Phase Behavior in the Nitrogen-Ammonia System

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Until the present investigation was undertaken, data which established satisfactorily the composition of the gas phase of heterogeneous mixtures of nitrogen and ammonia did not appear to be available. Such measurements were made, therefore, at temperatures between 40° and 250° F. and pressures as high as 4500 p.s.i.

The volumetric and phase behavior of nitrogen and of ammonia has been studied in sufficient detail for the purposes of an investigation of phase behavior in the nitrogen-ammonia system. A detailed study was made of the volumetric behavior of nitrogen in the gas phase (*8–10*). The volumetric and phase behavior of ammonia has been described (*4–6*), and the results are available also in tabular form (*3*). The solubility of nitrogen in ammonia was carefully investigated as part of a general study of the volumetric behavior of the nitrogen-ammonia system in the liquid phase (*13*); for this binary system, the data establish with reasonable accuracy the composition of the bubble point liquid as a function of pressure and temperature.

EQUIPMENT AND METHODS

A detailed description of the equipment used for this investigation is available (*12*). The sample of ammonia and nitrogen was confined over mercury in a stainless steel vessel provided with a mechanical agitator driven through a stainless steel wall by a rotating electromagnet. The assembly was placed within an agitated oil bath, the temperature of which was controlled by an electronic modulating circuit (*11*). Known quantities of mercury were added or withdrawn from the pressure vessel, thus permitting the total volume of the vessel available to the mixture of nitrogen and ammonia to be established with an uncertainty of the order of 0.25%.

The temperature of the system was measured with a platinum resistance thermometer of the conventional strain-free type (*7*). This thermometer was compared with a similar instrument calibrated by the National Bureau of Standards. Apparently, the temperature of the sample was known within 0.02° F. of the international platinum scale (*1*).

Pressure was determined with a balance (*12*) which was calibrated against the vapor pressure of carbon dioxide (*2*). Experience with the instrument indicates that the pressure of the system was established within 0.03% or 0.2 p.s.i., whichever was the larger measure of uncertainty.

The sample from the gas phase of the heterogeneous mixture of nitrogen and ammonia was withdrawn under isobaric-isothermal conditions after initial attainment of equilibrium. The composition of the sample was determined by measurement of its specific weight at known pressures and temperatures in the vicinity of atmospheric pressure and ambient temperature. The variation in specific weight with respect to composition of the gas phase near atmospheric pressure and ambient temperature was determined by preparing a series of samples of known composition and determining their specific weight. The deviations from ideal solution were small but systematic. Minor corrections for variations in pressure from sample to sample were made on the assumption that the measured deviations from ideal solution were independent of pressure.

The compositions of a number of samples were determined by a partial condensation technique. Satisfactory agreement between the results from the two methods of determining the composition was realized.

MATERIALS

The nitrogen used in this investigation was obtained from commercial sources and was reported to contain not more than 0.00004 mole fraction impurities. It was prepared for this study by passage through a condenser which was maintained at the temperature of liquid nitrogen. The ammonia was purchased as the anhydrous material and was dried by contact with anhydrous calcium sulfate. It was found that the vapor pressure of the ammonia varied with quality less than 0.02 p.s.i. at a constant temperature of 100° F. On the basis of these findings it was estimated that the ammonia contained less than 0.002 mole fraction impurities.

EXPERIMENTAL RESULTS

Experimental data concerning the composition of the gas phase withdrawn from heterogeneous mixtures of nitrogen and ammonia are given in Table I. The data are shown in Figure 1 upon a pressure-composition diagram. Compositions of the bubble point liquid as established from data given by Wiebe and Gaddy (*13*) are included in Figure 1. The measurements of Wiebe and Gaddy were not carried out at the temperatures covered in this investigation, so that in order to obtain the curves representing the composition of bubble point liquid shown in Figure 1, their experimental data were interpolated with respect to temperature.

The data of Figure 1 were smoothed with respect to pressure and temperature, and values of the mole fraction of nitrogen in the liquid and gas phases are recorded in Table II. Table II also includes values of an equilibrium ratio defined by

$$K_k = y_k/x_k \tag{1}$$

where y_k represents the mole fraction of component k in the gas

Table I. Experimental Measurements in the Gas Phase of the Nitrogen-Ammonia System

Pressure, P.S.I.	Compn., Mole Fraction Nitrogen	Pressure, P.S.I.	Compn., Mole Fraction Nitrogen
40° F.		160° F.	
142.12	0.4758	552.97	0.0819
236.21	0.6741	660.06	0.1811
288.77	0.7248	1021.61	0.4097
499.51	0.8315	1503.39	0.5360
776.29	0.8784	1783.91	0.5788
1308.68	0.9197	1947.25	0.5998
1993.60	0.9387	2508.88	0.6391
2934.75	0.9395	2908.66	0.6500
		2917.36	0.6553
100° F.		2993.96	0.6590
327.42	0.3259	2994.94	0.6537
393.37	0.4140	3446.23	0.6752
611.22	0.6022	3834.18	0.6866
949.24	0.7088	4473.32	0.6922
1007.03	0.7188	220° F.	
1348.16	0.7758		
1505.2	0.7851	1553.55	0.2094
1901.78	0.8115	2419.59	0.3272
1992.33	0.8142	2962.81	0.3535
2439.06	0.8417	3636.80	0.3565
3090.49	0.8479	4014.75	0.3603
3886.60	0.8635	4550.58	0.3103
		250° F.	
		1466.51	0.0422
		1761.17	0.0965
		2099.05	0.1358
		2300.68	0.1401
		2492.69	0.1323

Table II. Composition of the Coexisting Liquid and Gas Phases in the Nitrogen-Ammonia System

Pressure, P.S.I.	Composition Mole Fraction Nitrogen		Equilibrium Ratio	
	Dew Point	Bubble Point	Nitrogen	Ammonia
		40° F.		
73.3[a]	0	0	. . .	1.000
500	0.8364	0.0021	398	0.164
1000	0.9064	0.0043	211	0.094
1500	0.9270	0.0064	145	0.0735
2000	0.9361	0.0083	113	0.0644
2500	0.9395	0.0101	93.0	0.0611
3000	0.9400	0.0117	80.3	0.0607
3500	0.9405[b]	0.0131	71.8	0.0603
4000	0.9408	0.0142	66.2	0.0601
4500	0.9410	0.0152	61.9	0.0599
5000	0.9415	0.0161	58.5	0.0594
5500	0.9420	0.0168	56.1	0.0590
6000	0.9430	0.0175	53.9	0.0580
		100° F.		
211.9[a]	0	0	. . .	1.000
500	0.5200	0.0027	193	0.481
1000	0.7180	0.0071	101	0.284
1500	0.7905	0.0113	70.0	0.212
2000	0.8275	0.0152	54.4	0.175
2500	0.8461	0.0188	45.0	0.157
3000	0.8550	0.0221	38.7	0.148
3500	0.8605	0.0251	34.3	0.143
4000	0.8635	0.0278	31.1	0.140
4500	0.8655[b]	0.0303	28.6	0.139
5000	0.8675	0.0327	26.5	0.137
5500	0.8690	0.0349	24.9	0.136
6000	0.8700	0.0369	23.6	0.135
		160° F.		
492.8[a]	0	0	. . .	1.000
500	0.0103	0.0001	93.6	0.990
1000	0.4090	0.0084	48.7	0.596
1500	0.5408	0.0162	33.4	0.467
2000	0.6055	0.0239	25.3	0.404
2500	0.6452	0.0315	20.5	0.366
3000	0.6695	0.0389	17.2	0.345
3500	0.6820	0.0463	14.7	0.333
4000	0.6885	0.0530	13.0	0.329
4500	0.6920	0.0595	11.6	0.328
5000	0.6940[b]	0.0658	10.6	0.328
5500	0.6950	0.0718	9.68	0.329
6000	0.6955	0.0777	8.95	0.330
		220° F.		
989.5[a]	0	0	. . .	1.000
1000	0.0105	0.0005	21.0	0.990
1500	0.1975	0.0163	12.1	0.816
2000	0.2850	0.0324	8.80	0.739
2500	0.3333	0.0502	6.64	0.702
3000	0.3540	0.0700	5.06	0.695
3500	0.3640	0.0944	3.86	0.702
4000	0.3628	0.1262	2.87	0.729
4500	0.3200	0.1555	2.06	0.805
	250° F.	250° F.		
1347[a]	0	0	. . .	1.000
1500	0.0510	0.0089	5.73	0.958
2000	0.1290	0.0379	3.40	0.905
2500	0.1315	0.0696	1.89	0.934

[a] Vapor pressure of ammonia.

[b] Values at this and higher pressures extrapolated from data at lower pressures.

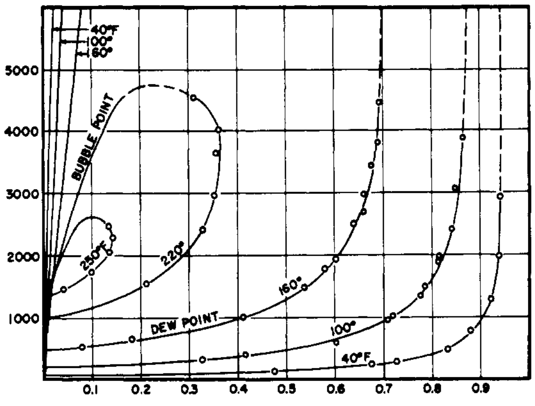

Figure 1. Pressure-composition diagram for the nitrogen-ammonia system

phase and x_k represents the mole fraction of component k in the liquid phase.

The standard deviation of the experimental data shown in Figure 1 from the smoothed values recorded in Table II was 0.005 mole fraction. In establishing the deviation no regard was taken of the different methods of analysis employed. It appears that there is no statistically significant difference between the data obtained by the partial condensation technique and those determined from specific weight measurements. The standard deviation of the experimental data of Wiebe and Gaddy from the smoothed values recorded in Table II was 0.005 mole fraction. The much smaller standard deviation of experimental data for bubble-point than for dew point is indicative of the greater difficulty experienced in establishing the composition of the gas phase in a heterogeneous mixture than in establishing the composition of the bubble point liquid. In addition, the mole fraction of nitrogen in the liquid phase is approximately one tenth that in the gas phase. This fact also would be expected to make the standard deviation of the measurements in the gas phase larger than in the liquid-phase.

The product of the pressure and equilibrium ratio, *PK*, for nitrogen and ammonia is portrayed in Figures 2 and 3, respectively. This product is utilized in order to present the data with higher precision than would be possible if the equilibrium ratio alone were employed.

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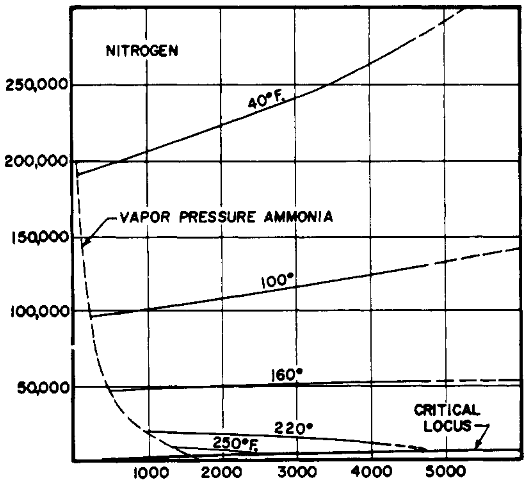

Figure 2. Equilibrium ratios for nitrogen in the nitrogen-ammonia system

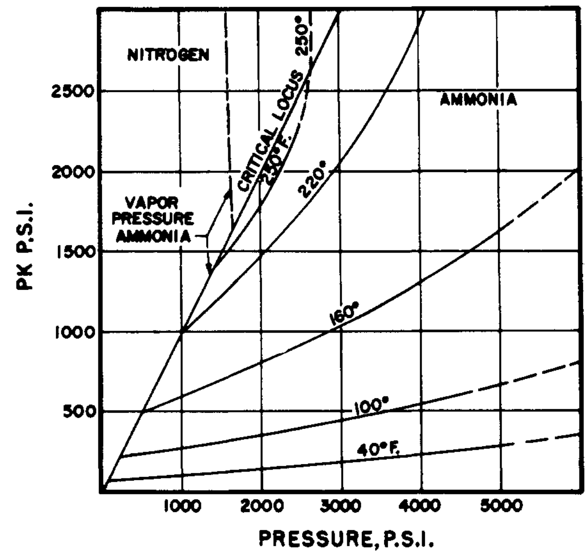

Figure 3. Equilibrium ratios for ammonia in the nitrogen-ammonia system

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Vapor Pressure and Boiling Point of Titanium Tetrachloride

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The published information on the volatility of titanium tetrachloride has consisted mainly of only three vapor pressure studies, one by Arii (*1*), one by Schäfer and Zeppernick (*14*), and one embodied in an equation by Dreisbach (*5*), based upon data obtained over the pressure range of about 100 to 760 mm. of mercury on material of high and tested purity. With widely varying degrees of precision, there are a number of measurements of the boiling point at ordinary pressures. Not all of this information is in satisfactory agreement. As a consequence, the vapor pressure has been redetermined over the temperature range from 90° to 142° C.

EXPERIMENTAL

Material. The original titanium tetrachloride was water-white and obtained from the Fisher Scientific Co., Pittsburgh, Pa., as the "purified" grade. It was further purified by fractionation in an isothermal, 1-cm. diameter, 120-cm. long column packed with 1/8-inch glass helices. A center cut was taken that came over at a constant temperature, within less than 0.1° C. Considerable care was taken to see that the titanium tetrachloride was stored and handled only in closed systems and only in glassware that had been carefully dried. However, in the transfer of the purified titanium tetrachloride from the distillation column to the vapor pressure measuring equipment, there was an instant of slight exposure to ordinary air as the 1-liter collection flask was shifted from one apparatus to another. After the transfer, to counteract any trace of water contamination, a front-end fraction was distilled off and discarded, after which a fraction was distilled into the vapor pressure measuring equipment.

Equipment and Procedure. The vapor pressures were measured in a modified Gillespie (*7*) still. The changes consisted of substituting Teflon plug-valves for the glass stopcocks, permitting the elimination of all stopcock grease; constructing the entire assembly as one closed, dry system; and using separate liquid- and vapor-sample traps similar to those of Thornton (*15*).

The pressure was regulated by a vacuum pump, a controlled leak of dry air into a surge reservoir, and a Cartesian manostat (*8*). The pressure was read to 0.3 mm. on a mercury manometer by means of a cathetometer. The readings were corrected to standard conditions, which include 0° C. The equilibrium temperature was measured in the Gillespie-type still with a 5-junction iron-constantan thermopile. It was calibrated to 0.01° C. by measuring the vapor pressure of water in the same still, with additional calibration points for the melting points of pure benzoic acid at 122.36° C. and of camphor at 172.98° C.

RESULTS AND DISCUSSION

The experimental results on the vapor pressure of titanium tetrachloride, in millimeters of mercury at 0° C., are presented in Table I, along with the predictions by Equation 1. The average deviation is 2.32 mm. of mercury.

A comparison was made between these results, those of Arii (*1*) and of Schäfer and Zeppernick (*14*), and the equation of Dreisbach (*5*). The vapor pressures of Arii were in all cases

Table I. Vapor Pressure of Titanium Tetrachloride

Temp., ° C.	Pressure, Mm. Hg (0° C.)		Temp., ° C.	Pressure, Mm. Hg (0° C.)	
	Obsd.	Calcd. (Eq. 1)		Obsd.	Calcd. (Eq. 1)
90.54	189.1	191.2	129.44	634.7	631.8
97.09	236.1	238.9	129.82	643.6	638.4
103.89	288.6	298.0	133.45	701.7	703.7
116.29	434.8	435.6	133.97	713.5	713.5
116.55	439.8	438.9	134.10	716.0	716.0
119.79	482.6	482.3	136.25	756.6	757.6
122.73	525.4	524.5	139.07	814.5	815.0
123.94	535.4	542.7	141.61	870.1	869.6
125.63	571.9	569.0			

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