The Phase Behavior and Solubility Relations of the Benzene-Water System

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In order to contribute to knowledge of the nature of the phase behavior of partially miscible liquid systems, a study of the benzene-water system was undertaken. The pressures at liquid- and vapor-phase boundaries of fifteen mixtures of benzene and water were determined within the temperature range of 200 to 357°C. Along with a complete numerical tabulation, these data are presented graphically as pressure-temperature, pressure-composition, and temperature-composition phase diagrams to show the nature of the boundaries.

Up to the three-phase critical end point, the benzene-water system develops in a manner usually ascribed to a partially miscible system in which the vapor composition at a point of univariance lies intermediate to the two liquid compositions. The three-phase critical end point occurs at 1,364 lb./sq. in. abs. and 268.3°C., and the composition of the critical phase is 25.8 weight % water, with the remaining liquid phase 92.8 weight % water.

The pressure, temperature, and composition of the critical solution end point are deduced as 2,300 lb./sq. in. abs., 306.4°C., and 59 weight % water, respectively. At temperatures between these two critical points the phase behavior is likened to that of a dense gas or fluid dissolved in a liquid. Definite limiting values of temperature and pressure are assignable to this behavior by the extension of the three-phase curve up to the critical solution end point. This extended curve is not a phase boundary, but the temperature and pressure at a given point on the curve represents in a mixture of fixed composition the limit of mutual solubility of the benzene-rich fluid phase and the water-rich phase. At a temperature above or a pressure below the given point the liquid phase begins to vaporize.

Above the critical solution end point the vapor-liquid phase boundaries are like those of a normal binary mixture.

Although the broad principles governing the *P-T-x* relations of partially miscible mixtures were set forth by van der Waals (*16*), van Laar (*9*), Keunen (*8*), and Roozeboom (*12*) in the early part of the present century, few systems exhibiting partial miscibility have been examined in a quantitative fashion over a wide range of temperature, pressure, and composition. Because of this paucity of data, the phase behavior in the region of the liquid-vapor critical state of one of the liquid layers is still greatly a matter of conjecture. In the critical region the compressibility of the liquid approaches that of the vapor, and so the mutual solubility of the liquid layers is greatly influenced by relatively small changes in pressure. In many chemical processes and especially in petroleum processing, where hydrocarbon-water mixtures are encountered, such phase behavior may be of great practical significance. The sparing solubility of oil, gas, and water mixtures, as they are known at the earth's surface, may very well present an entirely different mutual relationship when subject to high underground pressure and temperature.

To obtain a more quantitative picture of the phase behavior of partially miscible systems, the *P-T-x* relations of the benzene-water system have been determined throughout most of its saturated temperature range.

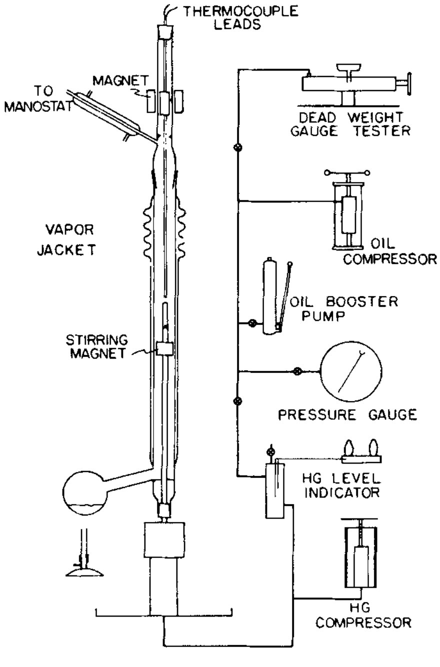

Fig. 1. Schematic diagram of assembled apparatus.

The phase behavior of this system is typical of systems for which the equilibrium vapor composition lies intermediate to the immiscible liquid-layer compositions. Aside from the possible industrial applications of the data, the benzene-water system is an interesting one to study from the point of view of interactions between two molecules representative of nonpolar and polar liquids. The vapor-pressure curves of these compounds intersect at 182°C. At lower temperatures benzene is the more volatile component, whereas at higher temperatures water is more volatile.

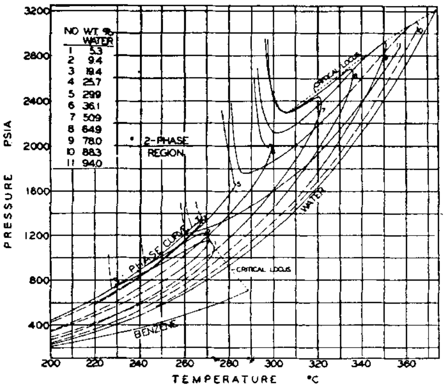

Fig. 2. 2 *P-T-x* space diagram for the benzene-water system.

Scheffer (*13*) has measured the three-phase vapor pressure up to the vaporization critical end point of the benzene-rich layer. Jaeger (*2*) has obtained data on the solubility of benzene in water over an extended temperature range, while others (*14*, *1*, *3*) have measured the mutual solubility in the vicinity of room temperature and atmospheric pressure.

EXPERIMENTAL METHODS AND APPARATUS

To determine the phase relations in the benzene-water system *P-T* border curves were obtained for fifteen mixtures varying in concentration from nearly pure benzene to nearly pure water. The apparatus employed was a modification of that described by Young (*17*) and Kay (*4*) and is shown schematically in Figure 1. Essentially a small air-free sample of each of the mixtures was confined over mercury, in a quartz capillary tube of 2-mm. bore and 8-mm. O.D. The tube was heated to a constant temperature by the condensing vapor of one of a series of organic liquids or mercury, which was confined in a vacuum-jacketed tube surrounding the capillary tube. The capillary tube was held in a compressor block filled with mercury, and the block in turn was connected to a hydraulic-pressure oil pump used to balance the pressure developed by the sample. The mercury-oil interface was kept at a constant level by means of a mercury-displacement pump and mercury-level indicator. The pressure was measured to within 1-lb./sq. in. by a precision Bourdon type of pressure gauge with a 16-in. diameter dial marked in 5 lb. increments from 0 to 5,000 lb./sq. in. The calibration of the gauge was checked by

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TABLE 1. THE PRESSURE-TEMPERATURE RELATIONS AT THE PHASE BOUNDARIES OF THE SYSTEM BENZENE-WATER AT EQUAL INTERVALS OF TEMPERATURE

Temperature, °C.	Pressure, lb./sq. in. abs.
Composition: 5.5 wt. % water	
200*	287
210*	351
220*	418
230*	495
240*	582
250*	662
260	807
270	963
273	1055
273.2	1085 $VL\text{-}T_m$
273	1100
272.2	1127 VC
271	1147
270.3	1150 $VL\text{-}F_m$
268	1140
265	1115
260	1060
250	951
240	948
230	745
227.5	720 $3p_m$
Composition: 9.4 wt. % water	
200*	343
210*	409
220*	482
230*	568
240	673
250	788
260	919
270	1116
271.0	1170 $VL\text{-}T_m$
270.5	1190
269.7	1207 VC
269.5	1211
269	1217
268.5	1220 $VL\text{-}P_m$
268.	1219
265	1193
260	1136
250	1011
242.5	924 $3p_m$
Composition: 19.4 wt. % water	
180*	290
190*	353
200*	419
210*	505
220*	598
230*	708
240	835
250	981
260	1150
267	1305
267.5	1322
267.8	1354 $VC\text{-}T_m$
267	1330
266	1316
265	1300
263.5	1278 $3p_m$
Composition: 25.7 wt. % water	
200*	417
210*	510
220*	615
230*	732
240*	869
250	1031
260	1212 Azeo
265	1303
266	1320
267	1338
268	1356
268.3	1361 VC
Composition: 29.9 wt. % water	
190*	320
200*	395
210*	483
220*	583
230*	698
240*	828
250	985
260	1158
270	1346
280	1572
283.1	1665 $VL\text{-}T_m\text{-}P_m$
282.8	1670 $2L\text{-}T_m$
282.5	1674
282	1710
281	1830
280	1938
277	2275
Composition: 36.1 wt. % water	
200*	348
210*	426
220*	515
230*	618
240*	737
250*	871
260	1020
270	1193
280	1391
290	1632
295	1778
299	1944
299.6	2000 $VL\text{-}T_m$
299.5	2015
299.4	2019
299.3	2022
299.2	2024
299.1	2025 $VL\text{-}P_m$
298.8	2022
298.6	2018
298.4	2015
298.2	2006
298.0	1998
297.5	1992 $2L\text{-}T_m$
297	1997
296	2025
294	2133
292	2405
Composition: 50.9 wt. % water	
210*	331
220*	410
230*	498
240*	601
250*	717
260*	855
270*	1012
280*	1183
290	1382
300	1616
310	1888
320	2240
321.6	2390 $VL\text{-}T_m$
321	2439
320.4	2443 $VL\text{-}P_m$
320	2441
315	2583
310	2327
306	2302 $2L\text{-}T_m$
304	2310
303	2327
300	2429
Composition: 64.9 wt. % water	
220*	363
230*	442
240*	535
250*	642
260*	766
270*	911
280	1073
290*	1249
300	1455
310	1697
320	1972
330	2300
336.2	2650 $VL\text{-}T_m$
336.1	2675
335	2685
330	2618
320	2467
310	2327
308	2307
306.4	2301 $2L\text{-}T_m$
305	2306
303	2335
300	2460
Composition: 69.9 wt. % water	
336.1	2711 VC
Composition: 78.0 wt. % water	
230*	417
240*	500
250*	597
260*	711
270*	840
280*	985
290*	1151
300*	1331
310*	1531
320	1773
330	2057
340	2376
350	2795
351.0	2890 $VL\text{-}T_m$
350.4	2920 $VL\text{-}P_m$
350.0	2916 VC
345	2845
340	2757
330	2552
320	2357
310	2195
305	2136
301.7	2118 $2L\text{-}T_m$
300	2125
298	2182
295	2334
293.7	2513
Composition: 88.3 wt. % water	
365	3110 VC(est)
335	2497
330	2386
320	2183
310	2011
300	1870
390	1772
287.5	1763 $2L\text{-}T_m$
287	1764
286	1770
283	1795
284	1865
282.8	2000
Composition: 94.0 wt. % water	
357	2863
358	2807
350	2667
340	2376
330	2149
320	1932
310	1752
300	1608
290	1475
280	1360
270	1372
265	1240
260.2	1215 $3p_m$

means of the dead-weight gauge. An iron-constantan thermocouple together with a sensitive potentiometer was used to measure the temperature of the vapor jacket to within 0.05°C. The couple was standardized against the melting point of ice and the condensing temperatures of water, naphthalene, benzophenone, and mercury all at 760 mm. of mercury pressure. Equilibrium between the liquid and vapor phases of the sample was established quickly by the movement of a small steel ball through the sample by means of a series of magnets (Figure 1).

Reagent-grade benzene, which had been dried over phosphorous pentoxide and rectified, and freshly prepared conductivity water were used in the preparation of the mixtures. Small quantities of the pure components were deaerated under high vacuum, and a measured quantity of each component was transferred by molecular distillation to the experimental tube attached to the high vacuum line. The procedure for the preparation of samples has been described elsewhere (*5*). Mixtures of a known composition could be prepared to within 0.002 weight fraction.

The reliability of the apparatus and procedures was checked by a comparison of the measured values of the vapor pressure of the pure components with accepted values from the literature. A summary of the observations showed that the temperature and pressure measurements were accurate to within 0.05°C. and 1 lb./sq. in., respectively.

EXPERIMENTAL RESULTS

The pressure at the liquid- and vapor-phase boundaries of fifteen mixtures of benzene and water were determined within the temperature range from 200° to 357°C. The smoothed data at increments of 10°C. in temperature for twelve of the mixtures are presented in Table 1. More extensive data are available (*10*). Table 2 gives values of the three-phase pressure at increments of 10°C. up to the critical end point temperature. These values are in excellent agreement with those reported by Scheffer (*13*). In addition, pressure-temperature data along the extension of the three-phase curve up to the critical solution point are shown.

Also indicated in these tables are the values of the unique states of each mixture noted as follows: the vaporization critical points (*VC*), the maximum temperature for the coexistence of vapor and liquid (*VL-T_m*), the maximum pressure for the coexistence of vapor and liquid (*VL-P_m*), the maximum three-phase temperature and pressure ($3p_m$), and the maximum temperature for two liquid phases (*2L-T_m*).

The values in the tables were read from large-scale plots of the experimental data as shown in Figure 2. Because of the limitations of the apparatus, the dew points of the mixtures could not be determined to as low a pressure and tempera-

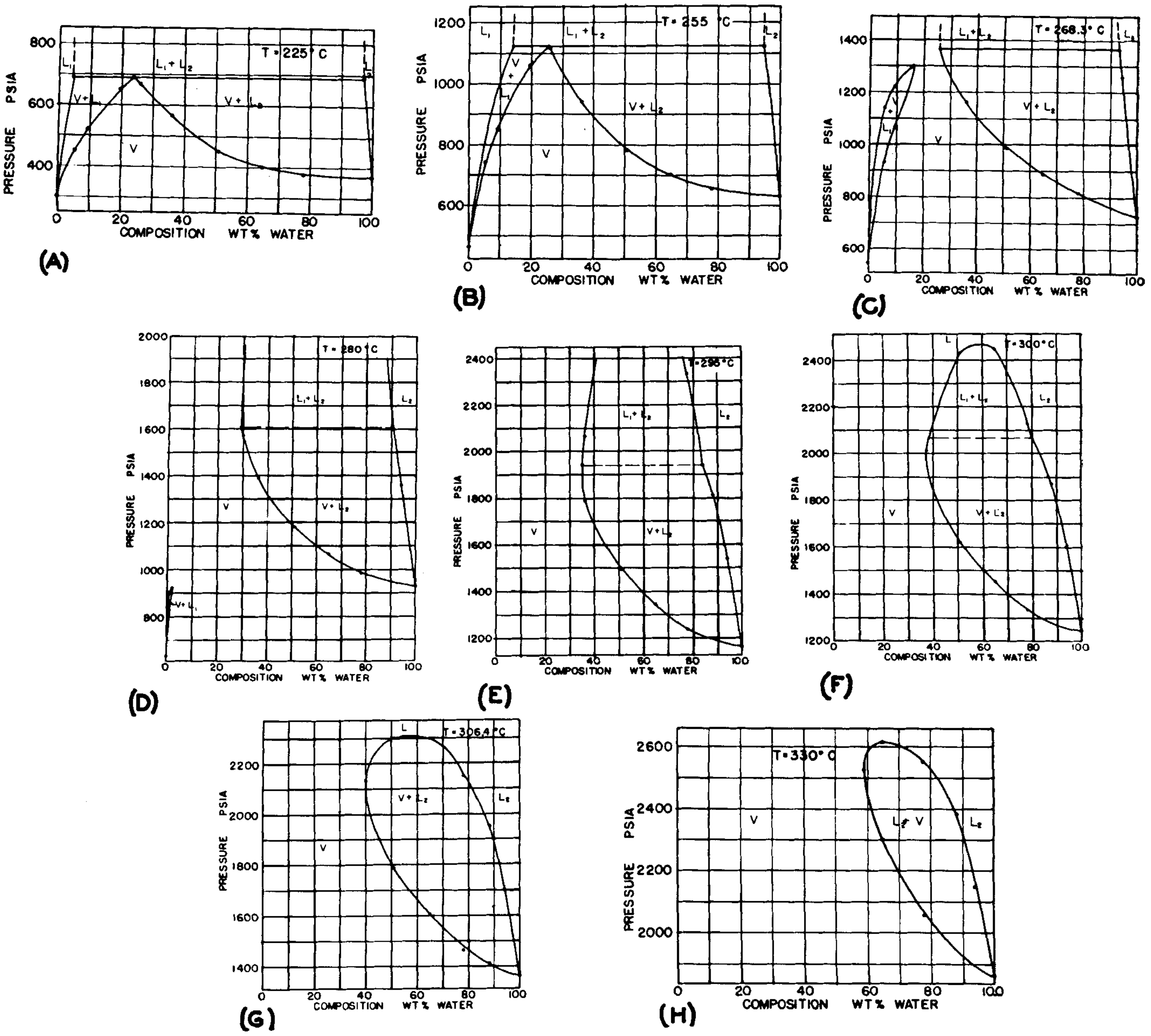

Fig. 3. Pressure-composition isothermal diagrams of the benzene-water system.

ture as desired. However these values were obtained by extrapolation of the measured portion of the curve, by the plotting of the logarithm of the absolute pressure vs. the reciprocal of the absolute temperature, and by the extension of the resulting straight line. The extrapolated curves are shown in Figure 2 by dashed lines, and the extrapolated values are shown in the table by asterisks.

The curves in Figure 2 are the *P-T* border curves of the various mixtures and the vapor-pressure curves of pure benzene and water. The latter curves were constructed with the vapor pressure reported for benzene by Kay and Nevens (*6*) and the vapor pressure of water given by Keenan and Keyes (*7*). These curves together form the *P-T-x* space diagram. The three-phase curve represents the pressure and temperature condition where two liquid phases and a vapor phase coexist in equilibrium; hence, when the pressure or temperature is set, the system is defined. The three-phase curve originates at the solid-liquid phase boundary and terminates in the critical end point. The coordinates of this point are 268.3°C., 1,364 lb./sq. in., and 25.8 weight % water. Immediately above the three-phase curve the system exists as two liquid phases, and below the curve the system is composed of a liquid and a vapor phase. The short, nearly vertical branches for mixtures 5 through 11 (Figure 2), as well as those extending upward from the three-phase curve, represent the phase boundaries separating the region of two liquid phases (to the left of the curve) from a region of a single homogeneous phase (to the right of the curve) for mixtures of the composition indicated. These curves extend into the high-pressure region and presumably are curved so that they intersect the solid-phase boundary at a lower temperature.

The critical locus is not continuous but is separated into two branches by a liquid miscibility gap (*10*). The lower branch of the curve originating in the critical point of benzene has a negative slope and terminates in the critical end point as noted above. The upper branch of the locus, beginning in the critical point of water, ends abruptly at the critical solution point of 306.4°C., 2,300 lb./sq. in., and 59 weight % water. In the miscibility gap between these compositions the phenomenon associated with the *L-V* critical point is observed only for the benzene-rich phase but not for the mixture as a whole.

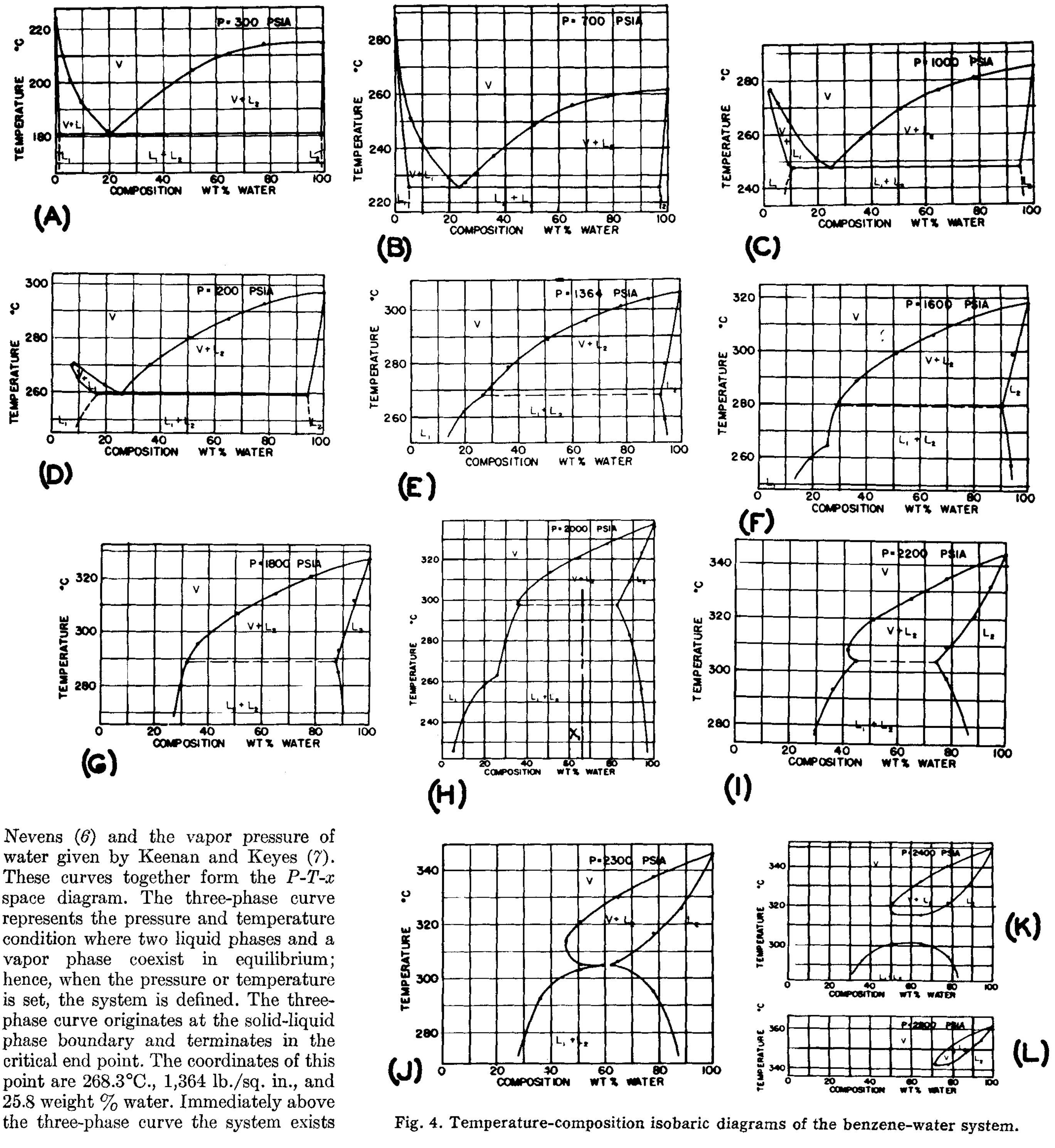

Fig. 4. Temperature-composition isobaric diagrams of the benzene-water system.

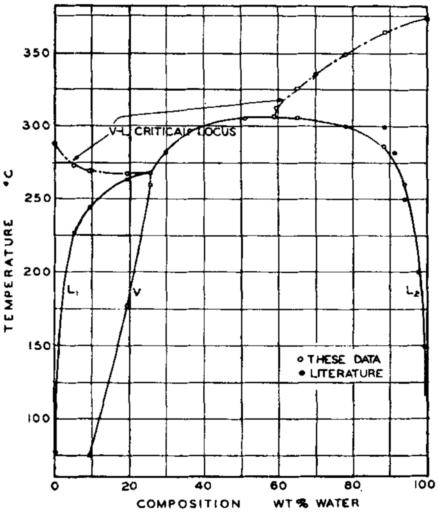

Fig. 5. Temperature-composition diagram for the benzene-water system.

TABLE 2. PRESSURE-TEMPERATURE RELATIONS ALONG THE THREE-PHASE CURVE AND THE EXTENSION OF THE THREE-PHASE CURVE, BENZENE-WATER SYSTEM

Temperature, °C.	Pressure, lb./sq. in. abs.
	Expt.
180	295
190	360
200	438
210	531
220	633
230	752
240	885
250	1038
255	1123
260	1212
265	1307
268.3	1364
270	1404
280	1610
290	1825
300	2070
306.4	2302 ($2L$-T_m)

INTERPRETATION OF THE DATA

From the graphically smoothed data and plots of Figure 2 a series of cross plots was prepared in order to interpret more fully the nature of the phase behavior.

Up to the three-phase critical end point (268.3°C.) the benzene-water system develops in a manner usually ascribed to a partially miscible system in which the vapor composition at a point of univariance lies intermediate to the two liquid compositions. This is clearly shown in the *P-x* phase diagrams at constant temperature, Figures 3*a*, 3*b*, and 3*c*, and the *T-x* phase diagrams at constant pressure, Figures 4*a*, *b*, *c*, and *d*. The point of intersection of the vapor curves with the constant-pressure line in each of the *P-x* diagrams and with the constant-temperature line in each of the *T-x* diagrams is a heteroazeotropic point (*15*). The three-phase curve is therefore the vapor-pressure curve of the heteroazeotrope or constant-boiling mixture formed by benzene and water. The variation of its composition with temperature is shown by the vapor curve in Figure 5.

The existence of an island in the *P-x* section (Figures 3*c* and *d*) is the result of the negative slope of the critical-locus curve. Referring to Figure 2, one can see that any isotherm taken in the range of temperatures from the three-phase critical end point to the critical point of pure benzene will have an island.

In the region of the three-phase critical temperature and pressure there can be detected the subtleties of the evolution of the surface to realign itself so as to continue on in another direction. Significantly Figure 5, the solubility diagram, shows the benzene-rich liquid-solubility branch going to the vapor branch abruptly at the three-phase critical end point. There is no smooth, rounded compromise meeting of the two curves. The vapor branch continues directly on above the three-phase critical, having taken on itself the meaning of both branches from which it evolved. Similarly the critical locus curve (Figure 5) goes through a minimum before reaching the three-phase critical to attain a positive slope and be directed toward its ultimate terminal, the critical point of water.

The three-phase curve extended beyond the critical end point temperature (268.3°C.) to the critical solution temperature (306.4°C.) does in effect continue to represent three-phase equilibrium. However the transition of one of the liquid phases to the vapor phase is continuous and accompanied by no volume change at constant temperature and pressure. The extension of the three-phase curve may be considered to represent a metastable three-phase equilibrium. A point on the curve would represent the limit of the solubility of a benzene-rich dense gas or fluid phase and a water-rich liquid phase at a temperature and pressure where the liquid is just beginning to vaporize. However the dense fluid and the vapor form a homogeneous mixture which is identified as a single phase.

When one traces the phase changes of a mixture of composition x_1 in Figure 4*h*, the foregoing interpretation is illustrated. At some low temperature, and a pressure of 2,000 lb./sq. in., the mixture will exist as two liquid phases. These two liquid phases increase mutually in solubility as the temperature is raised to approximately 264°C. With further increase in temperature the benzene-rich phase is no longer identified as a liquid but rather as a dense fluid, and the effect of increased temperature is a continued increase in solubility of the two phases. Upon reaching a temperature of 297°C. these two phases have reached their maximum solubility, which may in a broad sense be called the *limit of solubility* of the gas and liquid. At this temperature the water-rich phase begins to vaporize and the vapor which is formed is completely dissolved in the benzene-rich fluid. An increase in the temperature above 297°C. causes a normal pattern of behavior. In terms of solubility the liquid becomes more soluble in the vapor while the vapor becomes less soluble in the liquid.

Figure 5 outlines completely the solubility relations of the saturated liquids for the system. All mixtures become completely miscible at a temperature of 306.4°C., which corresponds to a pressure of 2.300 lb./sq. in. A mixture containing about 59 weight % water was deduced to be the composition which will be critical at this point. Mixtures which still retain two phases at temperatures and pressures above the critical solution point have phase boundaries like normal binary mixtures, Figures 3(*H*), 4(*K*), and 4(*M*).

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