Phase Behavior from Enthalpy Measurements

Benzene–Ethyl Alcohol and *n*-Pentane–Ethyl Alcohol Systems

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A FLOW CALORIMETER, utilizing a double jacket of boiling Freon 11, provides a rapid means of obtaining enthalpy-pressure-temperature data. The apparatus, starting from a relatively simple model, has been developed to provide reasonably accutate thermodynamic data (*4, 5*). The procedure consists of measuring the enthalpy at different pressures along an isotherm. If the temperature is below the critical value, the data include the subcooled liquid, two-phase, and superheated vapor regions.

The isotherms show two discontinuities. Starting at a low pressure, the first represents the saturated vapor (or dew point) pressure, and the second, the saturated liquid (or bubble point) pressure. For a pure component, these two pressures are identical, and measurements at different temperatures establish the vapor pressure curve for the material. However, for mixtures, the two pressures differ, and the results at various temperatures establish the dew point and bubble point curves for the system. Thus, the phase envelopes of a mixture can be determined from enthalpy measurements. If the temperature range is large enough, the complete, *P-T* curve, including the critical point, is obtainable. If measurements are made for the same system using samples of several different compositions, critical point–composition data become available.

The systems benzene-ethyl alcohol and *n*-pentane-ethyl alcohol have been investigated in a flow calorimeter from 250° to 500° F. at pressures from 50 to 1700 p.s.i.a. The phase behavior of these systems and that of the benzene-methanol system previously studied (*4*) are reported here. Enthalpy information is presented in the following article (*7*) concerned with the thermodynamic properties of polar molecules. Systems involving relatively nonpolar and relatively polar substances, such as hydrocarbon-alcohol mixtures, are particularly interesting in that the loci of critical points show minimum pressure or minimum temperature values.

EXPERIMENTAL

A schematic diagram of the apparatus and the details of the calorimeter have been described (*4*). In brief, the enthalpy measurement was based upon weighing the amount of Freon-11 evaporated in order to reduce the sample to the reference temperature of 77° F. Because the details of the apparatus are significant primarily for the enthalpy measurements, they are not repeated here. The pertinent problem for this investigation is the location of the phase boundaries separating the liquid-two-phase-vapor regions. The points of discontinuity on the measured pressure-enthalpy isotherm were located approximately by drawing the isotherm in three sections as indicated in Figure 1. This figure shows the experimental points obtained for the 25 mole % benzene-75% ethyl alcohol system. The enthalpy values are referred to a basis of H=0 for the pure components as liquids at 77° F. The method of correcting the experimental data to this basis is described in the following article (*7*). This approximate *P-H* diagram was then cross-plotted using temperature and enthalpy and pressure and temperature as coordinates. The final location of the discontinuities was established by making the three diagrams, *P-H*, *T-H*, and *P-T*, internally consistent.

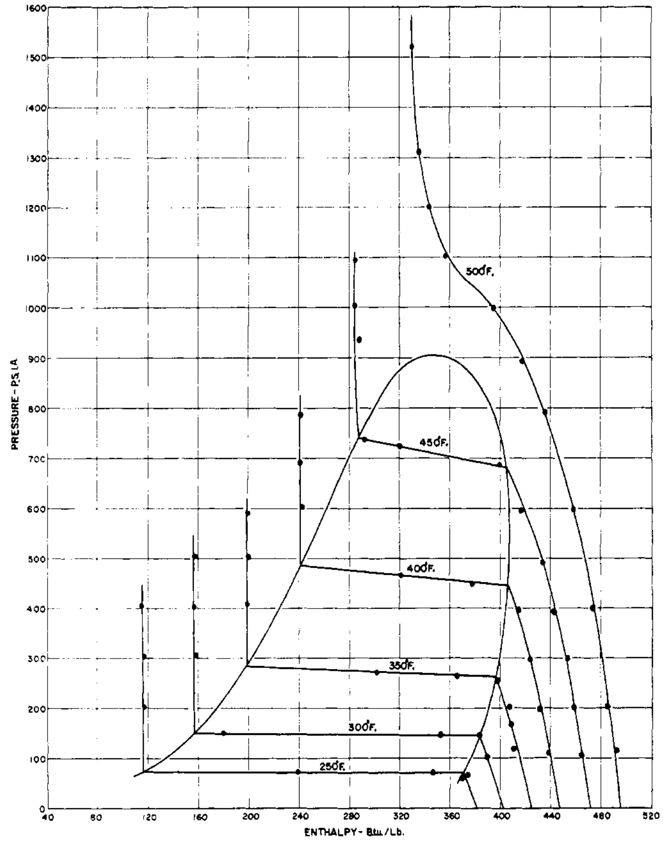

Figure 1. Pressure-enthalpy diagram
Mixture: 25 mole % benzene, 75 mole % ethyl alcohol
Datum: *H* = 0 pure liquid components at 77° F.

In the critical region, the senitivity of enthalpy to small pressure and temperature changes required additional data. These measurements were made at constant pressure at close temperature intervals. These additional results were first plotted on the temperature-enthalpy plane, and then this diagram cross-plotted to locate the *P-H* and *P-T* diagrams more firmly in the critical region.

The chemical analysis of the raw materials is as follows:

Ethyl alcohol was obtained from the Commercial Solvents Corp. (drum #386, 597, Nov. 4, 1957). The impurities were claimed to be less than 10 p.p.m. The water content was between 0.05 and 0.10 weight %.

Benzene from Merck and Co. conformed to ACS reagent grade specifications and was thiophene free. The boiling range was between 79.5° and 80.0° C.

n-Pentane was obtained from the Phillips Petroleum Co., who supplied the following analysis: *n*-pentane, 99.2; 2-methylbutane, 0.6; and cyclopentane, 0.2 mole %.

Methanol for the methanol-benzene results (*4*) was supplied by the Commerical Solvents Corp. and was said to have a minimum purity of 99.85 weight %. The maximum boiling range was 1.5° C. and included 64.5° C.

PRECISION OF DATA

It is difficult to estimate the precision of the dew point and bubble point curves on the *P-T* diagrams. The enthalpy data for the pure components could be compared with previously published information. A comparison with the results of Organick and Studhalter (*6*) indicated a mean error of 0.2 B.t.u. per pound and an average absolute

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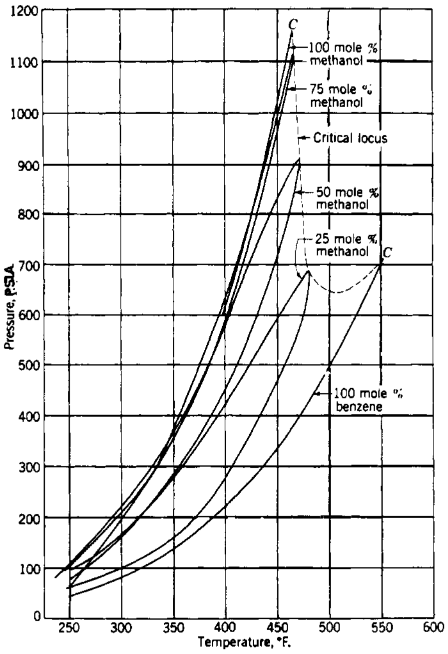


Figure 2. Pressure-temperature diagram for the benzene-methanol system

Table I. Dew Point and Bubble Point Temperatures (° F.) for the Methanol-Benzene System

Pressure, P.S.I.A.	100 Mole % Methanol Bubble Point and Dew Point	75 Mole % Methanol	
		Bubble point	Dew point
100	254	249	265
200	302	295	300
300	334	333	335
400	359	355	362
500	380	375	383
600	396	395	401
700	411	411	416
800	424	426	430
900	436	440	444
1000	448	452	456
1100	458	465	465
1110	...	468[a]	468[a]
1155	464[a]	...	...

Pressure, P.S.I.A.	50 Mole % Methanol		25 Mole % Methanol	
	Bubble point	Dew point	Bubble point	Dew point
100	244	269	255	300
200	295	318	318	371
300	330	355	355	407
400	360	386	392	434
500	384	410	433	457
600	406	430	455	475
650	...	...	469	479
680	...	...	480[a]	480[a]
700	427	448	...	...
800	446	463	...	...
850	457	470	...	...
900	470	470	...	...
908	472[a]	472[a]	...	...

Pressure, P.S.I.A.	100 Mole % Benzene Bubble Point and Dew Point
100	320
200	388
300	436
400	472
500	502
600	527
650	539
700	550
716	553[a]

[a] Critical temperature.

difference of 1.8 B.t.u. per pound. This indicated that the apparatus could be employed to obtain reliable enthalpy data for benzene. However, the graphical procedures used to locate phase boundaries introduced uncertainties. Also, saturation pressures are, in general, sensitive to small errors in other measurements. Hence, it is not expected that the *P-T* phase envelopes are as accurate as the single phase enthalpy data. The results are reported to 1° F. and 1 p.s.i.a., but probably are not accurate to these tolerances.

RESULTS

The phase envelopes for the benzene-methanol, benzene-ethyl alcohol, and *n*-pentane-ethyl alcohol are shown in Figure 2 to 4, and the corresponding data in Tables I to III. On these figures are shown the curves for the pure components and three compositions of the binary system. In contrast to hydrocarbon systems, the bubble point and dew point parts of the envelope for a given composition meet in a rather sharp point. In other words, the critical, cridonentherm, and cricondenbar points nearly coincide for these systems; while for mixtures of hydrocarbons these points may be widely separated. This behavior permits more accurate evaluation of the critical temperature and pressure.

For a binary system, the curve which connects the critical points of the two pure components and which is tangent to all of the *P-T* envelopes for intermediate compositions is the locus of the critical points. Such critical loci lines are shown dotted in Figures 2 to 4. The critical temperatures and pressures obtained in this manner are included in the data of Tables I to III.

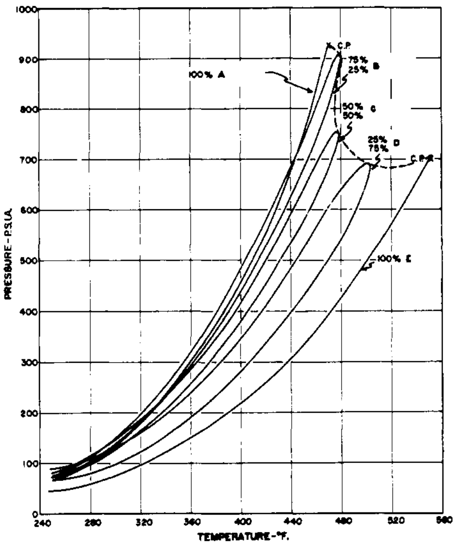
Table II. Dew Point and Bubble Point Temperatures (° F.) for the Ethyl Alcohol–Benzene System

Pressure, P.S.I.A.	100 Mole % Ethyl Alcohol Bubble Point and Dew Point	75 Mole % Ethyl Alcohol	
		Bubble point	Dew point
100	278	273	278
200	327	321	327
300	360	355	362
400	387	381	390
500	409	403	414
600	428	424	435
700	443	443	453
800	456	460	469
900	467	475	479
906	...	479[a]	479[a]
927	470[a]		

Pressure, P.S.I.A.	50 Mole % Ethyl Alcohol		25 Mole % Ethyl Alcohol	
	Bubble point	Dew point	Bubble point	Dew point
100	269	281	270	301
200	325	337	342	365
300	365	375	384	407
400	396	405	417	440
500	420	432	444	469
600	442	455	469	493
650	...	...	483	500
693	...	...	502[a]	502[a]
700	462	473	...	...
750	474	477	...	...
756	478[a]	478[a]	...	...

Pressure, P.S.I.A.	100 Mole % Benzene Bubble Point and Dew Point
100	320
200	388
300	436
400	472
500	502
600	527
650	539
700	550
716	553[a]

[a] Critical temperature.



	Ethyl Alcohol, %	Benzene, %
A.	100	
B.	75	25
C.	50	50
D.	25	75
E.		100

	Ethyl Alcohol, %	*n*-Pentane, %
A.	75	25
B.	100	
C.	50	50
D.	25	75
E.		100

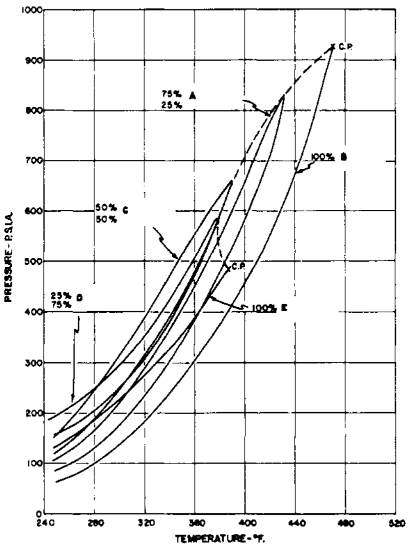


Figure 3. Pressure-temperature diagram for benzene–ethyl alcohol system

Figure 4. Pressure-temperature diagram for the *n*-pentane–ethyl alcohol system

The intersection of a dew point curve for one composition on Figures 2, 3, or 4 with a bubble point curve for a different composition would be expected to indicate the composition of vapor and liquid phases in equilibrium. This is true except when an azeotrope occurs between the two compositions. Minimum boiling azeotropes exist for both the benzene-methanol and benzene–ethyl alcohol systems, although they do not persist up to the critical pressure. Neither Figures 2 nor 3 exhibit a minimum in the critical temperature locus curve—i.e., the dotted lines in Figures 2 and 3 do not pass through a minimum temperature. For the benzene-methanol system, the azeotropic composition at 325° F. and 270 p.s.i.a. is 75 mole % methanol. This is the point where the dew point and bubble point curves of the phase envelope for 75 mole % methanol become tangent to each other, as seen in Figure 2. An azeotrope for this system exists up to a pressure somewhat above 600 p.s.i.a. In the benzene–ethyl alcohol system, the minimum boiling azeotrope disappears somewhat above 200 p.s.i.a. At atmospheric pressure Zmaczynski (*8*) noted a constant boiling mixture at 280° F. containing 59 mole % ethyl alcohol.

Table III. Dew Point and Bubble Point Temperatures (° F.) for the *n*-Pentane–Ethyl Alcohol System

Pressure, P.S.I.A.	100 Mole % Ethyl Alcohol Bubble Point and Dew Point	75 Mole % Ethyl Alcohol	
		Bubble point	Dew point
100	278	245	263
200	327	293	309
300	360	323	339
400	387	348	363
500	409	370	385
600	428	389	403
700	443	407	419
800	456	425	430
826	...	432^a	432^a
900	467	...	...
927	470^a	...	...

	50 Mole % Ethyl Alcohol		25 Mole % Ethyl Alcohol	
	Bubble point	Dew point	Bubble point	Dew point
200	265	284	253	276
300	296	317	302	318
400	323	342	334	345
500	347	364	359	365
550	...	...	370	373
582	...	...	378^a	378^a
600	372	381	...	...
650	386	389	...	...
657	390^a	390^a	...	...

	100 Mole % *n*-Pentane Bubble Point and Dew Point
100	223
200	287
300	330
400	363
450	378
485	387^a

^{a} Critical temperature.

Compositions of phases in equilibrium for a variety of temperatures and pressures can be obtained approximately by replotting the data in Figures 2 to 4 on temperature-composition diagrams. However, these results would be approximate because only three intermediate compositions are available for plotting the bubble and dew point curves.

The critical locus curve (Figure 4) for the ethyl alcohol–*n*-pentane system does exhibit a minimum critical temperature. This type of behavior was first observed by Kuenen (*1*) for the nitrous oxide–ethane system and later reaffirmed for acetylene-ethane and carbon dioxide–ethane mixtures (*2*). The minimum boiling azeotrope for this system exists up to the critical point. Its ethyl alcohol content increases with pressure up to the region of 50 mole % from 7.6 mole % (*3*) at atmospheric pressure.

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