SOME PECULIARITIES IN THE P–T BORDER CURVES OF MIXTURES OF HYDROGEN AND A PETROLEUM NAPHTHA[1]

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Received March 14, 1941

The solubility of hydrogen in a volatile petroleum naphtha has been investigated over a temperature and pressure range which included the critical region of the hydrogen–naphtha mixtures. At concentrations of hydrogen below about 18 cc. (at S.T.P.) per gram of naphtha the shapes of the *P–T* border curves, derived from the solubility data, are such as to suggest the existence of a region of isobaric retrograde condensation at temperatures relatively far removed from the critical region of the mixture. Additional evidence, in support of the suggestion that this behavior is a characteristic property of a general class of mixtures composed of a liquid and a slightly soluble gas, is provided by data given in the literature on the solubility of hydrogen and nitrogen in liquid ammonia.

In the course of an investigation of the solubility of hydrogen in a volatile naphtha, the *P–T* border curves of several mixtures of the naphtha and hydrogen were determined over a temperature range which included the critical region of the mixture. Within certain limits of hydrogen concentration the shapes of these curves are such as to suggest the existence of a region of isobaric retrograde condensation at temperatures far removed from the critical region of the mixture. As far as can be learned from the literature, the existence of such a region has not been pointed out before. The present report gives a summary of the experimental results on the hydrogen–naphtha mixtures as well as a discussion of the results on other mixtures reported in the literature which appear to have similar properties.

I. EXPERIMENTAL

The apparatus and experimental procedure used for determining the *P–T* border curves of a mixture have been fully described in previous papers (2, 3).

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[1] Presented at the Symposium on Reactions and Equilibria in Chemical Systems under High Pressure, which was held under the auspices of the Division of Physical and Inorganic Chemistry at the One-hundredth Meeting of the American Chemical Society, Detroit, Michigan, September 9–13, 1940.

The naphtha was a narrow-boiling fraction composed principally of the pentanes and hexanes. Its composition as determined by distillation, as well as data on other physical properties, are given in table 1. No attempt was made to remove the air dissolved at room temperature under atmospheric pressure. The hydrogen was commercially pure, cylinder hydrogen and was used without further purification. Mixtures of the naphtha and hydrogen were prepared by first loading the experimental tube with a small sample of the naphtha, calculating its weight from its volume and density, and then injecting into it a measured amount of hydrogen gas. Succeeding mixtures were prepared by adding additional amounts of hydrogen. Details of procedure are given in the papers referred to above.

TABLE 1

Inspection data on the petroleum naphtha used in the hydrogen–naphtha mixtures

COMPOSITION		A.S.T.M. DISTILLATION		
Component	Mole per cent	Volume per cent vaporized	°C.	°F.
Isopentane	7.8	Initial	43.3	110
n-Pentane	31.3	10	47.8	118
Cyclopentane	4.8	20	48.9	120
Neohexane	1.7	30	50.0	122
2,3-Dimethylbutane	1.7	40	51.1	124
2-Methylpentane	16.8	50	53.3	128
3-Methylpentane	18.4	60	55.0	131
n-Hexane	16.8	70	56.7	134
Residue	0.7	80	59.4	139
		90	62.2	144
		Maximum	67.2	153

Density at 15.55°C. (60°F.) = 0.6597 g. per cubic centimeter.

II. RESULTS

Three mixtures containing, respectively, 7.78, 15.22, and 30.21 cc. of hydrogen (at S.T.P.) per gram of naphtha, were prepared and their border curves were determined from about 100°C. upwards through the critical region. The experimental data are given in table 2 and shown graphically by the curves in figure 1. Unfortunately, the critical points were not determined with any great accuracy. However, their approximate locations on the curves are indicated. As will be noted, a minimum point occurs in the boiling-point section of the border curve of two of the mixtures, being most prominent in the mixture of lowest hydrogen concentration.

The relation between the total pressure and the solubility of the gas at constant temperature for several temperatures was determined graphically from figure 1 and is shown by the curves in figure 2. At the lower temperatures the amount of hydrogen dissolved is directly proportional to the pressure, but as the temperature approaches the critical temperature of the naphtha (about 220°C.), a slight deviation from the linear relation occurs. These constant-temperature lines intersect each other and, when extrapolated to zero amount of hydrogen, cut the pressure axis at what corresponds to the initial vapor pressure of the air-saturated naphtha.

TABLE 2

Boiling points and dew points of mixtures of hydrogen and petroleum naphtha

COMPOSITION: CC. OF H_2 (AT S.T.P.) PER GRAM OF NAPHTHA	TEMPERATURE	PRESSURE	
		Boiling point	Dew point
	°C.	*atmospheres*	*atmospheres*
7.78	55.2	34.8	
	93.3	30.6	
	130.6	29.4	
	148.9	30.3	
	165.6	31.7	14.1
	204.4	37.8	27.4
	216.5	39.5	33.9
15.22	93.3	55.3	
	148.9	47.5	
	165.6	46.8	14.5
	184.0	47.0	20.2
	204.0	47.4	28.8
	217.7	44.4	38.2
30.21	148.9	81.5	
	165.6	76.4	15.6
	183.3	71.7	21.8
	204.4	65.1	32.1
	217.0	53.8	43.1

III. PHASE BEHAVIOR

Unfortunately, the boiling-point curves which contain minimum points (figure 1) were not determined at low temperatures, but their shape may be deduced qualitatively from a knowledge of the solubility of slightly soluble gases in liquids at low temperature. Kuenen (4), reasoning from the known behavior of mixtures, has predicted that the solubility of a slightly soluble gas in a liquid passes through a minimum value at a temperature relatively far removed from the critical point of the liquid. This prediction has been amply confirmed in the investigations of Wiebe and Gaddy (7, 8) on the solubility of hydrogen and helium in water, and of

Wiebe, Gaddy, and Heins (10) and Saddington and Krase (6) on the solubility of nitrogen in water. In view of this property, the solubility of hydrogen in naphtha may be expected to pass through a minimum at some low temperature. As a consequence, the pressure along the boiling-point curve, beginning at the minimum point, will rise at first as the temperature is decreased, pass through a maximum at the temperature of minimum solubility, and finally decrease with decreasing temperature. The complete border curve, then, must look something like that shown in figure 3. The curve *KJHAC* is the boiling-point curve which meets the dew-point curve, *LBC*, in the critical point, *C*. The dotted curves represent curves of constant relative volumes of the liquid and vapor phases in equilibrium, expressed as volume per cent of liquid. In the case of the hydrogen–naphtha mixtures these curves might be expected to be spaced as indicated by the numbers, owing to the low solubility of hydrogen.

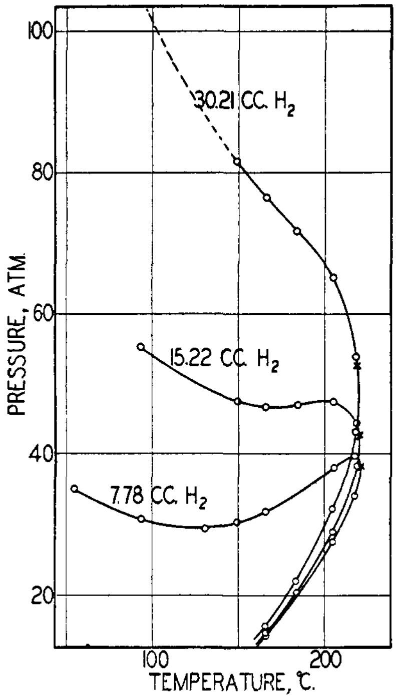

FIG. 1

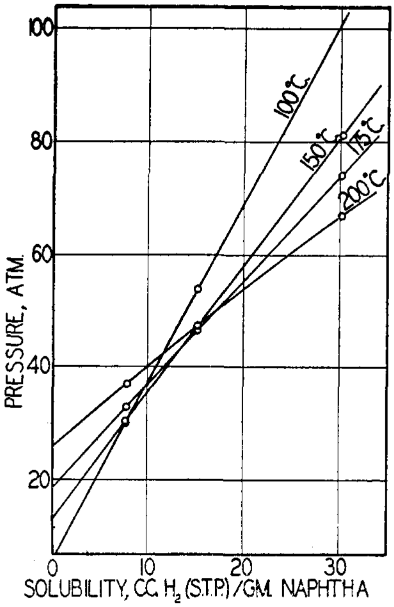

FIG. 2

FIG. 1. Border curves of hydrogen–naphtha mixtures. Composition in cubic centimeters of hydrogen (at S.T.P.) per gram of naphtha. ×, critical point.

FIG. 2. Effect of pressure on the solubility of hydrogen in naphtha

The phase behavior when the mixture is heated along the constant pressure line, $P'P''$, brings to light a certain interesting property. At low temperatures no change is observed until *D* is reached, when a bubble of vapor appears. Between *D* and *E* some of the dotted lines are cut twice, indicating that the liquid at first begins to vaporize in the normal manner with the volume of the vapor phase increasing; but as the temperature increases the vaporization comes to a halt, and condensation of the vapor begins and proceeds until it is complete at *E*. Continuing the heating, no change is observed until *F* is reached, when vaporization again begins and proceeds in a normal manner until the liquid has been completely vaporized at *G*. Over part of the path between *D* and *E* the phase behavior is the reverse of what usually occurs when a mixture is heated isobarically below its critical pressure. However, it is similar in all respects to what occurs above the critical pressure when the critical point, *C*, lies to the right of the point of maximum pressure, *A*. Likewise, it is similar to that described by Kuenen (5) when a mixture the critical point, *C*, of which lies below the point of maximum temperature, *B*, is compressed (or expanded) isothermally at a temperature between *C* and *B*. Kuenen called this isothermal process "retrograde condensation of the second kind" but did not give a name to the corresponding isobaric process. It would seem logical, there-

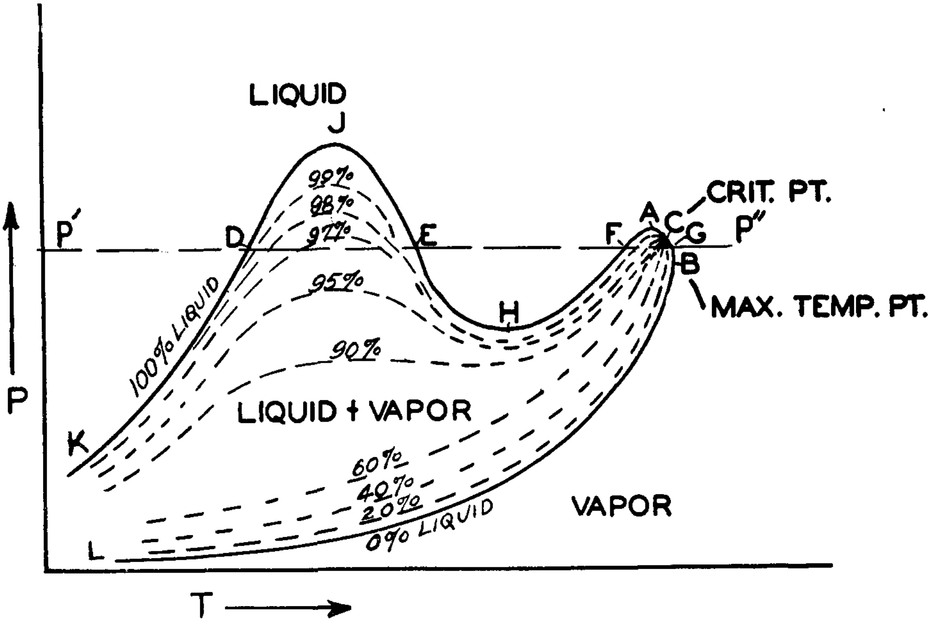

FIG. 3. *P–T* diagram illustrating the complete border curve of a mixture having a minimum point in its boiling-point curve.

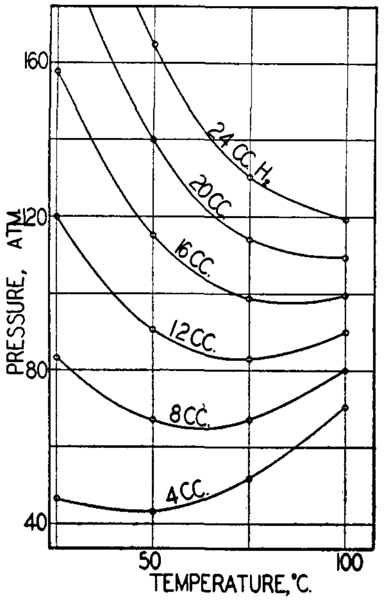

FIG. 4. Boiling-point curves of hydrogen-ammonia mixtures. Composition in cubic centimeters of hydrogen (at S.T.P.) per gram of ammonia. Data by Wiebe and Tremearne (J. Am. Chem. Soc. **56**, 2357 (1934)).

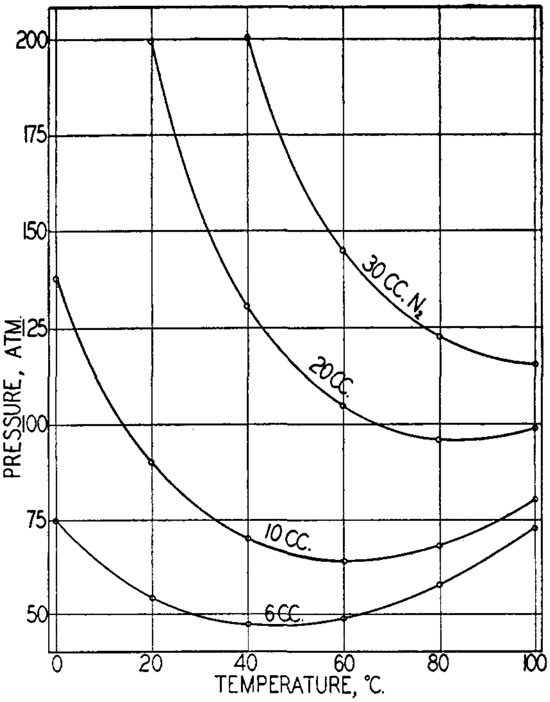

FIG. 5. Boiling-point curves of nitrogen-ammonia mixtures. Composition in cubic centimeters of nitrogen (at S.T.P.) per gram of ammonia. Data by Wiebe and Gaddy (J. Am. Chem. Soc. **59**, 1984 (1937)).

fore, to call it "isobaric retrograde condensation of the second kind" or, according to the nomenclature proposed by Katz and Kurata (1), "isobaric retrograde condensation between boiling points."

It will be noted from figure 3 that there are two *P–T* regions where isobaric retrograde condensation of the second kind occurs. One is associated with the critical region of the mixture and over the pressure range from *C* to *A*; the other, with the temperature region immediately below the point of minimum pressure, *H*, and between the maximum pressure, *J*, and a pressure somewhat below *H*.

V. OTHER MIXTURES WITH SIMILAR PROPERTIES

So far as can be determined from the literature, the existence of a minimum in the boiling-point curve has not been pointed out before. However, from the data of Wiebe and Tremearne (11) on the solubility of hydrogen in liquid ammonia and of Wiebe and Gaddy (9) on the solubility of nitrogen in liquid ammonia, boiling-point curves can be derived which show a minimum point. These curves are shown in figures 4 and 5. As in the case of hydrogen–naphtha mixtures, the minimum occurs only over a limited range of concentration from zero concentration of the gas. The temperature range of the data is too narrow to permit the derivation of the complete curves but, in general, they would be expected to be similar to that shown in figure 3.

It would seem that the phase behavior of hydrogen–naphtha, hydrogen–ammonia, and nitrogen–ammonia mixtures might be a characteristic property of a general class of mixtures composed of a liquid and a slightly soluble gas. The investigation of the solubility of such gases as hydrogen, helium, nitrogen, oxygen, and others, in a number of liquids over a wide range of temperature and pressure should prove of considerable interest in testing this generalization.

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