Phase Relations of Binary Systems that Form Azeotropes: I. The Ammonia–*n*-Butane System

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Binary systems that form azeotropes in the critical region of the system show a wide variation in their phase behavior. As part of an investigation of the factors responsible for this variation, the *P-V-T-x* relations of the ammonia-*n*-butane system were determined at the liquid-vapor phase boundaries from near room temperature to the highest temperature and pressure at which the liquid and vapor coexist. Ammonia and *n*-butane form an azeotrope whose composition varies from 81.7 mole % ammonia at 300 lb./sq. in. to 86.3 mole % at 1295 lb./sq. in. The critical locus possesses a minimum temperature point similar to other binary systems that form azeotropes in the critical region. The experimental results support the hypothesis that binary systems that form azeotropes exhibit a characteristic pattern of *P-T-x* relations in the critical region that is distinctively different from systems that do not form azeotropes.

In a previous paper (*2*) attention was called to the progressive change in the *P-T* critical loci of binary systems composed of hydrogen sulfide and the paraffin hydrocarbons, methane, ethane, and propane. This change, which ranged from a curve with a maximum pressure point in the case of the methane-hydrogen sulfide system to one with a minimum temperature point in the case of the propane-hydrogen sulfide system, was associated with the fact that hydrogen sulfide forms an azeotrope with ethane and with propane but not with methane. It was predicted, in the case of binary systems of hydrogen sulfide-hexane and higher members of the paraffin hydrocarbon series, that the critical locus would again possess a point of maximum pressure. This has been confirmed in part by the work of Reamer, Selleck, Sage and Lacey (*6*) on the hydrogen sulfide-decane system.

It was suggested that the relations exhibited by the binaries of hydrogen sulfide and the paraffin hydrocarbon series form a characteristic pattern of relations for binary systems composed of a compound termed an azeotropic agent and members of a homologous series of compounds. Within a certain temperature range wherein azeotropes are formed, a characteristic of the agent and the homologous series, the *P-T* critical loci will progress through a series of changes from a curve with a maximum pressure point, to one with a minimum temperature point, back to one with a maximum pressure point as the critical temperature of the agent changes from less than, to greater than, the critical temperature of the compound with which it is paired. The carbon dioxide-paraffin hydrocarbon systems studied by Poettmann and Katz (*5*) were cited as exhibiting this behavior.

To obtain further data for a test of this generalization and to investigate the variation in the form that the critical locus may take, the *P-V-T-x* relations of the ammonia-*n*-butane system were determined from 32°F. and 200 lb./sq. in. to the highest temperature and pressure at which the liquid and vapor phases can coexist. In this region the two components are miscible in all proportions.

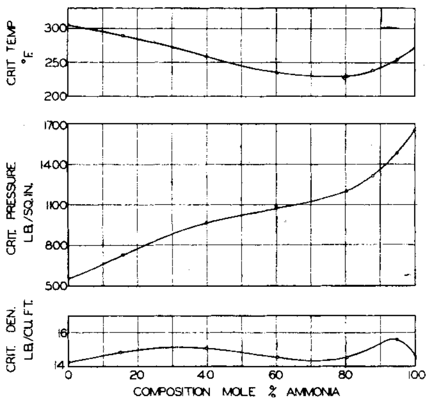

Fig. 1. Relations between composition and critical temperature, critical pressure and critical density; ammonia-*n*-butane system.

EXPERIMENTAL METHODS AND APPARATUS

The *P-V-T-x* relations of the ammonia-*n*-butane system at the liquid-vapor phase boundaries were obtained by the determination of the pressure-temperature border curves and temperature-density curves of a series of mixtures of known composition. The relations between any combination of the variables were derived by the construction of the appropriate cross plot of these curves.

The apparatus and experimental procedures for the preparation of mixtures of known composition and for the determination of the volume at different temperatures and pressures were the same as those employed in earlier investigations of a similar kind (*3*). The procedure was as follows:

A small air-free sample of the ammonia-*n*-butane mixture was confined over mercury in a thick-walled glass tube which was surrounded by a constant temperature bath. The tube was connected to a mercury-filled compressor with means for controlling the pressure on the sample. After the pressure had been properly adjusted and equilibrium attained by means of a magnetic stirrer, the volume of the sample was determined by measuring the length of the column of sample, this length having

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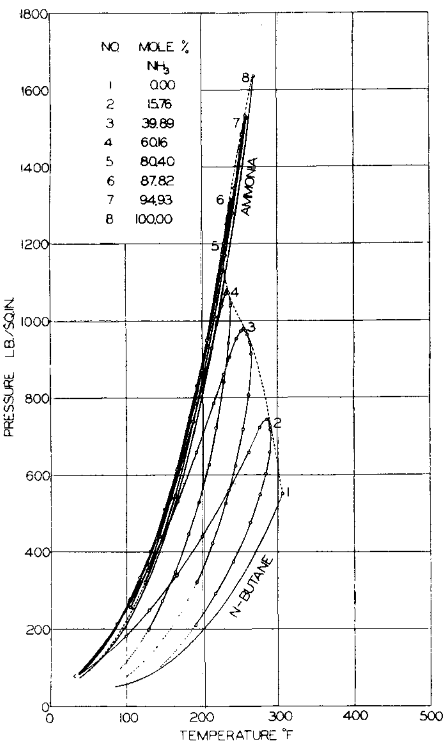

Fig. 2. The pressure-temperature-composition diagram; ammonia-n-butane system.

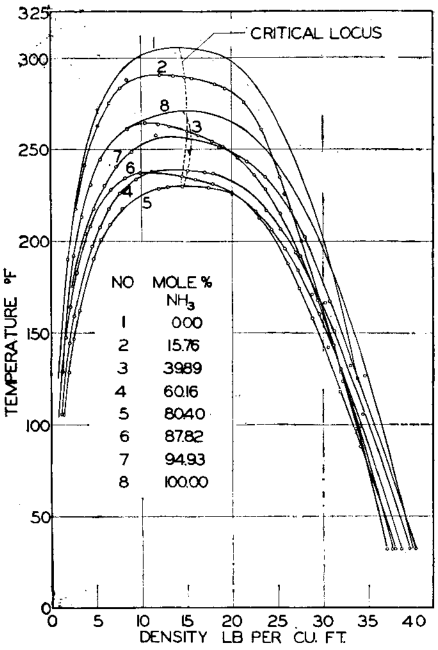

Fig. 3. The temperature-density-composition diagram; ammonia-n-butane system.

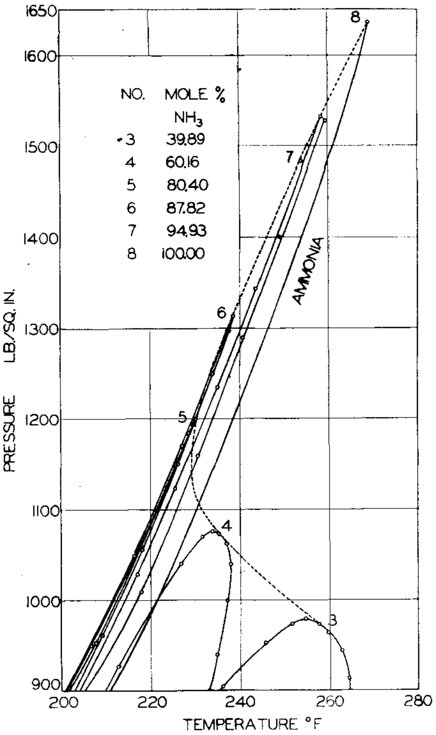

Fig. 4. Expanded P-T-x plot in the high-pressure region; ammonia-n-butane system.

been related to the volume by a prior calibration of the tube.

The temperature of the sample was measured to within 0.05°F. by means of a copper constantan thermocouple and a sensitive potentiometer. For the pressure, a dead weight gauge, similar to that previously described (*3*), was used. Its sensitivity was 0.02 lb./sq. in. The experimental tube in which the sample was confined was constructed of precision-bore capillary of approximately 2-mm. bore. It was carefully calibrated with mercury. By the use of a cathetometer, reading to 0.05-mm. and with a sample occupying a length never less than 15 mm. of the tube, the volume of the sample could be measured with a maximum error of about 0.6%. The methods employed in the calibration of the thermocouple, pressure gauge, and experimental tube have been described (*3*).

PREPARATION OF MATERIALS

The n-butane was furnished by Phillips Petroleum Company and was reported to be 99.78 ± .08 mole % n-butane. The ammonia was an anhydrous commercial sample, stated by the manufacturer to be better than 99 mole % ammonia.

Both the n-butane and ammonia were further purified by repeated distillation at low temperature and under high vacuum; the initial fraction and the residue were discarded, and the middle fraction was retained for the succeeding distillation. The deaerated n-butane and ammonia were then stored in the gaseous state by sealing them in glass ampoules (*3*).

Prior to their use, the n-butane and ammonia were tested for the presence of impurities by measuring, in the experimental apparatus, the difference between the bubble- and dew-point pressures at a constant temperature. The pressure change was 0.15 lb./sq. in. at 262.3°F. for n-butane and 1.4 lb./sq. in. for ammonia at 158.0°F.

Mixtures of ammonia and n-butane gas were prepared by first filling the experimental tube, under vacuum, with clean, freshly distilled mercury, then injecting into the tube a measured volume of each of the gases at a known temperature and pressure to make a mixture of the desired composition. The apparatus and procedure have been described (*3*). In the calculation of the amount of each gas, the deviation of the gas from the perfect gas law was taken into account. The composition arrived at in this way was accurate to within 0.05 mole %.

TABLE 1. COMPOSITION AND CRITICAL CONSTANTS OF MIXTURES OF AMMONIA AND NORMAL BUTANE

Composition mole % ammonia	Composition wt. % ammonia	Critical temperature °F.	Critical pressure lb./sq. in. abs.	Critical density lb./cu. ft.
0.00	0.00	305.40	548.9	—
15.76	5.45	289.49	725.6	14.78
39.89	16.28	259.79	963.9	15.05
60.16	30.68	235.26	1072.4	14.48
80.40	54.58	229.84	1200.0	14.50
87.82	67.87	238.51	1313.7	15.15
94.93	84.59	253.94	1484.4	15.60
100.00	100.00	269.53	1637.1	—

RESULTS AND DISCUSSION

The pressure and specific volumes of the liquid and vapor at the bubble and dew points were determined for six different mixtures of ammonia and n-butane at temperatures ranging from near the ice point to the cricondentherm of each mixture. Experimental data on the pure components were limited to the purity checks previously described, except that the critical point of ammonia was determined. For butane, the vapor pressure and orthobaric density data reported by Kay (*1*) were used, for ammonia the vapor pressure and density data given in Landolt-Bornstein (*4*). The critical constants of the mixtures are listed in Table 1, and their relation to the composition is shown by the curves in Figure 1. Likewise, the pressure-temperature and density-temperature data for the mixtures and the pure components are shown graphically by the curves in Figures 2 and 3 respectively. For some of the mixtures the bubble- and dew-point curves in the low-pressure region were extrapolated by plotting the experimental data as the logarithm of the pressure against the reciprocal of the absolute temperature and extending the straight line through the points to the desired temperature and/or pressure. This region is indicated by the broken line curves in the diagrams.

Values of the temperature and density

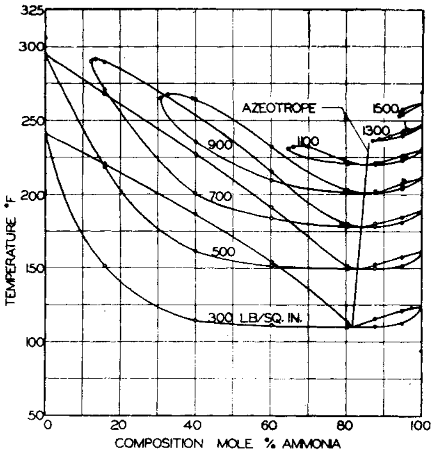

Fig. 5. Temperature-composition diagram; ammonia-*n*-butane system.

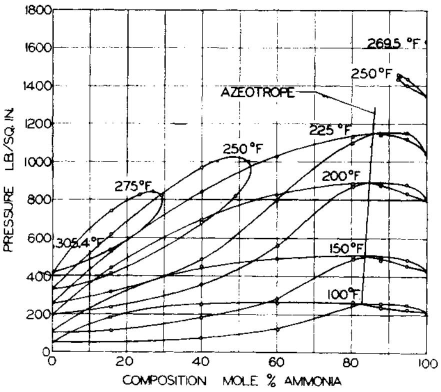

Fig. 6. Pressure-composition diagram; ammonia-*n*-butane system.

TABLE 2. TEMPERATURE-COMPOSITION RELATIONS IN *n*-BUTANE-AMMONIA SYSTEM AT CONSTANT PRESSURE

Ammonia mole %	Pressure 300 lb./sq. in.		Pressure 500 lb./sq. in.		Pressure 700 lb./sq. in.		Pressure 900 lb./sq. in.	
°F.	liquid °F.	vapor °F.	liquid °F.	vapor °F.	liquid °F.	vapor °F.	liquid °F.	vapor °F.
0	241.0	241.0	295.0	295.0	—	—		
10	171	228.5	244.0	278.1	—	—		
12.2	—	—	—	—	289.5	289.5		
13.4	—	—	—	—	280.9	297.0		
20	140.9	214.9	202.6	261.0	255.7	285.0		
30	123.5	201.0	176.1	244.4	223.2	220.4		
30.7	—	—	—	—	—	—	264.5	264.5
33.6	—	—	—	—	—	—	250.5	268.0
40	114.2	186.5	161.2	227.1	200.6	253.6	235.9	264.2
50	111.6	171.4	154.7	209.7	190.0	235.7	220.8	250.5
60	110.5	154.5	151.5	191.5	183.8	215.7	210.2	232.5
70	110.0	135.4	150.0	171.4	180.3	194.4	204.3	214.7
80	109.8	113.8	149.5	152.0	178.3	180.5	201.5	203.4
81.7a	109.8	109.8	—	—	—	—		
83.1a	—	—	149.5	149.5	—	—		
84.1a	—	—	—	—	178	178		
84.8a	—	—	—	—	—	—	201.4	201.4
90	110.7	117.5	149.8	154.0	178.7	181.2	201.5	203.3
95	—	—	151.7	157.5	181.3	184.8	204.1	207.3
100	123.5	123.5	161.0	161.0	188.5	188.5	211	211

Ammonia mole %	Pressure 1100 lb./sq. in.		Pressure 1300 lb./sq. in.		Pressure 1500 lb./sq. in.	
	liquid °F.	vapor °F.	liquid °F.	vapor °F.	liquid °F.	vapor °F.
64.4	230.7	230.7				
68	226.5	232.5				
70	225.0	232.0				
80	221.0	222.4				
85.6a	226.5	220.5				
87	—	—	236.6	236.6		
90	220.7	222.3	237.1	238.5		
94	—	—	—	—	254	254
95	223.0	220.3	239.7	242.7	—	—
96	—	—	—	—	256.0	258.7
98	—	—	—	—	258.7	260.2
100	230	230	246.5	246.5	261.2	261.2

at regular intervals of the pressure have been tabulated.*

The relations between pressure, temperature, and composition at the phase boundaries are represented by the *P-T-x* space diagram in Figure 2. Between approximately 80 mole % ammonia and pure ammonia the diagram is very narrow, and the liquid and vapor surfaces are curved and folded, a condition characteristic of a system whose components form a minimum boiling azeotrope. The nature of this portion of the diagram is more readily seen in Figure 4, which is an expanded view of the upper part of Figure 2.

The critical locus of the system possesses a point of minimum temperature. In this respect it differs from systems whose components are similar in chemical nature or whose critical temperatures are markedly different. For such systems the critical locus, in general, exhibits a point of maximum pressure.

The nonlinear relation between the density and composition is evident from an inspection of the temperature-density-composition space diagram (Figure 3). This is not surprising when one considers the difference in the chemical nature of the components.

The formation of an azeotrope with a minimum boiling temperature, which was indicated by the folding of the *P-T-x* space diagram, is clearly evident in the *T-x* and *P-x* diagrams shown respectively in Figures 5 and 6. The composition of the azeotrope is 81.7 mole % ammonia at 300 lb./sq. in., increasing to 86.3 mole % at 1295 lb./sq. in. The difference between the boiling point of the azeotrope and that of pure ammonia at 300 lb./sq. in. amounts to 13.5°F. and decreases to about 10°F. at 1295 lb./sq. in.

The effect of pressure on the vapor-liquid region is to be noted. Below 548.9 lb./sq. in. the *T-x* diagram extends from pure ammonia to pure *n*-butane; above this pressure the diagram terminates before the ordinate for pure *n*-butane is reached. For example, at 900 lb./sq. in. the *T-x* diagram terminates with a mixture of about 30.7 mole % ammonia, while at pressures above 1637 lb./sq. in. all mixtures are homogeneous regardless of the temperature. A summary of the *T-x* relations at equal intervals of the pressure is given in Table 2. These data were read from large scale plots of the curves in Figure 5.

The distribution of the components between the liquid and vapor phases at various pressures is shown by the curves in Figure 7 where the composition of the

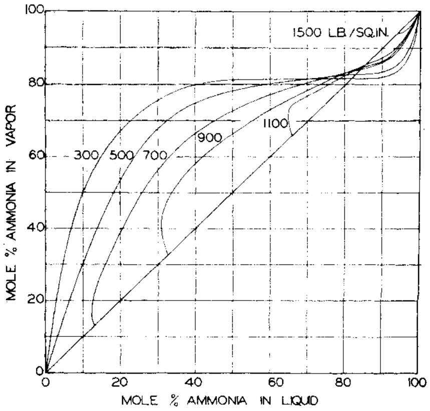

Fig. 7. Vapor-liquid composition diagram; ammonia-*n*-butane system.

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*Tabular material has been deposited as document 5718 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or $1.25 for 35-mm. microfilm.

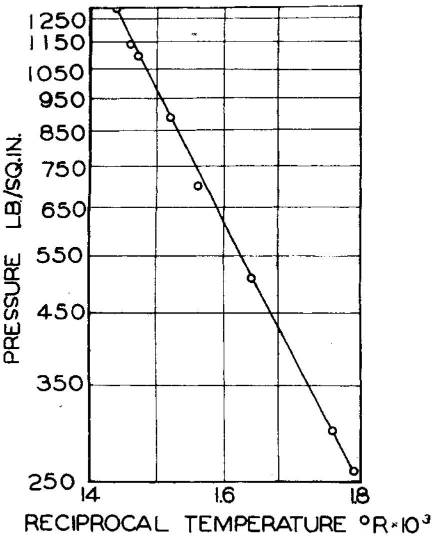

Fig. 8. Pressure-temperature relation for the ammonia-*n*-butane azeotrope.

vapor is plotted against the composition of the liquid. The existence of an azeotrope is indicated by the intersection of the curves with the diagonal where the compositions of the liquid and vapor phases are identical. With the aid of these curves, the composition of the azeotrope at different pressures (indicated in Table 2) was accurately determined.

Figure 8 shows a plot of the logarithm of the pressure vs. the reciprocal of the absolute temperature of the azeotropic point. From the linear form of the plotted curve it is evident that the relation between the pressure and temperature can be represented by the equation

$\log p = A + B/T$ as is the case for, a pure compound.

PHASE RELATIONS

The shape of the critical locus of the ammonia-*n*-butane system is in good agreement with the generalization deduced from a study of the critical loci of the carbon dioxide-hydrocarbon (*5*) and hydrogen sulfide-hydrocarbon systems. In accordance with this generalization, as the critical temperature of the component with the lower critical pressure increases relative to the critical temperature of the azeotropic agent, an inflection point develops in the critical locus near the critical point of the component with the lower critical pressure. As the difference in the critical temperatures becomes greater, the minimum critical temperature point disappears, and the inflection point gradually changes to a maximum critical-pressure point.

Since the critical temperature of *n*-butane is approximately 36°F. greater than the critical temperature of ammonia, it is to be expected that there will be an inflection point in the critical locus in the region of high butane content. The experimental results are in agreement with this prediction; as will be noted, a point of inflection occurs at about 50 mole % ammonia.

ACKNOWLEDGMENT

Grateful acknowledgment is made to Phillips Petroleum Company for furnishing the sample of *n*-butane.

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II. The Ammonia–Isooctane System

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Because of the paucity of data on the phase behavior of binary systems that form azeotropes, the *P-V-T-x* relations of the ammonia-isooctane system were determined at the liquid-vapor boundaries from room temperature to the critical temperature of isooctane. Evidence of an azeotrope existing over a very limited pressure and temperature range was obtained. The system is unique in that the critical locus contains a minimum temperature point as well as a minimum and a maximum pressure point. These relations are shown to fit a general pattern of phase relations characteristic of binary systems that form azeotropes in the critical region. This pattern serves as an aid for the qualitative prediction of the *P-T-x* relations of such systems.

According to the hypothesis proposed for the phase relations of binary systems that form azeotropes (*7*), it would be expected that the greatest diversity in phase relations would occur in systems in which the difference in the volatility of the components is large, but still within the range necessary for the formation of an azeotrope. For some systems, it seems probable that as the critical temperature of the component with the lower critical pressure increases relative to the critical temperature of the other component, a stage might be reached wherein the critical locus would exhibit a minimum and a maximum pressure point as well as a minimum temperature point. Such a system, however, has not been observed heretofore.

For systems composed of ammonia and a paraffin hydrocarbon the above relations might be expected to exist in a system composed of ammonia and a heptane or an octane. To test the hypothesis, the *P-V-T-x* relations of the ammonia-isooctane system were determined at the liquid-vapor phase boundaries from 32°F. to the critical temperature of isooctane. Below 140.3°F. the ammonia and isooctane are only partially miscible. Data were obtained in this region from which the mutual solubilities of the liquids were determined.

EXPERIMENTAL

The apparatus and procedure were similar to those employed in the study of the ammonia-*n*-butane system (*6*). The dead-weight pressure gauge, thermocouple, and experimental tube were calibrated as previously described (*7*). Pressures and temperatures were measured to within ±0.1 lb./sq. in. and 0.05°C., whereas volume measurements varied in accuracy over a wide range, depending upon the length of the tube which a particular sample occupied. Expressed in terms of density, the uncertainty in the values was somewhere between 0.0015 g./cc. for the liquid and .00015 g./cc. for the vapor samples.

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