Solid-Liquid Phase Behavior of Binary Solutions at Elevated Pressures

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The formation of a solid phase as the result of isothermally increasing pressure on a binary solution is analyzed from a thermodynamic point of view. Exact thermodynamic equations are presented for the case in which there are no more than one liquid and one solid phase in equilibrium for the entire range of compositions. Approximate relations incorporating the additional assumption of ideality in both solid and liquid phases are also presented. Experimental data for the system ethylene bromide-ethylene chloride are reported and compared with predicted values. Incomplete data for the system benzene-*n*-heptane are also reported.

The successful operation of many separation processes is dependent on the difference in composition and density of two phases in equilibrium. Phase behavior is influenced by both temperature and pressure; however investigations concerning the effect of pressure on condensed phases of binary mixtures have been relatively scarce.

The most extensive work done in this broad area has been the study of solubilities of solids in liquids under variable pressure. One of the first to investigate this phenomenon was Cohen (*3*), who, in 1909, reported data on the change in solubilities with pressure of aqueous zinc sulfate and cadmium sulfate solutions. A comprehensive review of the literature in this field was presented by Tsiklis (*14*) in 1945.

The effect of pressure on binary liquid-liquid systems was studied primarily in the first thirty years of this century. Timmermans (*10, 11, 12*) has reviewed the literature rather completely up to 1923.

Eutectic forming solid-liquid systems were studied as early as 1912 by Pushin and Grebenshchikov (*8*). However the work done in this realm was chiefly empirical until 1938, when Adams (*1*) presented thermodynamic equations for the prediction of pressure composition phase diagrams for eutectic type of mixtures. Binary systems forming solid solutions have been considered at variable pressures only superficially. In 1926 Pushin (*7*) obtained isothermal liquidus curves of the system chloronitrobenzene-bromonitrobenzene at several temperatures. Swallow and Gibson (*9*) determined the liquidus curve of the system monomethylaniline-dimethylaniline to 2,000 atm. in a visual observation type of cell.

There exist in the literature no relations which would permit the prediction of isothermal solid liquid phase behavior for mixtures forming solid solutions. For this reason it was decided to attempt a development of such relations and make an experimental study to compare with the resulting equations.

THERMODYNAMIC ANALYSIS

The simplest type of solid-liquid system was chosen for analysis, that is a system in which no more than one liquid and one solid phase exist in equilibrium. A thermodynamic viewpoint was taken as the most straightforward approach to the problem.

Rigorous Analysis

For phases in equilibrium the partial molal Gibbs free energy of the *i*th component is equal in all phases. For a liquid and a solid phase in equilibrium at pressure *P*

$$\overline{G}_{ilP} = \overline{G}_{isP} \qquad (1)$$

The partial molal free energy of component *i* in phase *j* at pressure *P* can be determined from its value at $P_j°$ at the same temperature if partial molal volume data are available:

$$\overline{G}_{ijP} = \overline{G}_{ijP_j°} + \int_{P_j°}^{P} \overline{V}_{ij}\, dP \qquad (2)$$

If activity-coefficient data are available with a standard state of the pure component *i* in the *j* phase at $P_j°$ and the temperature in question, the partial molal free energy of component *i* in solution at this pressure and temperature is expressed as

$$\overline{G}_{ijP_j°} = G_{ijP_j°} + RT [\ln \overline{\gamma}_{ijP_j°} + \ln X_{ij}] \qquad (3)$$

In order to take advantage of the equilibrium relation which exists between pure liquid and pure solid at pressure P_i, use is made of volumetric data for pure component *i*:

$$G_{ijP_j°} = G_{ijP_i} + \int_{P_i}^{P_j°} V_{ij}\, dP \qquad (4)$$

Combination of Equations (2), (3), and (4) provides a relation between the partial molal free energy of component *i* at equilibrium in solution at pressure *P* and the molal free energy of pure component *i* at equilibrium at pressure P_i:

$$\overline{G}_{ijP} = G_{ijP_i} + \int_{P_i}^{P_j°} V_{ij}\, dP + RT[\ln \overline{\gamma}_{ijP_j°} + \ln X_{ij}] + \int_{P_j°}^{P} \overline{V}_{ij}\, dP \qquad (5)$$

At pressure P_i the solid and liquid

phases of pure component i are in equilibrium; therefore

$$G_{ilP_i} = G_{isP_i} \qquad (6)$$

If Equation (5) is applied to one component of a binary system in both phases, l and s, Equations (1) and (6) serve to eliminate the free energy and yield an expression relating the composition X_{ij} to the activity coefficient and volumetric data:

$$\int_{P_i}^{P_s^o} V_{is}dP + RT[\ln \bar{\gamma}_{isP_s^o} + \ln X_{is}] + \int_{P_s^o}^{P} \bar{V}_{is}dP = \int_{P_i}^{P_l^o} V_{il}dP + RT[\ln \bar{\gamma}_{ilP_l^o} + \ln X_{il}] + \int_{P_l^o}^{P} \bar{V}_{il}dP \qquad (7)$$

Two equations of this type are obtained by considering each of the components in a binary system, and they can be solved in combination with the two basic relations

$$\sum_{i=1}^{2} X_{ij} = 1.0 \qquad (8)$$

to yield the four equilibrium mole fractions X_{ij}. The results presented below have been rearranged for convenience in calculating the desired results when the necessary data are available:

$$RT\ln\alpha_s = \sum_{1}^{2} (\Gamma v_i + \overline{\Gamma v_i}) - RT \ln \left[\frac{\bar{\gamma}_{1sP_s^o}\ \bar{\gamma}_{2lP_l^o}}{\bar{\gamma}_{1lP_l^o}\ \bar{\gamma}_{2sP_s^o}} \right] \qquad (9)$$

$$(X_2)_s = \frac{1}{(\alpha_s - 1)} \left[\alpha_s \frac{\bar{\gamma}_{2lP_l^o}}{\bar{\gamma}_{2sP_s^o}} \exp \left\{ -\frac{1}{RT} (\Gamma v_2 + \overline{\Gamma v_2}) \right\} - 1 \right] \qquad (10)$$

The following definitions have been used to simplify the presentation of Equations (9) and (10):

$$\alpha_s \equiv \frac{(X_{1s})(X_{2l})}{(X_{2s})(X_{1l})} \qquad (11)$$

$$\Gamma v_i \equiv (-1)^i \left[\int_{P_l^o}^{P_i} \bar{V}_{il}\, dP - \int_{P_s^o}^{P_i} V_{is}\, dP \right] \qquad (12)$$

$$\overline{\Gamma v_i} \equiv (-1)^i \left[\int_{P}^{P_l^o} \bar{V}_{il}\, dP - \int_{P}^{P_s^o} \bar{V}_{is}\, dP \right] \qquad (13)$$

In applying these equations α_s is first calculated from Equation (9) and then $(X_2)_s$ is determined from Equation (10). Combination of Equations (8) and (11) then yields X_{2l}:

$$X_{2l} = \frac{\alpha_s\ (X_{2s})}{[1 + (\alpha_s - 1)X_{2s}]} \qquad (14)$$

The remaining mole fractions are then easily obtained from Equation (8).

In order to solve the equations as described it is necessary to have the following data:

1. Volumetric data for both solid and liquid phases of the pure components, 1 and 2, over the pressure ranges indicated by the integral terms involving the molal volume V_i.
2. Solution behavior data in terms of activity coefficients, for both solid and liquid solutions at pressures P_s^o and P_l^o, respectively.
3. Volumetric data for both solid and liquid solutions over the pressure ranges indicated by the integral terms involving the partial molal volume $\bar{V}_i$.

If such data are available, the calculation procedure repeated at several pressures yields sufficient results to plot the pressure composition, solid liquid phase diagram for a binary mixture.

Ideal Case

Much of the data necessary for the solution of the rigorous equations is generally not available, and therefore it is instructive to simplify the equations with the assumptions of ideal solution behavior in both phases; that is

$$\bar{\gamma}_{ijP_j^o} = 1.0 \qquad (15)$$

and

$$\bar{V}_{ij} = V_{ij} \qquad (16)$$

The rigorous equations are simplified considerably when these ideal solution behavior conditions are applied:

$$RT\ln\alpha_s = \int_{P_1}^{P} [V_{1l} - V_{1s}]\, dP + \int_{P}^{P_2} [V_{2l} - V_{2s}]\, dP \qquad (17)$$

$$X_{2s} = \frac{1}{(\alpha_s - 1)} \left[\alpha_s \exp \left\{ \frac{1}{RT} \int_{P_2}^{P} [V_{2l} - V_{2s}]\, dP \right\} - 1 \right] \qquad (18)$$

$$X_{2l} = \frac{\alpha_s\ (X_{2s})}{[1 + (\alpha_s - 1)X_{2s}]} \qquad (14)$$

In order to predict the pressure of the phase change as a function of composition in a binary mixture with these equations it is only necessary to have volumetric data for the pure components. However such predictions will be accurate only to the extent of the validity of the assumption of ideality in both phases.

It should be pointed out that the integral of V_{1l} with respect to pressure is for a hypothetical situation, since component 1 is a solid at these conditions. Similarly the integral of component 2 in the solid phase is hypothetical, since this component is a liquid at the pressures involved.

Sample Calculation

The data available for calculation do not always correspond precisely to those required for direct solution of the above equations. The following sample calculation illustrates the use of available data and explains the assumptions which were made to compete the calculations.

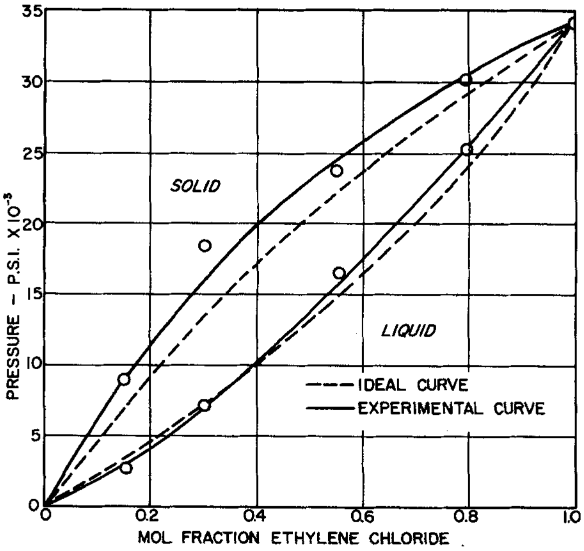

Fig. 1. Experimental and predicted results for ethylene bromide-ethylene chloride system.

The following data are reported in the literature:

	Ethylene bromide	Ethylene chloride
V_{ilP_o}–cc./g.mole	86.2(*4*)	78.8(*4*)
V_{is}/V_{il}	0.897(2)	---
$\bar{\beta}_{il}$–atm.$^{-1}$	———	44 (*15*)
P_i–atm.	1.0(4)	2380 (This work)

Lack of data indicated by – – – in the above listing necessitated the assumptions that $V_{is}/V_{il} = 0.897$ for ethylene chloride and $\bar{\beta}_{il} = 44$ atm.$^{-1}$ for ethylene bromide.

These data are incorporated into the integrals involved in Equations (17) and (18) and the integration performed between the arbitrary limits P_a and P_b:

$$\int_{P_a}^{P_b} [V_{il} - V_{is}]\, dP = 0.103\, V_{ilP_o}$$

$$(P_b - P_a) \left[1 - \frac{\bar{\beta}}{10^6}\left(\frac{P_b + P_a}{2} - P_o\right)\right] \tag{19}$$

In applying this equation some pressure P between P_1 and P_2 is chosen, and Equation (19) is evaluated and used in Equations (17) and (18). For example for P = 476 atm. Equation (17) yields a value of α_s = 2.22, Equation (18) predicts X_{2s} = 0.160, and Equation (14) yields X_{2l} = 0.297.

Similar calculations carried out at other pressures yield the curve shown as the dotted lines in Figure 1.

EXPERIMENTAL STUDY

Apparatus

An experimental study was deemed necessary in order to examine a system whose properties might be nearly ideal and whose phase diagram could thus be compared with the solution of the ideal equations. Complete equipment was designed and constructed, including a high-pressure cell which allows visual observation of the hydrocarbon system through sapphire windows.

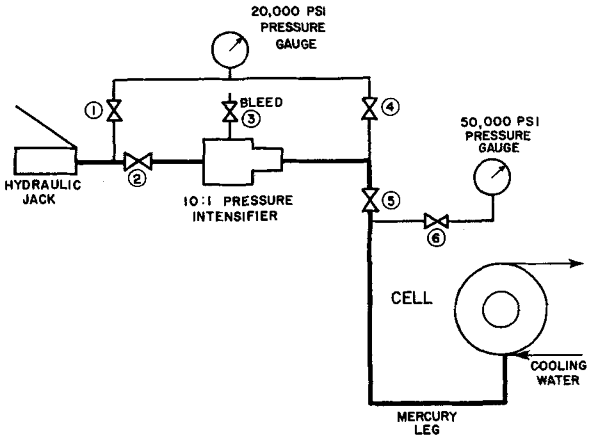

Fig. 3. Experimental apparatus.

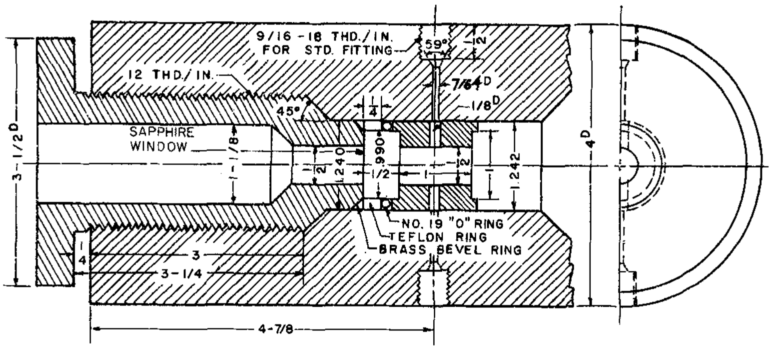

Fig. 2. High-pressure cell.

High-Pressure Cell—The high-pressure cell in shown in detail in Figure 2. It is a steel cylinder, 9¾ in. long by 4 in. in diameter, machined out of No. 4340 alloy steel heat treated to 43 Rockwell C. Two 1/16-in. holes were drilled along a diameter of the cell midway along the length. The hole at the top of the cell is used both for insertion of the sample mixture and for temperature measurement. The bottom hole is used to connect the cell to the pressure elevation apparatus. The outer ends of the holes were machined to accept ¼ in. high-pressure fittings.

The pressure chamber, in the center of the cell, is bounded by two 0.5 in. thick cylindrical sapphire windows which butt against two threaded end plugs; these end plugs were constructed of the same material as the cell body. To permit visual observation of the hydrocarbon system in the pressure chamber the end plugs are hollow along their longitudinal axes.

The system under observation is contained inside the steel filler plug in the center of the cell by two loosely fitting sapphire windows. The actual pressure seal is made by two silicone rubber *O* rings, each of which is bounded by the filler plug, cell wall, sapphire window, and a Teflon ring of rectangular cross section. Triangular brass washers fit between the Teflon rings and the end plugs.

The seal has proved to be extremely efficient against pressure leakage. No pressure drop was observed on the gauges when the cell was left with a pressure of 40,000 lb./sq. in. for a period of 16 hr.

Complementary Pressure Equipment—The pressure elevation equipment is shown diagrammatically in Figure 3. Pressure is initiated by means of a 10,000 lb./sq. in. maximum hydraulic jack. Hydraulic oil transmits the pressure through ¼ in. high-pressure tubing to a valve 2. The pressure is then increased approximately ten times by means of a piston type of intensifier. The intensified pressure is then transmitted by means of hydraulic oil through a 60,000 lb./sq. in. two-way valve which serves as both a tee and valve 4. Value 5 is a 60,000 lb./sq. in. valve which, when closed, allows pressure to be maintained on the cell alone. The line from valve 5 is connected through a 60,000 lb./sq. in. tee to the bottom opening in the high-pressure cell. Since the fluid transmitting the pressure comes in direct contact with the hydrocarbon system under observation, it is necessary that this fluid be essentially immiscible with hydrocarbons. For this reason this line was filled with mercury.

A line filled with hydraulic oil passes from the tee situated downstream from value 5 to a 50,000 lb./sq. in. bourdon tube pressure gauge. A 60,000 lb./sq. in. valve was installed in this line in order to avoid damage to the gauge when pressures above 50,000 lb./sq. in. were obtained.

Another supplementary line was constructed, bypassing the intensifier. The main purpose of this line is to permit hydraulic reversal of the intensifier piston. A 20,000 lb./sq. in. bourdon tube pressure gauge was installed between valves 1 and 4.

Temperature Control—A length of ⅜-in. copper tubing was wrapped around the cell and sealed to it with high-conductivity cement. The copper coil surrounding the cell was then wrapped with insulating material. Water from a bath whose temperature is controlled to ± 0.2°F. is continuously pumped through this copper coil during any experiment in order to maintain constant temperature of the test mixture in the high-pressure cell.

Safety Precautions—For reasons of safety the entire apparatus is situated behind a ¼ in. thick steel barricade. Only the necessary valve handles and pressure gauges protrude. A hole was cut in the wall to allow visual observation of the

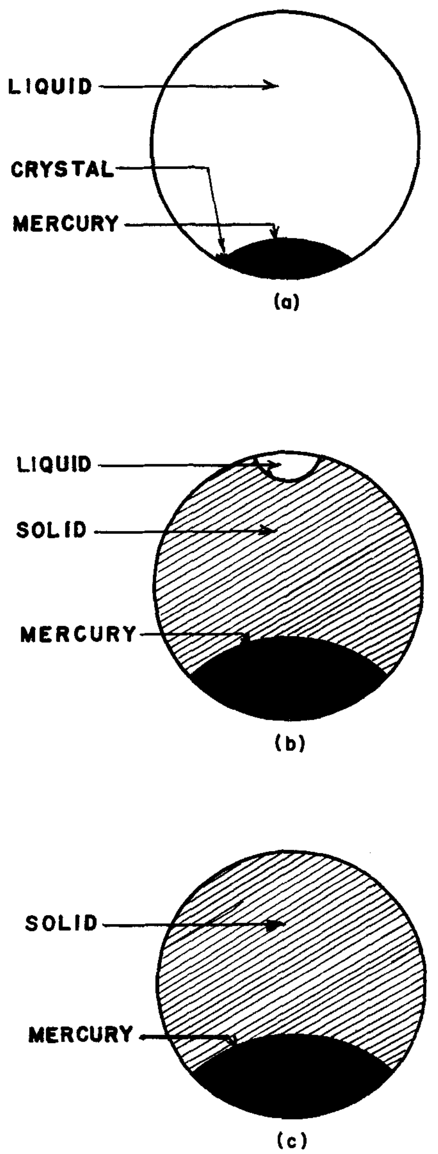

Fig. 4. Views of experimental liquidus and solidus points.

hydrocarbon system in the cell. The cell was displaced a foot from the opening and viewed through a periscope and magnifier which protect the observer from any fragments in the case of failure.

PROCEDURE

The experimental phase diagrams were obtained by determining, for several mixtures of known concentrations, both the liquidus pressure, or point where the first crystal is in equilibrium with the liquid, and the solidus pressure, or point of complete crystallization.

Preliminary

Test mixtures were analyzed to determine their exact concentrations by means of their refractive indices and placed in the cell through the top or sample entry port. This opening was then sealed by means of the high-pressure thermocouple fitting.

TABLE 1. EXPERIMENTAL RESULTS FOR THE ETHYLENE BROMIDE-ETHYLENE CHLORIDE SYSTEM AT 51°F.

Mole fraction ethylene chloride	Initiation pressure, lb./sq. in.	Liquidus pressure, lb./sq. in.	Solidus pressure, lb./sq. in.
0	—	14.7[†]	14.7[†]
0.145	6,000	2,600	9,000
0.310	14,000[*]	7,200	18,400
0.550	19,700	16,500	23,800
0.796	29,000	25,400	30,100
1.00	35,000	34,300	34,300

[*] Pressure here was probably increased too rapidly.

[†] Accepted as normal freezing point for ethylene bromide.

Liquidus Determination

Pressure on the system was slowly increased until initiation of crystallization. The pressure was then slowly decreased until the last visible crystal remained in apparent equilibrium with the liquid. The approximate size of this crystal is sketched in Figure 4*a*. At least 1 hr. was allotted to enable the system to reach this equilibrium. This pressure was then recorded as the liquidus pressure for this concentration.

It is interesting to note that the initiation pressure was considerably higher than the pressure recorded as the liquidus point. For the benzene-*n*-heptane system it was about twice as great; that is a mixture whose liquidus point was 20,000 lb./sq.in. would not initiate crystallization until about 40,000 lb./sq.in. pressure was applied. For the ethylene bromide–ethylene chloride system initiation averaged about 3,000 lb./sq.in. above the liquidus pressure. The same effect was noted by Swallow and Gibson (*9*) using a similar experimental technique.

Solidus Determination

After the liquidus point had been recorded, the pressure was increased in increments of approximately 100 lb./sq.in. each until the entire mixture became homogeneously translucent.[*] This was recorded as the solidus pressure, or point of total solidification. The solidus point is more difficult to obtain with any accuracy than is the liquidus point.

After both the liquidus and solidus points were obtained, a check of the index of refraction was made, the cell was cleaned, and the procedure repeated with a mixture of different concentration. Five successful trials were carried out for the system ethylene bromide–ethylene chloride, and six for the system benzene-*n*-heptane.

Pressure Measurement

Pressure measurement is made by either of the two bourdon tube gauges. Pressures under 20,000 lb./sq.in. can be read directly on either gauge. When the pressure lies between 20,000 and 50,000 lb./sq.in. measurements can be made directly with the 50,000 lb./sq.in. gauge or can be determined upstream from the intensifier with the 20,000 lb./sq.in. gauge. Pressures in excess of 50,000 lb./sq.in. can be measured only indirectly upstream from the intensifier with the 20,000 lb/sq.in. gauge. All pressure measurements made directly are believed to be accurate to within 0.1% of the maximum gauge reading. Details of the calibration of the gauges are given by Winnick (*16*).

Two results in Table 2 were obtained by indirect measurement upstream from the intensifier. Although attempts were made at calibration of the intensifier, the failure of these calibrations to prove consistent caused the measurements so obtained to be extremely approximate.

Temperature Measurement

Temperature measurement is achieved by use of a specially designed thermocouple probe which is inserted into the opening in the top of the cell. The base of the thermocouple probe protrudes into the sample mixture approximately 0.1 in., the temperature being measured at that point.

The probe was constructed of 1/8-in. O.D. by 1/32-in. I.D. high-pressure tubing. The outside diameter was machined down to 3/32 in. to enable it to fit into the cell opening. One end of the probe was attached to a small section of ¼ in. high-pressure tubing, threaded to accept a 60,000 lb./sq.in. fitting. One junction of a copper-constantan thermocouple was sealed inside the other end with silver solder. The voltage from the thermocouple is measured with a potentiometer. Its precision is approximately ± 0.02 mv. or about ± 1°F.

Reagents and Analysis

Pure grade *n*-heptane was used exclusively. The benzene, ethylene bromide, and ethylene chloride were reagent grade chemicals.

A refractometer was used to determine the concentrations of the test mixtures. With the refractive index of the experimental solutions it is pos-

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[*] A view of the pressure chamber at a pressure within 1,000 lb./sq. in. of the experimental solidus point is seen in Figure 4*b*. At the top a small area is observed which appears brighter than the remaining area. It is assumed that this area is mostly liquid. In Figure 4*c* the view at the experimental solidus point is seen. The brighter area has gradually disappeared, and the entire mixture is now believed to be crystallized. Because change is so gradual, accurate ascertainment of the pressure of complete solidification is difficult.

sible to determine their concentrations with an estimated accuracy of ± 0.5%.

RESULTS AND CONCLUSIONS

The experimental results for the ethylene bromide–ethylene chloride system are recorded in Table 1. The experimentally determined phase diagram is shown as smooth curves drawn through the five liquidus and solidus points plotted on Figure 1. The discrepancies between the experimental (solid) and predicted (broken) curves are probably due both to errors in the experimental and predicted results.

The visual observation technique employed undoubtedly led to some error in the solidus point determinations, but the main experimental error was probably caused by nonequilibrium. Mixing through the liquid with no mechanical agitation is slow; diffusion through the solid phase is many times slower. It should be noted in Figure 1 that although the experimental liquidus points lie close to the predicted liquidus curve, all of the solidus points are above the predicted solidus curve. This can be explained on the basis of incomplete mixing in the solid phase. Under such conditions the liquid phase becomes rich in ethylene chloride, causing a higher pressure necessary for final solidification.

Two factors led to inaccuracies in the location of the predicted curve. Although the system ethylene bromide-ethylene chloride has been reported to form near-ideal solid solutions at 1-atm. pressure (*13*), there may be sizeable deviations from ideality in one or both phases at higher pressures, rendering the ideal equations inaccurate for description of the system. To make matters worse, many approximations had to be made in applying the ideal equations, owing to the lack of compressibility and specific volume data for the pure components at the higher pressures.

It is impossible to say whether experimental or calculational error is more responsible for the lack of agreement. If complete thermodynamic data ($\overline{V}$ and $\overline{\gamma}$) were available to permit evaluation of the rigorous equations, it would have been possible to determine the experimental error. If, on the other hand, the experimental results were assumed correct and sufficient data were available, the true activity coefficients for the system could be obtained by substituting these values into the rigorous equations. As these data are not available, no such calculations were possible.

The results for the benzene-*n*-heptane system are presented in Table 2. Although liquidus point data were obtained only to *n*-heptane concentrations of 72.5%, a mixture of 86% *n*-heptane was tested. No initiation was observed for this mixture at an approximate pressure of 80,000 lb./sq.in., the pressure limit of the present equipment.

TABLE 2. EXPERIMENTAL RESULTS FOR THE BENZENE-*n*-HEPTANE SYSTEM AT 35°F.

Mole fraction *n*-heptane	Initiation pressure, lb./sq. in.	Liquidus pressure, lb./sq. in.
0	—	14.7
0.151	4,100	2,000
0.237(5)	7,300	4,100
0.465	16,000	11,200
0.533	29,000	13,300
0.594	(32,000)*	17,100
0.725	49,000	30,000
0.860	>(80,000)*	

* Approximate values determined from measurements made upstream from the intensifier.

No solidus points were reported for this system, although the mixtures did appear to become homogeneously translucent. The reason for this is as follows: benzene-*n*-heptane has been reported to be an eutectic forming mixture (*6*). That is the mixtures are mutually insoluble in the solid phase. As the pressure is increased, pure benzene crystallizes. However great occlusion of *n*-heptane occurs in the benzene crystals, causing what appears to be a homogeneous solid (*5*). The eutectic is expected to be reached at a pressure in excess of 100,000 lb./sq.in. (*2*) and a mole-fraction of approximately 0.93 n-heptane (*6*).

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NOTATION

$\overline{G}_{ijP}$ = partial molal free energy of component i in phase j at pressure P

$\overline{G}_{ijP_j^\circ}$ = partial molal free energy of component i in phase j at pressure P_j°

$G_{ijP_j^\circ}$ = molal free energy of pure component i as phase j at pressure P_j°

G_{ijP_i} = molal free energy of pure component i as phase j at pressure P_i

P = pressure of system

P_j° = pressure at which solution behavior (activity coefficient) data are available for phase j

P_i = pressure at which solid and liquid phases of pure component i are at equilibrium

R = gas constant

T = temperature

$\overline{V}_{ij}$ = partial molal volume of component i in solution in phase j

V_{ij} = molal volume of pure component i as phase j

X_{ij} = mole fraction of component i in phase j

Greek Letters

α_s = defined by Equation (11)

$\overline{\beta}$ = isothermal compressibility

$$= \frac{10^6[(V_i)_l^\circ - (V_i)_l]}{(V_i)_l^\circ(P_i - P^\circ)} \quad (15)$$

$\overline{\gamma}_{ijP_j^\circ}$ = activity coefficient of component i in solution in phase j at pressure P_j°

Γ_{Vi} = defined by Equation (12)

$\overline{\Gamma_{Vi}}$ = defined by Equation (13)

Subscripts

i = component i

j = phase j

l = liquid phase

s = solid phase

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