

That is, that the velocity of precipitation for the same energy, applied to the particle, would be 20,000 times as great for smokes as for sols. This confirms the experimental evidence of the very slow precipitation.

Summary

The author has investigated the effect of high potentials upon colloidal suspensions in non-conducting liquids. There has been no precipitation detected in the range $10^4 - 2 \times 10^5$ volts, either alternating or direct current.

It is shown that the rate of precipitation would be 1/20000 of that for smoke for the same energy applied to the particle.

The author wishes to acknowledge his gratitude to Mr. William Haggenbotham for the valuable assistance rendered him in the course of the investigation.

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THE EQUILIBRIUM IN LIQUID MIXTURES OF AMMONIA AND XYLENE

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Introduction

Franklin and Kraus have observed that mixtures of ammonia and *meta*-xylene have an upper critical end-point¹ a little below room temperatures. Since the vapor-pressure curves of only a few such systems have been studied thus far,² it appeared worth while to investigate this system in some detail. In as much as the vapor pressure of xylene is low compared with that of ammonia, the total-pressure curves will differ little from the partial-pressure curves.

In the present investigation the vapor pressure of various liquid mixtures has been determined together with the composition of the liquid phases of the monovariant system. The latter data were determined in a separate series of experiments.

The critical end-point was determined in a special experiment by direct observation of the temperature at which the two phases become identical. For this purpose ammonia and *meta*xylene were sealed in a heavy walled

¹ This is sometimes called the critical point of solution. Since such a point also occurs in the diphasic system, it appears preferable to designate the critical point of the three-phase system as critical end-point, as has been suggested by Büchner.

² The literature relating to systems of this type has been collected by Büchner in Part 2, Vol. II, of Roozeboom's "Die Heterogenen Gleichgewichte vom Standpunkte der Phasenlehre," and detailed references may accordingly be omitted here.

glass tube provided with an electromagnetic stirrer. This tube was placed in a bath, contained in a Dewar tube, the temperature of which was allowed to rise slowly. Keeping the mixture vigorously stirred, the temperature was noted at which the two-phase system disappeared. The mean value so found for the critical end-point was 14.7° .

The Vapor Pressure of Liquid Mixtures of Ammonia and Xylene

Apparatus.—The boiling point of the *metaxylene* used in this work was found to be close to 139.2° , the value given in Landolt-Börnstein's Tables of Physico-chemical Constants for the boiling point of pure *m*-xylene. The ammonia was drawn from a container in which it had been purified by the method given by Franklin and Kraus.³ The arrangement of the apparatus used to measure the total pressure of the vapor of mixtures of liquid ammonia and liquid xylene is shown in Fig. 1.

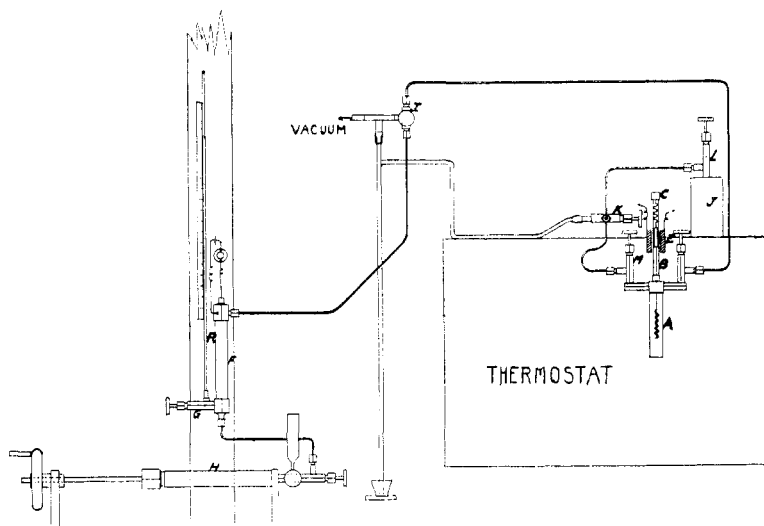


Fig. 1.—The apparatus employed in determining the vapor pressure of the monovariant system.

All parts of the apparatus which were under pressure were constructed of metal, with the exception of the mercury column *R*, which was made of glass tubing of 1 mm. thickness and 4 mm. internal diameter.

The liquid mixture was contained in a thin walled steel tube *A* of 2.75 cm. internal diameter and 15 cm. length. This tube was suspended in a thermostat containing kerosene which was vigorously stirred and whose temperature could readily be controlled within 0.01° . The total volume of the liquid mixture in Tube *A* varied from 30 cc. to 70 cc., depending on the composition. A brass tube, *B*, 12 mm. o. d. by 9 mm. i. d., and 20 cm. long, was screwed and soldered to *A*. A steel core, having a diameter of 8 mm. and a length of 7.5 cm. was supported in the bore of the brass tube by a steel piano wire spring of No. 31 B. and S. gage. This spring was fastened to the brass cap *C* which was

³ Franklin and Kraus, *Am. Chem. J.*, **23**, 284 (1900).

screwed into a conical seat on the top of the tube *A*. A plunger stirrer was suspended from the steel core by means of a heavy steel wire. The core was actuated by means of a solenoid *E* in which the current was interrupted once per second by means of a motor driven contact breaker. The degree of stirring could be regulated by adjusting the position of the solenoid along the axis of the brass tube and by resistance placed in the solenoid circuit.

Connection was made with the manometer *R* by means of a mercury reservoir *F* of thin walled steel tubing of 27 mm. i. d. and 17.5 cm. length. To its ends were welded 2 short pieces of hexagonal steel which were machined to take the various connections. Connection with the mercury column was made through the valve *G*. The column had a height of 7.2 meters. A plug carrying an insulated platinum contact point was screwed into the top of *F*. By means of this contact point, which projected into a small opening near the top of the mercury reservoir, the level of the mercury could be maintained at a fixed point with ease and precision. The position of the platinum point was transferred to a point on a steel tape suspended alongside the manometer column. Contact of the mercury with the platinum point was indicated by means of a small electric lamp. The amount of mercury in the reservoir was regulated by means of the mercury displacement piston *H*.

Connection between the tube *A*, containing the liquid ammonia-liquid xylene, and the mercury reservoir *F*, was made by means of a small bore steel tube as shown. This capillary steel tube connection was provided with a valve at *I*, by means of which the space above the mercury in the reservoir and the tube *F* and in the connecting tube could be evacuated.

The ammonia supply was contained in a light steel cylinder *J*. The steel capillary tube connecting this container and the tube *A* could be evacuated at will through the valve *K*. The desired quantity of ammonia was distilled from the container *J* into the tube *A* on opening valves *L* and *M*. During the distillation, the temperature of the thermostat was maintained near 8°, while the ammonia container was slightly warmed by resting it on a small electrically heated plate. The quantity of ammonia, which distilled into *A*, was obtained by difference in the weight of the container before and after the distillation.

The description of the method of determining the total vapor pressure of a mixture of liquid xylene and liquid ammonia by means of this apparatus follows.

Experimental Method.—For a mixture of a desired composition, the proper amount of xylene was introduced into *A* through *B* by means of a weight pipet having a long stem. *B* was then closed by Cap *C*, and *A* was evacuated. The desired quantity of ammonia was next distilled into *A* from *J* in the manner described above. The plunger stirring the liquid in *A* was then set in motion and the temperature of the bath was brought to the value desired.

The valve *G* connecting the mercury column and the mercury reservoir was then cautiously opened and the column allowed to adjust itself to the pressure in the apparatus, after which mercury was forced into the reservoir by means of the displacement piston *H* until contact was made with the platinum point. The position of the top of the mercury column was read on a graduated steel tape suspended with its zero point near the top of the column. As soon as the position of the meniscus of the mercury

column became constant, two readings were made at intervals of 10 minutes. The height of the column of mercury was given by the difference in reading of the position of the platinum point and the position of the top of the mercury column. The temperature of the column was obtained from thermometers placed at 120cm. intervals along its height. The barometric height and the temperatures were read for every measurement of the height of the manometer column, and the temperature of the room in the immediate neighborhood of the apparatus was noted. The temperature of the thermostat was then changed to the one next desired and the procedure for measuring the pressure, as just described, was repeated.

In general, for a given composition, the run was started at 8° and measurements of the pressure were made at 8° , 10° , 12° , 14° , 15° , 17° and 20° . In some cases, for a mixture of given composition, the pressure measurements were repeated at the various temperatures as the temperature was varied from 8° to 20° and back from 20° to 8° by the intervals given above. The agreement of the measurements in any such case was found to lie well within the limits of error involved in other parts of the experimental work.

Experimental Results.—In Table I are given in detail the data as obtained for a complete run at some one composition. In Table II are

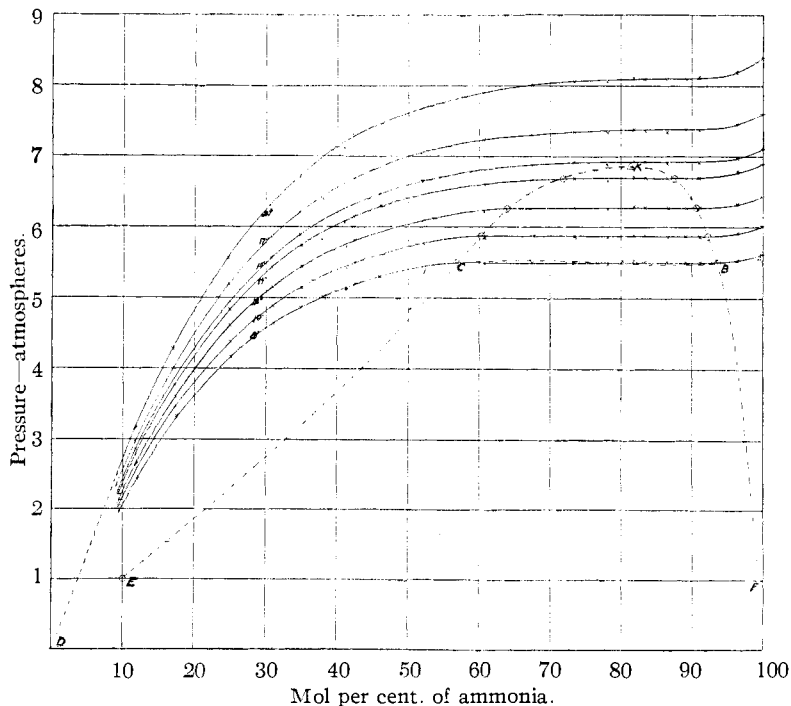


Fig. 2.—Isotherms of the mixtures.

given the values of temperature, pressure, and mean composition for all experiments which were considered satisfactory. It was necessary to correct the total composition of the liquid ammonia-xylene mixtures for the amount of ammonia in the vapor above the liquid in *A* and in the tube connecting this reservoir with *F*. The volume, the pressure and the temperature of the vapor filling this space were in all cases known, and from these data the weight of ammonia in the vapor space was calculated, assuming the laws of perfect gases to hold. While this is far from true for ammonia⁴ at these high pressures, yet the error introduced was negligible, since the correction for ammonia in the vapor was in any case small compared with the total amount of ammonia present. This correction has been applied to the compositions given in Table II.

The temperatures given in Tables I, II and IV are subject to the corrections indicated in Table III, which were obtained by comparing the laboratory thermometer used in this investigation with a thermometer standardized by the Reichsanstalt.

TABLE I
DETAILED DATA FOR A RUN

Run No. 6. Position of platinum point (transferred to steel tape), 22.917 ft.

Temperature of Thermostat ^a ° C.	Position of top of mercury column on steel tape	Height of mercury column Cm.	Average temp. of mercury column ° C.	Height of mercury column corrected for temp. ^b	Barometer corrected for temp. Cm.	Pressure of mixed xylene-ammonia vapors	
	Ft.			Cm.		Cm.	Cm.
8	20.375	77.48	23	77.19	72.89	150.08	1.975
10	20.167	83.82	25	83.49	72.92	156.41	2.058
12	19.962	90.07	25	89.71	72.98	162.69	2.141
14	19.750	96.53	26	96.11	72.97	169.08	2.224
15	19.641	99.85	26	99.43	72.97	172.40	2.268
17	19.416	106.70	26	106.25	72.98	179.23	2.358
20	19.078	117.00	26	116.52	72.99	189.51	2.493

^a Temperature subject to corrections given in Table III.

^b Corrections obtained from "Physikalische-Chemische Tabellen" by Landolt-Börnstein.

In Fig. 2 the pressures given in Table II are plotted as ordinates against the temperatures as abscissas. The horizontal portions of the isotherms represent the mean composition of the mixture for which 2 liquid phases are present. The end-points of the horizontal portions give the composition of the 2 liquid phases in equilibrium with each other. These points, at which the isotherms become horizontal, can be estimated only roughly from the plots. As it was desirable to know the composition of the 2 liquid phases somewhat more accurately, a separate set of experiments was carried out for their determination.

⁴ Lange, *Z. angew. Chem.*, 1903, pp. 511-13.

TABLE II

VAPOR PRESSURE AND MEAN COMPOSITION OF MIXTURES AT DIFFERENT TEMPERATURES

Temperature of thermostat ^a ° C.	Pressure of mixed xylene-ammonia vapors in atm.		Composition of the liquid phase Mol. per cent. ammonia		Pressure of mixed xylene-ammonia vapors in atm.		Composition of the liquid phase Mol. per cent. ammonia		Pressure of mixed xylene-ammonia vapors in atm.		Composition of the liquid phase Mol. per cent. ammonia	
	Run 4				Run 5				Run 6			
8	4.64	31.0			3.32	17.5			1.97	9.5		
10	4.89	30.9			3.47	17.4			2.06	9.5		
12	5.15	30.9			3.59	17.3			2.14	9.5		
14	5.43	30.8			3.76	17.3			2.22	9.4		
15	5.56	30.8			3.85	17.2			2.27	9.4		
17	5.86	30.8			4.01	17.2			2.36	9.3		
20	6.30	30.7			4.27	17.1			2.49	9.3		
	Run 8				Run 9				Run 11			
8	2.46	12.0			4.16	25.2			4.87	35.2		
10	2.57	11.9			4.37	25.1			5.14	35.1		
12	2.67	11.9			4.60	25.0			5.43	35.0		
14	2.79	11.8			4.83	25.0			5.73	35.0		
15	2.85	11.8			4.94	25.0			5.88	34.9		
17	2.97	11.8			5.19	24.9			6.20	34.8		
20	3.15	11.7			5.56	24.8			6.70	34.8		
	Run 12				Run 13				Run 14			
8	5.01	38.1			5.18	42.6			5.29	46.1		
10	5.31	38.1			5.49	42.5				
12	5.61	38.0			5.81	42.5				
14	5.92	37.9			6.14	42.3			6.30	46.1		
15	6.10	37.9			6.31	42.2			6.46	45.9		
17	6.40	38.0			6.68	42.4				
20	6.93	37.9			7.31	42.2				
	Run 15				Run 16				Run 17			
8	5.42	50.1			5.43	54.2			5.48	64.6		
10	5.70	50.2				
	Run 18				Run 19				Run 20			
8	5.48	78.1			5.50	86.5			5.51	89.1		
10	5.86	78.1			5.87	86.5			5.88	89.1		
12	6.25	78.1			6.28	86.6			6.29	89.1		
14	6.66	78.1			6.70	86.6			6.70	89.1		
15	6.89	78.0			6.91	86.5			6.93	89.1		
17	7.34	78.0			7.36	86.4			7.39	89.1		
20	8.06	78.0			8.10	86.4			8.10	89.1		
	Run 21				Run 22				Run 23			
8	5.50	91.2			5.54	96.4			5.62	Pure ammonia		
10	5.86	91.1			5.92	96.3			6.02	Pure ammonia		
12	6.28	91.1			6.33	96.3			6.44	Pure ammonia		
14	6.70	91.0			6.79	96.3			6.90	Pure ammonia		
15	6.92	91.0			6.98	96.3			7.11	Pure ammonia		
17	7.39	90.9			7.46	96.3			7.60	Pure ammonia		
20	8.13	90.8			8.19	96.3			8.39	Pure ammonia		

	Run 24		Run 26		Run 28	
8	5.60	98.7	5.50	95.1	5.37	50.2
10	6.00	98.7	5.88	95.0
12	6.41	98.7	6.30	95.0
14	6.86	98.7	6.73	95.0
15	7.09	98.7	6.95	95.0
17	7.56	98.7	7.41	95.0
20	8.33	98.7	8.18	95.0
	Run 30		Run 31		Run 32	
8	5.12	41.3	5.39	52.3	5.47	60.8
10	5.42	41.3	5.74	52.3	5.84	60.8
12	5.71	41.6	6.09	52.1	6.22	60.7
14	6.06	41.1	6.46	52.1	6.61	60.7
15	6.24	41.1	6.65	52.1	6.82	60.7
17	6.58	41.1	7.05	51.9	7.24	60.6
20	7.13	40.9	7.68	51.9	7.91	60.5
	Run 33		Run 34		Run 35	
8	5.49	67.5	5.50	73.4	5.53	80.2
10	5.86	67.4	5.88	73.4
12	6.26	67.4	6.28	73.4
14	6.67	67.4	6.69	73.4
15	6.88	67.3	6.91	73.4
17	7.31	67.3	7.35	73.4
20	8.01	67.3	8.06	73.4
	Run 36		Run 37			
8	5.53	81.8	5.51	83.4		
10	5.89	81.8	5.89	83.4		
12	6.30	81.8	6.28	83.4		
14	6.72	81.8	6.70	83.4		
15	6.94	81.8	6.92	83.4		
17	7.39	81.8	7.37	83.4		
20	8.12	81.8	8.10	83.4		

^a All temperatures given in Table II are subject to the corrections given in Table III.

TABLE III
THERMOMETER CORRECTIONS

Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.	Reading on laboratory thermometer °C.	Reading on Reichsanstalt's thermometer °C.
8	7.83	15	14.79
10	9.82	17	16.79
12	11.81	20	19.80
14	13.79

Composition of the Liquid Phases

Apparatus.—In Fig. 3 is shown the apparatus by means of which the composition of the 2 liquid phases was determined. In a preliminary experiment, the relative volumes of the 2 phases were determined by observations made on mixtures contained in a glass tube of uniform diameter. The mean composition of the liquid mixture used in this preliminary experiment corresponded to that at the critical point, *K*, which was esti-

mated from the plot shown in Fig. 2. The relative volumes of the 2 layers in the glass tube changed only a few per cent. for a temperature change from 8° to 14.7° , the temperature of the critical end-point. With this knowledge of the volumes occupied by the 2 phases of a mixture of known mean composition, the apparatus shown in Fig. 3 was designed. The volumes of the chambers *A*, *B* and *C* were so proportioned that, when in an upright position, the surface separating the two liquid layers should always come within the mid section *B* for temperatures from 8° to 14° .

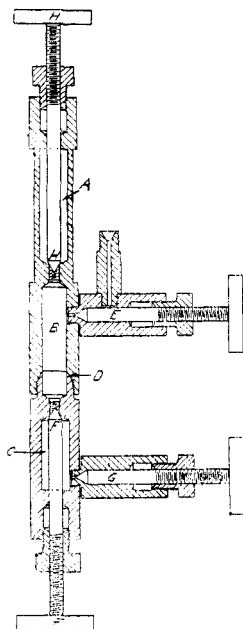


Fig. 3.—Apparatus employed in determining the composition of the liquid phases.

Procedure.—The procedure adopted in making a determination of the composition of the two liquid phases at a given temperature is as follows. The desired quantity of xylene was run into Chamber *C* from a weight pipet. The two parts of the apparatus were then screwed together at the conical joint *D*, and the whole was then placed in the thermostat in an upright position with Chamber *C* at the bottom. The outlet valve *E* was connected by means of a steel tube to the valve *K*, shown in Fig. 1. After evacuation, the desired quantity of ammonia was distilled into the apparatus. The quantity of ammonia introduced was obtained by difference in the weight of the container. Valve *E* was then closed and the whole apparatus was shaken at brief intervals, for a period of half an hour. The apparatus was then allowed to remain at rest for 10 or 15 minutes to allow thorough separation of the layers. Valve *F* was then closed, thus sealing a portion of the lower, heavier layer in Chamber *C*. A valve shown at *G* was next opened to allow for the expansion of the liquid due to temperature rise when the apparatus was removed from the bath. The valve *H* was then closed, sealing a portion of the upper, lighter layer in the chamber *A*. The apparatus was then removed from the bath, the portion in the mid section *B* was discarded through valve *E*, after which the two parts of the apparatus were separated at the conical joint *D*. Each portion of the apparatus was weighed. The ammonia in *A* and *C* was determined by running these portions into known quantities of standard sulfuric acid and titrating back with sodium hydroxide. The empty parts of the apparatus were then again weighed, and the weight of the sample of the liquid layer was obtained by difference.

Experimental Results.—The following are the data in detail as obtained in one of these determinations.

EXPERIMENT 6 AT 12°

Wt. of part of apparatus containing upper portion of xylene-ammonia mixture.....	481.630 g.
Wt. of apparatus empty.....	480.326 g.
Wt. of sample of xylene-ammonia.....	1.304 g.
Vol. of 0.953 N H ₂ SO ₄ neutralized by xylene-ammonia sample.....	49.89 cc.
Ammonia in sample.....	0.04760 mols \approx 0.810 g.
Xylene in sample.....	0.494 g. \approx 0.00467 mols
Mol per cent. of ammonia.....	90.3
Wt. of part of apparatus containing lower portion of xylene-ammonia mixture.....	429.648 g.
Wt. of apparatus empty.....	427.585 g.
Wt. of sample of xylene-ammonia.....	2.063 g.
Vol. of 0.953 N H ₂ SO ₄ neutralized by xylene-ammonia sample.....	27.27 cc.
Ammonia in sample.....	0.0260 mols \approx 0.442 g.
Xylene in sample.....	1.621 g. \approx 0.0153 mols
Mol per cent. of ammonia.....	63.0

In Table IV are given the results of the determinations of the composition at 8°, 10°, 12° and 14°. In Fig. 2, these values of the composition are represented on their respective isotherms as points surrounded with circles.

TABLE IV
COMPOSITION OF THE TWO LIQUID PHASES AT DIFFERENT TEMPERATURES

Run	Temp. ° C.	NH ₃ in upper layer %	NH ₃ in lower layer %
12	8	93.7	56.5
13	8	93.4	56.8
14	8	93.4	56.8
3	10	92.0	60.5
4	10	92.4	60.3
5	10	91.7	59.5
15	10	92.3	60.4
6	12	90.3	63.0
7	12	90.3	64.0
11	12	90.9	64.3
8	14	87.2	..
9	14	87.2	71.8
10	14	88.1	71.8
Av.	8	93.6	56.7
Av.	10	92.2	60.4
Av.	12	90.5	63.8
Av.	14	87.5	71.8

The composition of the two liquid phases was determined at the boiling point of liquid ammonia at atmospheric pressure by means of another apparatus. In this experiment a known weight of xylene was run into a glass tube which was provided with a stirrer and which was immersed

in liquid ammonia contained in a Dewar flask. After exhausting, ammonia was distilled into the tube until 2 phases appeared, the liquid being vigorously stirred in the meantime. The amount of ammonia distilled over was determined by the change in the weight of the supply container. By this means the composition of the solution rich in xylene was determined.

To obtain the composition of the phase rich in ammonia, the above procedure was repeated, but with a small amount of xylene present at the beginning. The point was noted at which the xylene phase disappeared. From the known weights of xylene and ammonia present, the composition of the phase rich in ammonia was thus found.

It was difficult to determine accurately the appearance of a second phase or the disappearance of the first phase, and the results obtained in this part of the work may be in error by several per cent. The values found were 10.0 mol per cent. of ammonia for the phase rich in xylene, and 0.56 mol per cent. of xylene in the phase rich in ammonia.

The broken line curve shown in Fig. 2, passing through the circles on the isotherms, represents the composition of the liquid phases in equilibrium with each other.

Discussion

The form of the pressure-concentration isotherms shown in Fig. 2 places the system ammonia:*metaxylene* among Büchner's first type,⁵ in which the pressure of the 3-phase system lies intermediate between that of the pure components. In general, it has been found that liquid pairs having relatively high boiling points fall within this class, while liquid pairs whose boiling points are comparable fall within the class in which the pressure of the 3-phase system is higher than that of the components.

Büchner has found, as a result of an examination of a large number of systems of this type, that a temperature difference of at least 100° must exist between the boiling points of the two compounds, in order that they should fall within this class. There are, however, several exceptions to this rule. Büchner finds also that the ratio of the critical temperatures of the pairs which belong to this group has a value equal to, or greater than, 1.4. The system ammonia:xylene fulfils both these conditions, the difference in the boiling points being 172.7°, while the ratio of the critical temperatures is 1.41.

Considering the isotherms, the behavior of the mixtures of ammonia and xylene is such as might be expected. At temperatures below the critical end-point, the isotherms appear very much flattened at compositions approaching those of the 2 liquid phases. So, also, above the critical point, the isotherms at compositions in the neighborhood of the critical composition are comparatively flat. This system differs from other systems

⁵ Ref. 2, p. 34.

most largely, perhaps, in that the critical region is relatively contracted on one side of the figure. Whereas in many cases the critical composition lies in the neighborhood of 50% of the 2 components, in this system the critical composition has a value of approximately 82 mol per cent. of ammonia. As may be seen from Fig. 2, the composition of the 2 liquid phases diverges largely at lower temperatures, so that at the boiling point of liquid ammonia the phase rich in xylene contains only 10 mol per cent. of ammonia while that rich in ammonia contains only 0.56 mol per cent. of xylene. From the form of the curve, it may be inferred that this system will not exhibit a lower critical end-point. In any case, the freezing point of ammonia is reached at a temperature of approximately -76° , and a solid phase thus intervenes. It is doubtful, however, whether this system may be looked upon as having a lower critical end-point, even in the metastable regions.

Very striking is the large deviation of the pressure curves, which in this case are practically identical with the partial pressure curves of ammonia, from Raoult's law at low concentrations of xylene. It is theoretically necessary that, at the ammonia axis, the pressure curves shall become tangent to the straight line joining the pressure of this component with the origin on the opposite side of the diagram. It is evident, from the form of the curves, that the deviations from Raoult's law must be large even at relatively low concentrations. There is thus an intimate relation between the deviations from Raoult's law, that is to say, the deviations of a real system from that of an ideal one, and the appearance of new phases in the system. Our knowledge of the fundamental causes leading to a separation of a system into 2 phases is as yet too limited to enable us to interpret the phenomena observed, but it is clear, even now, that the appearance of new phases involves appreciable deviations from the laws of ideal systems. The greater the difference in the physical properties and constitution of the components in a mixture, the lower is the concentration at which the deviations from ideal systems reach appreciable values; and the lower is the concentration of the second component at which a new phase may appear. This is strikingly illustrated in the case of the system sodium: liquid ammonia, in which a critical phase appears having a composition of approximately 97 mol per cent. of ammonia.⁶ This corresponds to a concentration a little above normal.

It follows from the theory of liquid mixtures that the isotherms in the homogeneous regions are two branches of a continuous curve, which represents the pressure of a homogeneous system over the complete concentration range. Between the compositions of the 2 liquid phases, however, the homogeneous states are metastable and unstable, and are therefore only realizable in part, excepting on the critical isotherm. It has not

⁶ KRAUS, THIS JOURNAL, 29, 1557 (1907). Ruff and Zedner, *Ber.*, 41, 1948 (1908).

been found possible thus far to evolve a theory of mixtures sufficiently general in nature to include the case of systems in which one or both of the components are abnormal liquids. It is clear, however, that the theoretical isotherm must exhibit a maximum and a minimum in this region. In the figure, the broken line connecting the points B and C indicates such a form of the curve. It may be inferred, since the isotherms immediately above the critical end-point as well as in the homogeneous regions adjacent to the 3-phase equilibrium are comparatively flat, that the theoretical isotherm throughout the metastable and unstable regions will be comparatively flat.

Summary

1. The total vapor pressure of liquid mixtures of ammonia and *meta*-xylene has been determined for the entire range of compositions at temperatures of 8°, 10°, 12°, 14°, 15°, 17° and 20°. Mixtures of liquid ammonia and *meta*xylene exhibit a critical end-point at 14.7° at a pressure of 6.85 atmospheres and a composition of 81.4 mol per cent. of ammonia.

2. The composition of the liquid phases in equilibrium with each other in the 3-phase system has been determined at the temperatures given above and at -33.5°. At lower temperatures the percentage of ammonia in the phase rich in xylene decreases very markedly with the temperature.

3. The significance of the results obtained is briefly discussed.

WORCESTER, MASSACHUSETTS

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THE COMPOSITION AND CRYSTAL STRUCTURE OF NICKEL NITRATE HEXAMMONIATE

BY RALPH W. G. WYCKOFF¹

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1. Introduction

When an excess of ammonia is added to a concentrated solution of nickel nitrate in water, faintly blue isotropic octahedra are obtained to which have been assigned the composition $\text{Ni}(\text{NO}_3)_2 \cdot 4\text{NH}_3 \cdot 1$ (or 2) H_2O . By the slow cooling of a solution of appropriate concentration, large and perfect crystals of this salt are readily obtained. These crystals, however, decompose rapidly at room temperature, so that diffraction measurements were possible only after covering the crystal with a protecting coating of wax.

Comparison reflection spectra prepared in the usual manner² from a

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² Wyckoff, *THIS JOURNAL*, **42**, 1100 (1920).