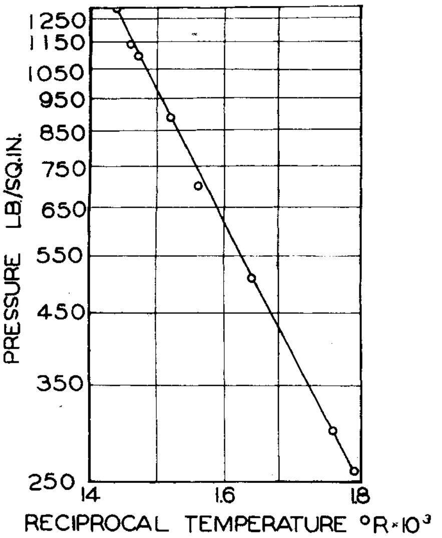

Fig. 8. Pressure-temperature relation for the ammonia-*n*-butane azeotrope.

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

WEBSTER B. KAY and F. MORGAN WARZEL
Ohio State University, Columbus, Ohio

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.

F. Morgan Warzel is with Phillips Petroleum Company, Idaho Falls, Idaho.

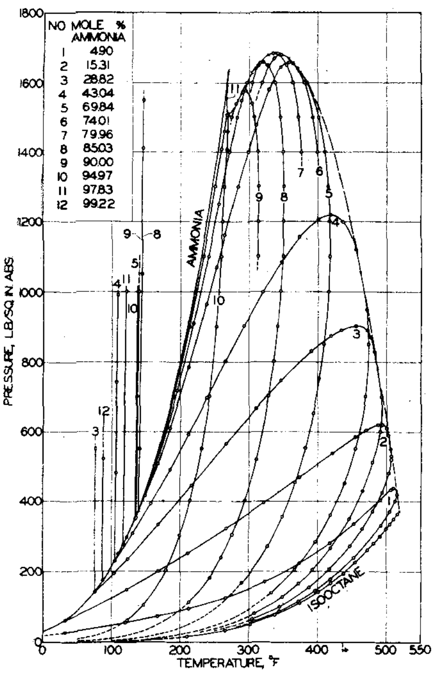

Fig. 1. Pressure-temperature diagram for ammonia-isooctane system.

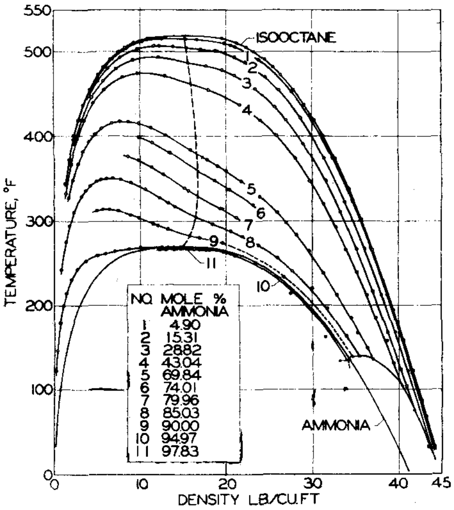

Fig. 2. Temperature-density diagram for ammonia-isooctane system.

Table 1. Composition and Critical Constants of Mixtures of Ammonia and Isooctane

	Critical constants			Max. pres. pt.		Max. temp. pts.	
mole % ammonia	pressure lb./sq. in.	temp. °F.	density lb./cu. ft.	pressure lb./sq. in.	temp. °F.	pressure lb./sq. in.	temp. °F.
0	371.9	519.22	15.2	—	—		
4.90	430.7	515.14	15.28	438	512 ± 1	424 ± 2	516
15.31	570.4	504.46	15.45	621	490 ± 1	530 ± 5	507
28.82	783.9	487.00	15.61	904	456 ± 3	670 ± 10	494
43.04	1055.3	461.98	15.91	1220	418 ± 2	830 ± 20	474
69.84	1630.5	375.55	17.23	1658	359 ± 1	1150 ± 20	418
74.01	1670.3	359.04	16.78	1681	348 ± 2	—	—
79.96	1680.1	329.05	16.68	1686	337 ± 2	—	—
85.03	1628.6	304.12	16.50	1660	320 ± 1	1280 ± 20	351
90.00	1550.3	282.51	15.74	1579	294.5	1270 ± 20	314
94.97	1514.8	268.57	14.87	1515	268.3	1508 ± 2	269.5
97.83	1557.6	266.72	13.96	1557	266.6	1558 ± 2	266.7
99.22	—	—	—	—	—	—	—
100.00	1637.1	269.53	14.76	—	—	—	—

PREPARATION OF MIXTURES

The ammonia was a sample of that purified and used in the study of the ammonia-*n*-butane system (*6*). The isooctane was from the same sample that was used for the determination of its vapor pressure and saturated liquid and vapor densities (*8*). It was furnished by Phillips Petroleum Company and was stated to be 99.87 ± 0.05 mole % isooctane. No further purification was undertaken except that possible traces of moisture were eliminated by distilling the sample in the presence of phosphorus pentoxide, into the degassing and loading train of the vapor-pressure apparatus.

Mixtures of ammonia and isooctane were prepared by loading the experimental tube with a sample of pure isooctane, calculating the weight from the measured volume and density and then adding a measured volume of ammonia gas at a known temperature and pressure to make a mixture of known concentration. The apparatus and procedure have been described in previous publications, (*4, 7*).

To determine if any decomposition of the ammonia occurred at the high temperatures to which the ammonia was subjected in the course of the measurements, a test sample of ammonia was loaded in the experimental tube and the bubble-point pressure determined at 158°F. before and after the sample was heated for about 13 hr. at 480°F. and 800 lb./sq. in. An increase of 3.7 lb./sq. in. was noted. Since 13 hr. represents the maximum period of time that any of the mixtures was heated at an elevated temperature, the error introduced into the data by the decomposition of the ammonia sample is believed to be insignificant.

RESULTS

The pressure-specific volume-temperature relations at the liquid-vapor phase boundaries of twelve different mixtures of ammonia and isooctane were determined in order to define the pressure-temperature-composition (*P-T-x*) and the temperature-density-composition (*T-p-x*) diagrams of the ammonia-isooctane system. The experimental data are represented by the curves in Figures 1 and 2, and a summary of the smoothed data at regular intervals of the pressure, read from large-scale plots of the curves was prepared.* The critical constants of the mixtures are listed separately in Table 1, and have been plotted in Figure 3 to show the relations with the composition.

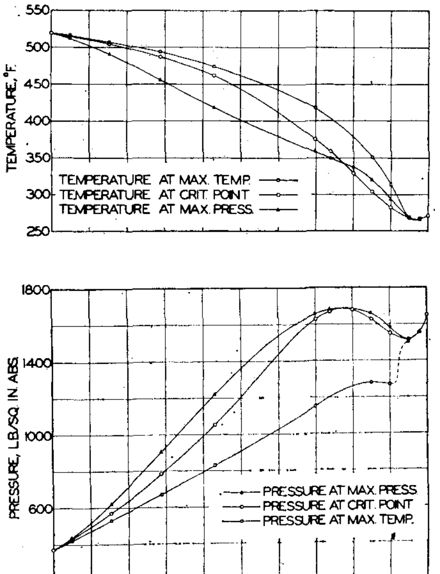

Fig. 3. Critical constants of mixtures of ammonia-isooctane system.

In the *P-T-x* space diagram, Figure 1, are shown the *P-T* border curves of the various mixtures, the critical locus, the vapor-pressure curves of the pure components, the three-phase vapor pressure curve and the curves defining the homogeneous and heterogeneous liquid regions.

As will be noted, the critical locus possesses three unique points: a minimum and a maximum pressure point and a minimum temperature point. The values of the pressure, temperature, and composition at each of the points are as follows:

Maximum pressure: 1688 ± 2 lb./sq. in. abs. at 342 ± 2°F. and 77.5 ± 1.0 mole % NH_3

Minimum pressure: 1513 ± 2 lb./sq. in. abs. at 270 ± 1°F. and 94.7 ± 0.3 mole % NH_3

Minimum temperature: 266 ± 0.7°F. at 1560 ± 10 lb./sq. in. abs. and 98.0 ± 0.5 mole % NH_3.

The critical temperature of ammonia was found to be 269.53°F. at 1637.1 lb./sq. in. abs.

The bubble-point curves of the mixtures in Figure 1 intersect the three-phase vapor pressure curve in the low temperature region. The points of intersection represent the conditions under which a liquid phase (composing the bulk of the sample and therefore having a composition very near the over-all mixture

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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.

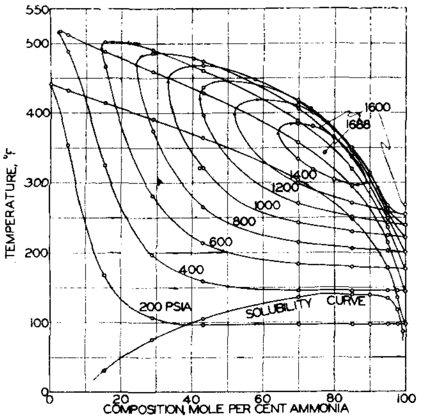

Fig. 4. Temperature-composition diagram of ammonia-isooctane system.

composition) is in equilibrium with a second liquid phase and a vapor phase. The second liquid phase and the vapor phase are present only in infinitesimal amounts. The three-phase vapor pressure curve very nearly coincides with the vapor pressure curve of ammonia, except in the region near the critical solution point, where it is situated slightly below that for ammonia (6 lb./sq. in. below, at the critical solution temperature, 140.27°F.) The fact that the three-phase curve is below rather than above the ammonia curve indicates that in this region the system is nonazeotropic.

The nearly vertical curves at the left in Figure 1, show the effect of pressure on the miscibility temperature of the various mixtures. These curves have a positive slope indicating that an increase in pressure decreases the mutual solubility of the two components over the range investigated. The experimental *P-V-T* data, including the points of intersection of the curves with the three-phase curve, are listed in Table 2.

Table 2. Pressure-Temperature-Density Relations at Miscibility Point, Ammonia-Isooctane System

Composition mole % NH_3	Pressure lb./sq. in. abs.	Temp. °F.	Density lb./cu. ft.	
28.82	141.5	75.07	41.88	SP
	551.4	76.24	41.88	L
43.04	228.9	105.10	40.43	SP
	481.8	106.30	40.29	
	741.4	107.49	40.46	
	991.8	108.55	40.58	
69.84	352.9	135.32	37.07	SP
	701.1	137.34	37.27	
	1000.8	139.12	37.38	
85.03	373.6	139.44	35.47	SP
	551.4	140.54	35.40	L
	1051.1	143.60	35.66	L
	1410.8	145.67	36.05	L
90.00	372.7	139.08	34.58	SP
	551.4	140.27	34.73	L
	1051.0	143.19	34.90	L
	1550.6	146.14	35.17	L
94.97	346.9	133.90	33.2	SP
	1000.9	137.73	33.2	L
97.83	278.0	117.39	33.85	SP
	1001.0	120.74	34.82	L
99.22	175.0	86.45	36.90	SP
	522.3	87.67	37.26	L

SP = tiny bubble of vapor + tiny drop of liquid with remainder in liquid phase.
L = tiny drop of liquid phase in presence of 2nd liquid phase.

Table 3. Temperature-Composition Relations at Constant Pressure

Mole % ammonia	Liquid °F.	Vapor °F.	Liquid °F.	Vapor °F.	Liquid °F.	Vapor °F.	Liquid °F.	Vapor °F.
	200 lb./sq. in. abs.		600 lb./sq. in. abs.		1000 lb./sq. in. abs.		1400 lb./sq. in. abs.	
0	441	441	—	—	—	—	—	—
4.90	353.7	431.6	—	—	—	—	—	—
15.31	167.6	414.0	465.6	501.9	—	—	—	—
28.82	107	391.0	281.0	490.6	—	—	—	—
43.04	96.5	364.2	214.2	460.5	320.8	467.6	—	—
69.84	96.5	302.8	183.5	387.8	242.8	416.1	298.0	410.5
74.01	—	—	—	—	—	—	—	399.4
79.96	—	—	—	—	—	—	—	376.1
85.03	96.5	248.3	179.4	319.8	229.9	346.0	271.1	349.6
90.00	—	—	—	—	—	—	—	312.5
94.97	96.5	178.6	177.3	235.2	223.8	256.3	258.8	267.0
97.83	96.5	134.9	—	—	—	—	—	—
100	96.5	96.5	176	176	221	221	254	254
	400 lb./sq. in. abs.		800 lb./sq. in. abs.		1200 lb./sq. in. abs.		1600lb./sq.in.abs.	
0	(above critical)		—	—	—	—	—	—
4.90	488.8	512.6	—	—	—	—	—	—
15.31	325.1	487.9	—	—	—	—	—	—
28.82	197.0	458.8	374.0	485.5	—	—	—	—
43.04	159.1	428.2	265.3	474.0	396.2	437.1	—	—
69.84	145.6	357.7	214.4	405.9	269.9	417.6	333.1	384.0
74.01	—	—	—	—	—	—	318.8	380.8
79.96	—	—	—	—	—	—	304.3	364.0
85.03	144.8	293.8	206.2	336.0	251.0	350.4	296.4	338.1
90.00	—	—	—	—	—	314	—	—
94.97	144.8	214.2	202.7	248.4	242.4	261.9	—	—
97.83	144.8	—	—	—	—	—	—	—
100	143.8	143.8	200.2	200.2	238.3	238.3	268	268

The data for the construction of the vapor-pressure curve of ammonia are those taken from the literature (*3*), except the critical point which was experimentally determined. The vapor pressure data of isooctane are those reported from this laboratory (*8*).

In the *T-ρ-x* diagram, Figure 2, a point of maximum critical density is to be noted for a mixture of approximately 77 mole % ammonia which is the mixture that exhibits a maximum critical pressure. There is experimental evidence (not shown) to indicate that a point of minimum critical density exists for the mixture that exhibits the minimum critical temperature of the system. The region of two liquid phases appears as an area in the lower right side of the diagram.

The relations between temperature and the composition of the coexisting liquid and vapor phases (Figure 4) were determined graphically from crossplots of Figures 1 and 2. The temperatures corresponding to the points of intersection of the constant pressure line with the bubble and dew curves of the mixtures that were studied are listed in Table 3. Below the critical pressure of isooctane, 372 lb./sq. in., the *T-x* diagram extends from pure ammonia to pure isooctane. Above this pressure the liquid-vapor region terminates before the ordinate for pure isooctane is reached. For example, at 400 lb./sq. in., the *T-x* diagram on the isooctane-rich side terminates with a mixture containing 2.2 mole % ammonia. Up to 1513 lb./sq. in., the minimum pressure on the critical locus, the liquid-vapor region is represented by a single area. At higher pressures, however, this area splits into two separate areas. Thus, at 1600 lb./sq. in. one liquid-vapor area exists in the composition range from 64.4 to 89.0 mole % ammonia, the other between 99 and 100 mole % ammonia (too small to be shown). This ammonia-rich region diminishes with increased pressure and disappears when the critical pressure of ammonia is reached, leaving a single-liquid vapor region. The latter decreases as the pressure is further increased and finally disappears at 1688 lb./sq. in. Above this pressure the system is completely homogeneous.

In the region of high concentration of ammonia at pressures of 1400 lb./sq. in. and above, the vapor-liquid composition curves approach each other and appear to coincide. Such a condition indicates the presence of an azeotrope. Unfortunately, sufficient data to establish completely the curves in this region were not obtained. However, the fact that ammonia forms azeotropes with members of the paraffin series of lower molecular weight, leads to the prediction that ammonia would form an azeotrope with isooctane, provided that the difference in volatility of the components is not too great. That this difference is within the range for the formation of an azeotrope is indicated by the existence of a point of minimum temperature on the critical locus. The latter relation is based on the observation that systems that possess a minimum temperature point in their critical locus show an azeotrope (*1, 7, 9–11*). It is estimated, therefore, that an azeotrope exists in mixtures of ammonia and isooctane between 98 and 100% ammonia at pressures above 1400 lb./sq. in.

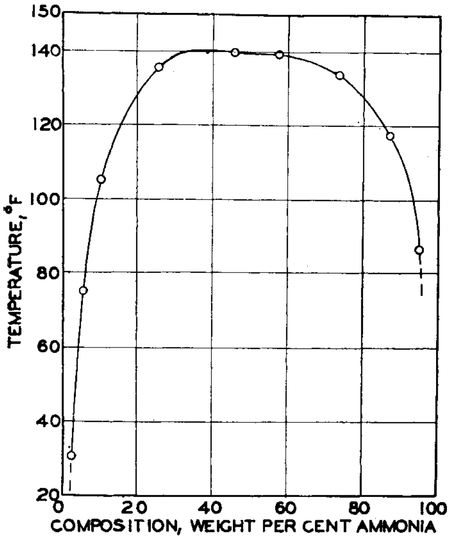

Fig. 5. Solubility curve for ammonia-isooctane at the three-phase pressure.

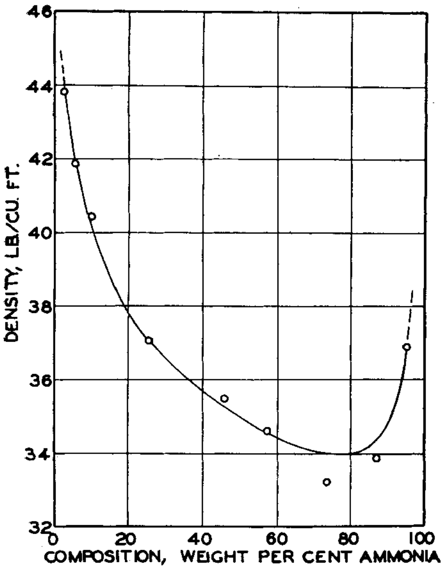

Fig. 6. Density of the saturated liquid phases in equilibrium with each other in ammonia-isooctane system.

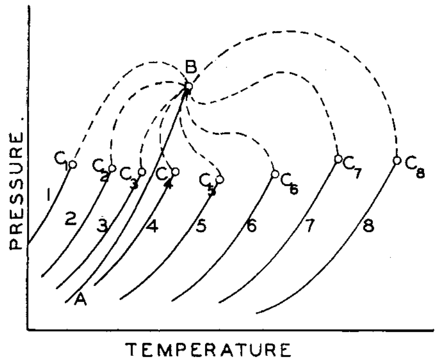

Fig. 7. Pattern of phase relations for binary systems that form azeotropes.

The solubility curve in the *T-x* diagram represents the mutual solubility of ammonia and isooctane at the 3-phase pressure. Since the effect of pressure on the solubility is very small, the variation of pressure along the curve may be ignored as far as its effect on the composition of the coexisting liquid phases is concerned. In Figure 5 the solubility is expressed in terms of weight percent. The critical solution temperature was found to be 140.27°F. and the composition 37 ± 5 wt. % ammonia (79 ± 4 mole % ammonia.) The critical solution temperature given in the literature for this system is 141.8°F. (*1*). The densities of the liquid phases as a function of the composition are given in Figure 6.

GENERAL PHASE RELATIONS WHEN AZEOTROPES ARE FORMED

The experimental data on the binary systems of ammonia with *n*-butane and with isooctane, as well as data on other systems (*5, 10*), indicate a general pattern which is illustrated schematically by the curves in Figure 7. Curves 1 through 8 represent the vapor pressure curves of similar kinds of compounds, such as members of an homologous series. Curve *A*, on the other hand, represents the vapor pressure curve of a compound whose chemical nature is sufficiently different so that it forms solutions with these compounds that deviate greatly from ideal solutions. Such mixtures are characterized by the formation of azeotropes which exist up to the critical region, provided the critical temperatures of the components do not differ greatly from each other. The broken line curves C_1B, C_2B, . . . C_8B represent the critical loci of the binary systems that *A* forms with each of the compounds 1 through 8. The curves C_1B and C_8B are those for systems whose components differ in their critical temperatures to such an extent that an azeotrope is not formed. These curves exhibit a maximum pressure point only.

For smaller differences in the critical temperatures, azeotropes are formed and the general shape of the critical locus depends to a large extent on whether the critical temperature of compound *A* is greater or less than the critical temperature of the compound with which it is mixed. When the critical temperature of *A* is greater, the locus may take the shapes illustrated by C_2B and C_3B. C_2B shows both a minimum-temperature and a maximum-pressure point whereas C_3B shows only a minimum temperature point. When the critical temperatures of both components are about the same, the locus is nearly symmetrical about a constant pressure line drawn through the minimum temperature point. As the critical temperature of the second component becomes greater than the critical temperature of the component *A*, the minimum temperature point moves toward the critical temperature of *A* and an inflection point in the curve appears near the critical point of the other component, as illustrated by curve C_5B. With a further increase in the difference between the critical temperatures, the inflection point moves toward the critical point of *A* and the locus may show minimum- and maximum-pressure points as well as a minimum-temperature point, (C_6B and C_7B), as in the case of the ammonia-isooctane system. Eventually, the difference between the critical temperatures becomes sufficiently great so that an azeotrope is not formed and the locus reverts to a simple curve with a maximum-pressure point.

These relations refer to systems in which minimum boiling azeotropes are formed. No experimental data are available on systems that form a maximum-boiling azeotrope in the critical region. However, it is presumed that the relations would be similar except that the point of minimum critical temperature would be replaced by a point of maximum critical temperature.

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