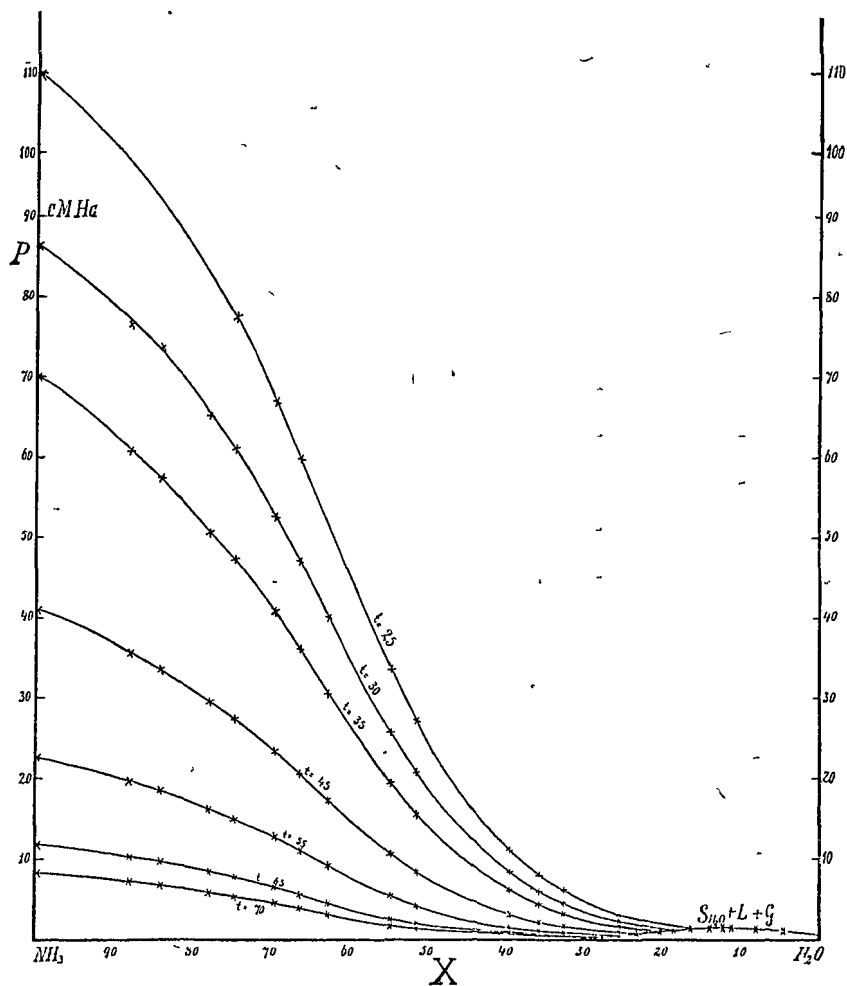


Fig. 4.

tion of the system sulphur-chlorine, and by Dr. DE LEEUW<sup>2)</sup> in the system aldehyde-alcohol.

Still more interesting is the consideration of the liquid lines of the  $(p,x)T$ -sections, which are represented in fig. 4 for the temperatures  $-25^{\circ}$ ,  $-30^{\circ}$ ,  $-35^{\circ}$ ,  $-45^{\circ}$ ,  $-55^{\circ}$ ,  $-65^{\circ}$ , and  $-70^{\circ}$ .<sup>3)</sup>

<sup>1)</sup> Z. f. phys. Chem. 54, 55, (1906).

<sup>2)</sup> loc. cit.

<sup>3)</sup> The vapour phases of the mixtures need not be investigated, as it appeared from a preliminary investigation that they practically consisted only of  $\text{NH}_3$  at the examined temperatures, as was indeed to be expected a priori.

We see that at all the temperatures mentioned here these liquid lines exhibit the type of negative liquid lines<sup>1)</sup>, as was met with by KONNSTAMM and VAN DALFSEN<sup>2)</sup> for the system ether-chloroform, and by GERLACH<sup>3)</sup> for water and glycerin, while as BAKHUIS ROOZEBOOM remarked, such a line may also be derived from the investigation carried out by SCHREINEMAKERS<sup>4)</sup> for the system acetone-phenol.

Nor do liquid lines of the  $(p,x)T$ -sections give the least indication of the existence of compounds in the liquid phase, and it is most remarkable that this even applies to the liquid lines corresponding to a temperature of  $-70^{\circ}$ , so only  $9^{\circ}$  above the temperature at which the compounds separate out of the liquid; an indubitable proof therefore that the compounds found undergo a dissociation in the liquid, much greater than would have been expected.

To complete the investigation the most important lines of the  $PT$ -projection of the spacial figure were also determined, the result of which is expressed in fig. 5, in which the three-phase lines of the

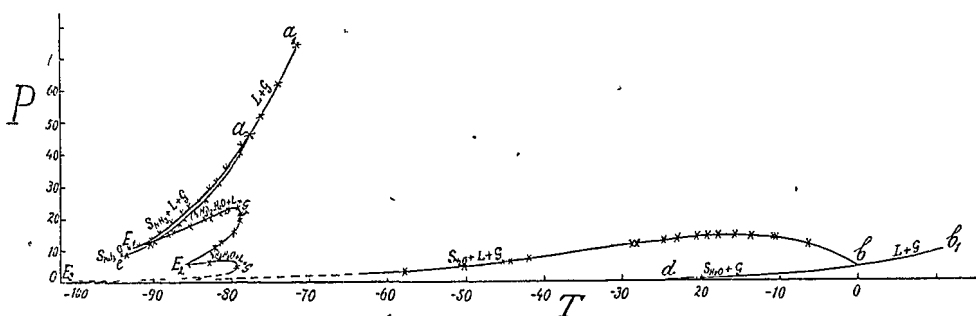


Fig. 5.

two compounds are very apparent. The difference in triple point pressure of the two compounds amounts to  $\pm 17$  m.m. Hg.

Finally also the plaitpoint curve was partially determined; as was to be expected this curve does not present any particularity either.

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*Amsterdam, May, 1914.*

1) BAKHUIS ROOZEBOOM. Die Heter. Gleichgew. II 40 (1904).

2) Verslagen d. Kon. Akad. v. Wet. 1901, 156.

3) Z. f. anal. Chem. 24, 106 (1885).

4) Z. f. phys. Chem. 39, 500 (1902).