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and

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The P-V-X Behavior of the Liquid System Acetone-Carbon Disulfide at Elevated Pressures

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The change in volume on mixing for a system showing large positive deviations from ideality is examined at one temperature to pressures of 100,000 lb./sq.in. Original atmospheric pressure density data and compression measurements over the entire mole fraction range for this system, acetone–carbon disulfide, are reported at 0°C. These are correlated with the semiempirical Tait equation to yield change in volume on mixing as a function of mole fraction and pressure. This volume change is found to decrease from the maximum of 1 cc./mole at atmospheric pressure to about 0.4 cc./mole at 100,000 lb./sq.in. The maximum also shifts during this pressure increase from 0.53 mole fraction acetone to 0.74.

Simultaneous determination of pressure, specific volume, temperature, and composition provides some of the most fundamental thermodynamic data. Relatively few measurements of this type on liquids have been reported in the literature.

Although some cursory investigations of the effect of pressure on the properties of liquids were conducted in the latter part of the 19th century, comprehensive studies of this type began with Bridgman in the early part of this century (*1*). It was the work of Bridgman which raised the limits of obtainable working pressures to over 1,000,000 lb./sq. in. However, his work was devoted exclusively to pure compounds (*2* to *6*). The effect of pressure on the physical properties of liquid mixtures has, as would be expected, received less attention. Aside from compressibilities at 1 atm., calculated from velocity of sound measurements (*7* to *9*), the works of Gibson (*10*), Eduljee (*11*), Reamer (*12*), and Cutler (*13*), concerning binary liquid compressions for a total of nine systems, stand alone. The prediction of the pressure effect on liquids has been almost completely limited to single component systems (*14* to *16*).

The purpose of this investigation was to obtain isothermal P-V-X data for the system acetone–carbon disulfide over the entire range of composition and for pressures up to 100,000 lb./sq. in. These data were then to be used in a study of the liquid-liquid phase behavior of this system.

THERMODYNAMIC RELATIONS

Isothermal P-V-X data over the entire range of composition and over a considerable pressure range result from experimental determinations of mixture densities at one atmosphere pressure and compressibility measurements from one atmosphere up to elevated pressures. Interpretation and application of such data are facilitated by the use of several thermodynamic relations summarized in the following paragraphs.

Densities at 1 Atm.

Experimental density data, originating under isothermal and isobaric conditions, may be correlated by first converting the data to change in volume on mixing:

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$$(\Delta V^m)^o = \left[\frac{X_1 (MW)_1 + X_2 (MW)_2}{\rho^o{}_m} \right] - \left[X_1 \frac{(MW)_1}{\rho^o{}_1} + X_2 \frac{(MW)_2}{\rho^o{}_2} \right] \quad (1)$$

Then, if the solutions are regular, these values may be fit using the equation given by Hildebrand and Scott (*26*):

$$(\Delta V^m)^o = \frac{- K_{12} X_1 X_2 V^o{}_1 V^o{}_2 \left[X_1 (\partial V_1/\partial P)^o{}_T + X_2 (\partial V_2/\partial P)^o{}_T \right]}{[X_1 V^o{}_1 + X_2 V^o{}_2]^2} \quad (2)$$

Nonregular solutions are also able to be fit with this equation. However, the value of K_{12} will be as strong a function of composition as the mixture is nonregular.

Compression Data

No satisfactory theory presently exists for the accurate prediction of the effect of pressure on liquid densities. In 1888, however, Tait (*17*) showed that the isothermal compressibility of liquid water could be well represented with the two-constant equation:

$$-\left(\frac{dV}{dP} \right)_T = \frac{J}{L + P} \quad (3)$$

Since that time this equation has been used with considerable success for many liquids (*11, 18* to *22*) and some liquid mixtures (*11, 23*). The constant L seems to be a function of temperature, while J seems to be nearly temperature independent for a given substance. Both are independent of pressure up to about 200,000 lb./sq. in. The dependence even then is slight (*24*).

Recently, this equation has been shown to have theoretical justification. Using association theory, Ginnell has arrived at a relationship for liquid compressibilities of identical form to the Tait equation (*25*).

The Tait equation can be integrated to yield:

$$\frac{V}{V^o} = 1.0 - \frac{J}{V^o} \ln \left(\frac{L + P}{L + P_o} \right) \quad (4)$$

EXPERIMENTS

Equipment

Densities at 1 Atm. Criteria mentioned elsewhere (*27*) made it necessary to use 0°C. for the study. However, literature values for the densities of acetone–carbon disulfide mixtures at 0°C. (*34* to *36*) as shown later, were found to be inconsistent. This necessitated determination of these data. A high-volatility pycnometer was used in a straightforward manner. All measurements were made in a room maintained at 0°C. (*27*).

Compressibilities—P-V-T Cell. In order to ascertain the change in volume on mixing as a function of pressure over the entire range of composition, a piezometer similar to that used by Bridgman (*28*) was used. Figure 1 shows the piezometer and high pressure enclosure. The cell consists of a 4-in.-diameter hardened steel vessel with a 6-in.-diameter sleeve shrunk over it. The diameter of the enclosure, shown in Figure 1, is 1 in. The pressure seal is made with a rubber O ring, **17**, a lead washer, **18**, and a steel ring, **19**.

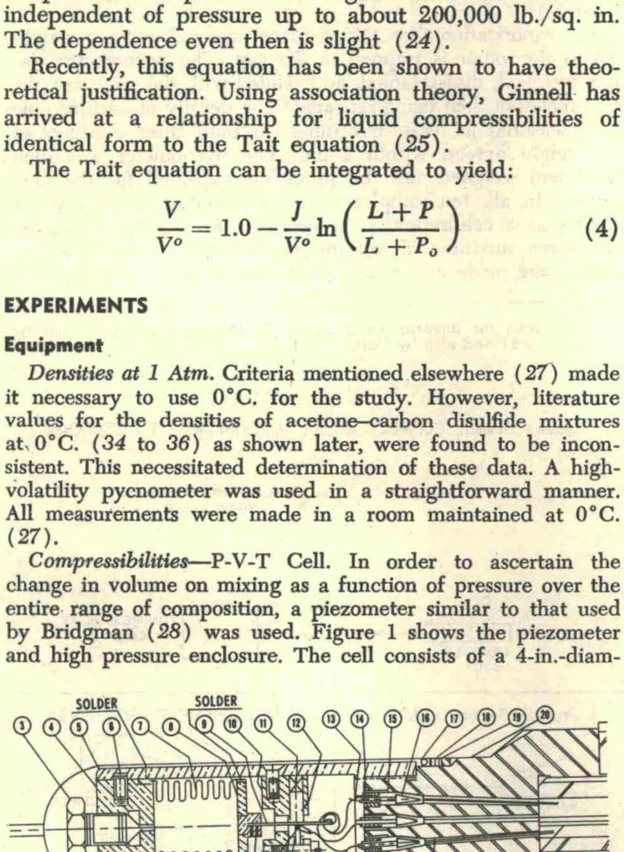

Fig. 1. P-V-T cell

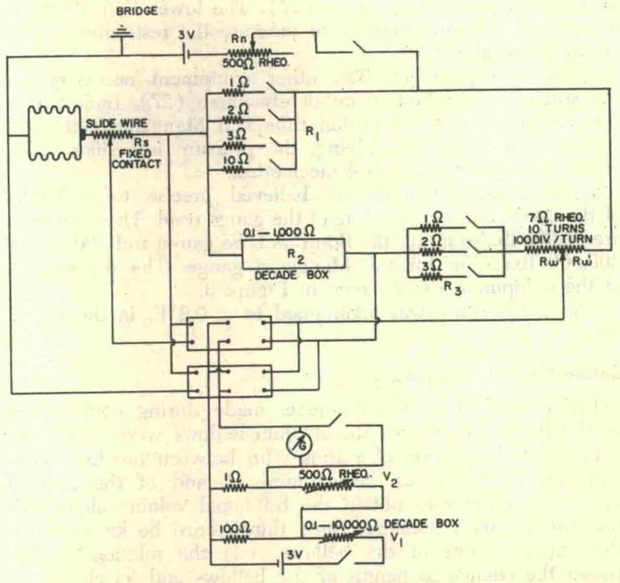

Fig. 2. Resistance measuring bridge.

The mixture under observation is contained in a brass sylphon bellows, **7**, which is sealed by means of the cap screw, **3**. This bellows is held firmly in place at one end by three brass screws, **6**, to the retainer, **5**, also made of brass. The other end of the bellows is free to move. A piece of Karma wire, **9**, is fixed at one end to this free end of the bellows by a set screw, **24**, and at the other to two flexible electrical connections, **13**. One is a current and the other a potential lead. This arrangement eliminates the necessity of correcting for lead wire resistance. The connections are led out of the cell through porcelain insulators, **14**. The Karma wire passes across a fixed contact, **25**, to which it is firmly pressed by a spring, **11**, and Teflon piston, **12**. An electrical lead from the fixed contact, **30**, as well as the leads from a Chromel-Alumel thermocouple, are brought out of the pressure chamber in the same manner as the Karma wire leads. The thermocouple junction lies in the space to the right of the Teflon piston, **12**. The bellows is removed from the cell body by unscrewing the entire end plug from the cell body. The three brass screws, **6**, holding the bellows to the retainer, **5**, and the screw, **24**, holding the Karma wire to the bellows are then removed, releasing the bellows for cleaning and refilling.

The entire cavity around the bellows is filled with the pressure transmission fluid, JP-4 jet fuel. This was chosen for its comparatively low viscosity at high pressures and low temperatures, its low cloud point, and its relatively low cost. As pressure is applied to the pressure transmission fluid, the bellows contracts, equilibrating the pressure within it to that without. This movement occurs along its longitudinal axis due to the design of the bellows (*28*). The Karma wire is pulled past the fixed contact, and a change in the resistance between either end of the wire and the fixed contact is observed. Suitable calibration yields change in volume as a function of change in resistance.

Measuring Bridge. The electrical bridge used to note the change in resistance is shown as Figure 2. When the slide wire has ceased to move on the fixed contact, the resistance of the segment between fixed contact and the right hand end of the wire is balanced against the lower section of the bridge by closing the upper DPDT switch to the left, and adjusting the 500 ohm-rheostat. A Rubicon Instrument Company Galvanometer indicates the null in the circuit. The upper DPDT switch is then closed to the right and the upper portion of the bridge is balanced against the lower by adjusting the 7-ohm rheostat, *Rw-Rw'*. This configuration eliminates the need of a standard potential source (*27*). The lower DPDT switch is used in the same manner to measure the resistance of the entire Karma slide wire.

Auxiliary Equipment. The other equipment necessary for the study is described in detail elsewhere (*27*). Included in this category are the Bourdon tube and Manganin coil pressure gauges (*29*), the valving, the pressure intensifier (*29*), and the temperature control mechanism.

Pressure measurements are believed precise to ± 0.25% of the maximum scale reading of the gauge used. These maxima are 50,000 lb./sq.in. for the Bourdon tube gauge and 100,000 or 200,000 lb./sq.in. for the Manganin gauge. The orientations of the equipment can be seen in Figure 3.

The temperature was maintained to ± 0.2°F. in the P-V-T cell.

Calibration of Equipment

P-V-T Cell. The measurements made during compression of the liquid samples in the sylphon bellows were of the resistance of the section of Karma wire between the fixed contact and flexible leads (see Figure 1) and of the applied pressure. In order to obtain the fractional volume change of the samples with pressure, three things must be known: (1) the initial volume of the bellows; (2) the relationship between the change in length of the bellows and its change in volume; and (3) the relationship between the change in resistance of the Karma wire and its length, and hence, the length of the bellows.

The first of these, the initial volume of the bellows, was calculated from the weight of the sample within it and the density at 1 atm. Instead of determining the other two relations separately, it was decided to carry out a calibration incorporating both.

If a linear relationship is assumed between the change in volume of the bellows with pressure and the change in resistance of the Karma wire segment with length, then

$$\Delta V = K \Delta R_S \tag{5}$$

Then, dividing by V^o, the initial volume of the bellows

$$\Delta (V/V^o) = \frac{K}{V^o} \Delta R_S \tag{6}$$

a relationship is obtained which describes the fractional volume change of a sample with pressure. The constant K is determined by making use of the literature data (*30*) for the compressibility of pure carbon disulfide at 0°C. These literature data were fitted to the Tait equation:

$$\frac{V}{V^o} = 1 - J'_{cs2} \ln \left[\frac{L_{cs2} + P}{L_{cs2}} \right] \tag{7}$$

A least square curve fitting routine was used to determine J'_{cs2} while L_{cs2} was preset with that value obtained from fitting in a similar manner the raw experimental data of this investigation for pure carbon disulfide at 0°C. to obtain the best values for Ro,* $(J_r)_{cs2}$, and L_{cs2}:†

$$R_S = R_O - (J_r)_{cs2} \ln \left[\frac{L_{cs2} + P}{L_{cs2}} \right] \tag{8}$$

The literature values of V/V^o, available only to 15,000 lb./sq.in., were fitted in this manner with a maximum deviation of 0.0002 and an average deviation of 0.00008 cc./cc.

If the above mentioned linearity assumption between volume and resistance is valid, then

$$K = \frac{J'_{cs2} (V^o)_{cs2}}{(J_r)_{cs2}} \tag{9}$$

and the resistance values from experimental runs with samples of any concentration can be fitted using an equation similar to Equation (8). The values for V/V^o vs. P for any sample i are then calculated as

$$\frac{V}{V^o} = 1 - J_i' \ln \left[\frac{L_i + P}{L_i} \right] \tag{10}$$

To evaluate the effect of higher pressures on the linearity assumption, two tests were carried out. First, the change in bellows volume with length was determined over a large range in volume and second, the resistance of the Karma wire was measured as a function of pressure. These tests are described elsewhere** (*27*).

The results showed the bellows to be as linear as was able to be determined (± 0.5% during a compression of 10%). Bridgman has found, however, with bellows of much more crude construction, that the linearity is better than 0.1% (*28*). Also, because any small nonlinearity would not cause a measurable error in the volume change on mixing values (these being determined by relative and not absolute compressibilities), no attempts were made to correct for these small effects.

The bellows constant K as determined to 15,000 lb./sq.in. was used unaltered over the entire range of pressures.

Procedure

Densities at 1 Atm. The pycnometer mentioned earlier was used to determine the density-composition diagram of the system acetone–carbon disulfide at 0°C.

Samples of known mole fraction were made using the method of Powers (*31*), whereby samples of the pure liquids are injected into a preweighed, rubber-covered glass bottle using a hypodermic needle and syringe.

The pycnometer was filled with the liquid in question and placed in the ice bath up to the neck. After 20 min. the stopper was inserted rather abruptly so as to cause a jet of liquid to be ejected through the hole in its center. The stopper and outer ground glass joint on the pycnometer body were then carefully dried so as to leave the level of liquid exactly even with the top of the stopper and the cap firmly pressed in place.

Any vaporization then taking place does not cause a weight loss as the vapor is trapped in the cap. The pycnometer was then weighed, disassembled, and refilled with the same sample, the procedure then being repeated. The density of each sample was measured at least four times, or until three readings of the weight agreed within 1 mg. The pycnometer was then dried and weighed and the procedure repeated for the next sample. In all, ten samples were run; doubly distilled water serving as a calibration, pure acetone, pure carbon disulfide, and seven mixtures of varying mole fractions. All measurements were made in a room maintained at 0°C.

* The value for R_o could not be determined experimentally. Vapor bubbles caused expansion of the bellows to an unknown degree at atmospheric pressure.

† The fiducial pressure P_o is neglected in these equations because the error in L is greater in absolute magnitude than P_o.

** The tests for linearity were essentially the same as those used by Bridgman (*28*) and also by Cutler (*13*).

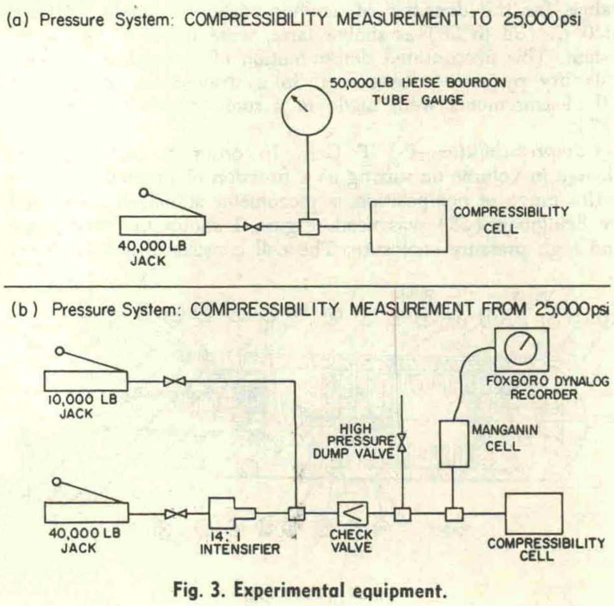

Fig. 3. Experimental equipment.

P-V-T Measurements. For determination of the isotherm of each of the acetone-carbon disulfide mixtures, the vessel shown in Figure 1 was used in combination with the measuring bridge (Figure 2). The cell was maintained at 0°C. at all times. In preparation for the determination of an isotherm, a sample was prepared in the same manner as for the density measurements. The bellows was removed from the Karma wire and retainer, cleaned thoroughly with acetone and then ether, dried by vacuum, and weighed along with the screw cap. The sample was then inserted by compressing alternately the bellows and then slowly filling with a hypodermic needle and syringe as the bellows was allowed to expand. When no air bubbles were seen during the compressions, the bellows was assumed full of liquid. An excess of liquid was allowed to remain which was then forced out as the cap was screwed in. The bellows was then rinsed in ether and vacuum dried. Special care was exercised in drawing out liquid which remained in the threads of the opening. When the bellows ceased to lose weight on standing, the weight was recorded and the bellows reinserted into the retainer, the Karma wire fixed into its housing on the bellows, and the entire assembly replaced into the cell. About 3 hr. were allowed to assure temperature equilibrium. Although the thermocouple potential would stabilize after about 20 min., the bellows and its contents were not assumed to be at temperature equilibrium until no change in resistance with time was noted on the measuring bridge. This indicated the bellows was no longer contracting. Pressure was then applied in an increment of 2,500 lb./sq.in. and after thermal equilibrium was again attained the resistance of the section of Karma wire between the fixed contact and the flexible leads was recorded. About 20 min. was usually sufficient to assure this equilibrium. The change in the resistance during a pressure change of 2,500 lb./sq.in. was about 0.005 ohm. Subsequent pressure applications were similarly made until the upper limit was reached. The procedure was then repeated as the pressure was decreased.

Eighteen samples of different mole fractions were investigated. Twelve of these were examined from 1 atm. to 30,000 lb./sq.in., the pressure limit for the needle valve between the jack and the P-V-T-cell, using the arrangement shown in Figure 3*a*. The other six were examined from 1 atm. to their upper pressure limit using the arrangement shown in Figure 3*b*. The measurements were divided into these two groups in order to obtain the best possible accuracy in pressure measurement in the low pressure range where the compressibilities are high. The Heise Bourdon tube gauge allowed pressure measurement to ± 50 lb./sq.in. With the Manganin gauge and recorder, the precision dropped to ±250 lb./sq.in. However, in the high pressure range, the compressibility is lowered, so the precision in the calculation of relative volume is not greatly affected.

The freezing point of pure acetone is believed to be about 90,000 lb./sq.in. at 0°C. (*32*) and that of carbon disulfide 150,000 lb./sq.in. (*33*) at the same temperature. No studies have been made on the freezing pressure of mixtures of the two. Because freezing may permanently distort the bellows and render it useless, samples of high acetone concentrations were taken no higher than 85,000 lb./sq.in. The samples richer in carbon disulfide were compressed up to 100,000 lb./sq.in. and pure carbon disulfide up to 122,000 lb./sq.in.

Table 1. Results of Density Determinations

Acetone—carbon disulfide   0°C.   1 atm.

X_1 (acetone)	ρ^o, g./cc.	(V^o_m) raw, cc./g.-mole	(V^o_m) calc., cc./g.-mole
0.00000	1.29339	58.871	58.871
0.08742	1.23702	60.277	60.262
0.17477	1.18488	61.598	61.603
0.26538	1.13310	62.962	62.940
0.40644	1.06024	64.892	64.908
0.55761	0.98805	66.870	66.867
0.76863	0.89741	69.377	69.355
0.87559	0.85600	70.457	70.471
1.00000	0.81299	71.440	71.440

Density of pure acetone (literature) (*37*) = 0.81248. Density of pure carbon disulfide (literature) (*37*) = 1.29319.

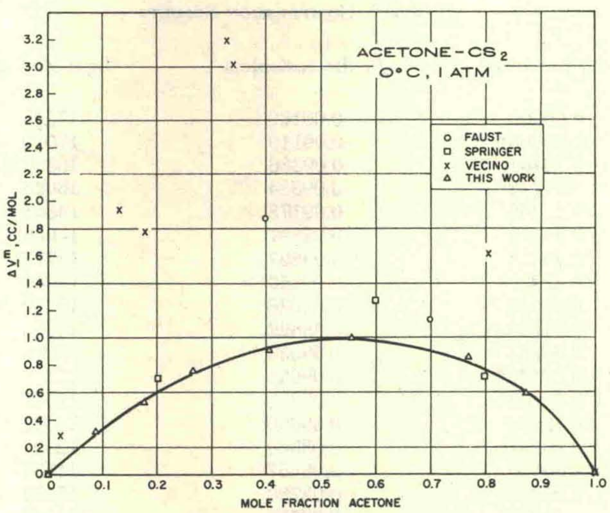

Fig. 4. Volume of mixing at 1 atm.

EXPERIMENTAL RESULTS

Densities at 1 Atm.

The densities of the nine acetone-carbon disulfide mixtures of different composition were calculated directly from the weight of the sample and volume of the pycnometer obtained from the water calibration. These results are shown as columns 1 and 2 in Table 1.

The molal volume of each sample (column 3) was calculated from the density and mole fraction of the sample:

$$(V^o{}_m)_{\text{raw}} = \frac{X_1(MW)_1 + X_2(MW)_2}{\rho^o} \tag{11}$$

The change in volume on mixing at 1 atm. was calculated with Equation (1) and plotted in Figure 4. Also shown in this figure are the other available data (*34 to 36*). The consistency of the data, shown especially with this severe test, can be seen.

P-V-T Measurements

The results of the compressions of the eighteen samples at 0°C. were fitted to the Tait equation and the best values for J' and L obtained. These results are shown in Table 2. The average error introduced by the fit was about 0.05%. That is, for any run, the difference between the value of V/V^o actually observed and that calculated using the Tait equation and these constants is roughly 0.0005.

The original data can be obtained from the junior author.

TREATMENT OF DATA

Densities at 1 Atm.

The experimental density data at one atmosphere pressure and 0°C., obtained with the pycnometer, were fitted using Equation (2). If the solutions were truly regular, the experimental values for density and for isothermal compressibility of pure compound j at 1 atm.

$$\left(\frac{\partial V_j}{\partial P}\right)^o_T = \frac{J'_j V^o{}_j}{L_j} \tag{12}$$

would yield a constant value for K_{12} when substituted into Equation (2). For these data, however, K_{12} varied

TABLE 2. COMPRESSION RESULTS

X_1 (acetone)	J'_i, dimensionless	L_i, lb./sq. in.
0.00000	0.09180	17170
0.00000*	0.09110	17010
0.10401	0.09366	16800
0.15436	0.09334	16625
0.22262*	0.09178	14601
0.25778	0.08897	14006
0.40473	0.09227	14775
0.42235*	0.09250	14046
0.50608	0.09036	13879
0.51046	0.08822	13159
0.60187	0.08939	13210
0.60720*	0.09084	12838
0.75209	0.08323	11517
0.75209*	0.09080	13036
0.89391	0.08966	12900
1.00000	0.08467	11554
1.00000	0.08783	12472
1.00000*	0.09273	14626

* Indicates high pressure trial.

with concentration. It was thus necessary to relate K_{12} with X_1 with an equation of the form:

$$K_{12} = K_o + B \exp (CX_1) \quad (13)$$

The values $K_o = 9.45 \times 10^4$, $B = 10.7$, $C = 6.74$ represented the data with an average deviation of 0.016% and a maximum deviation of 0.035%. The results are shown as column 4 in Table 1 and as the curve in Figure 4. Little theoretical significance is attributed to the fit. However, it provides a reasonable method of interpolation for the fiducial densities.

Compression Data

The data from each of the eighteen experimental compressions were fitted to the Tait equation to determine the best values of R_o, J'_i, and L_i as mentioned previously. In order to facilitate further computation using these results (38), the values of J'_i and L_i were fitted to a third-order polynomial against mole fraction. The results are shown below:

$$\overline{J'}_m = 0.09158 + 0.008499\, X_1 - 0.03482\, X_1^2 + 0.02415\, X_1^3 \quad (14)$$

$$\overline{L}_m = 17191. - 8455.2\, X_1 - 131.52\, X_1^2 + 4291.7\, X_1^3 \quad (15)$$

The average error introduced by the entire smoothing operation amounts to about 0.1%. That is, at any composition the difference between the value of V/V^o actually observed and that calculated using Equations (14) and (15) with the appropriate value of X_1 is about 0.0010.

The magnitude of the error can be seen with the aid of Figure 5. In this figure is plotted molar volume vs. mole fraction acetone at five representative pressures, including atmospheric. The circled points are calculated directly from the compression results of Table 2 and the relationship from Equation (10):

$$V_m = V^o{}_m \left[1 - J'_i \ln \left(\frac{L + P}{L} \right) \right] \quad (16)$$

The curves shown in Figure 5 were calculated in exactly the same manner, except that the smoothed constants, $\overline{J'}_m$ and $\overline{L}_m$ were used.

The molar change in volume on mixing can be found at any pressure and composition. Equation (17) is obtained from appropriate substitution of Equation (10) into the definition of the volume change on mixing at pressure P:

$$\left[\Delta V^m = (\Delta V^m)^o - (V_m)^o \overline{J'}_m \ln \left(\frac{\overline{L}_m + P}{\overline{L}_m} \right) + X_1 (V_1)^o J'_1 \ln \left(\frac{L_1 + P}{L_1} \right) + X_2 (V_2)^o J'_2 \ln \left(\frac{L_2 + P}{L_2} \right) \right]_{T,x} \quad (17)$$

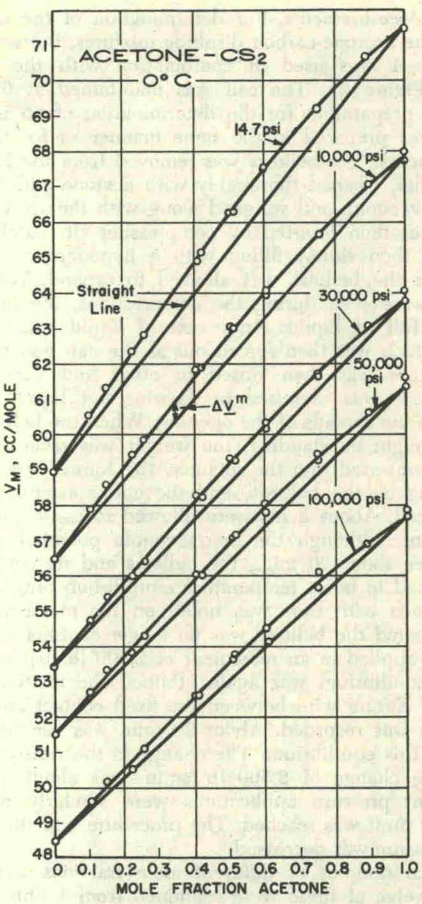

Fig. 5. Molar volume at representative pressures.

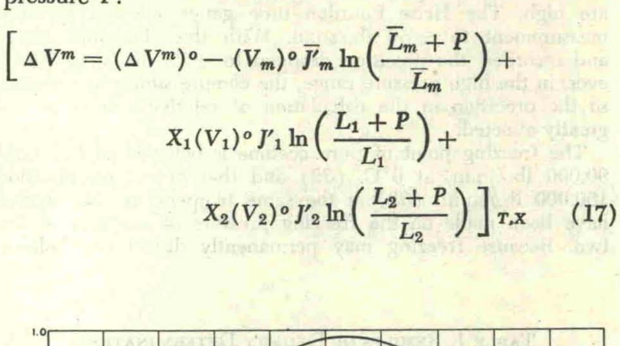

Fig. 6. Volume of mixing at representative pressures.

where values of J'_j and L_j for the pure components from Equations (14) and (15), respectively, with $X_1 = 1.00$ for pure component 1 and $X_1 = 0.0$ for pure component 2. The resultant curves at some representative pressures are shown as Figure 6.

The second smoothing operation is seen to allow the calculation of ΔV^m at any pressure and mole fraction. This is especially useful if calculations are to be carried out using these results. Such a calculation is reported in a subsequent study (38).

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NOTATION

B = constant defined in Equation (13)
C = constant defined in Equation (13)
J = Tait equation constant, cc.
J'_1 = Tait equation constant for pure compound 1, dimensionless
J'_2 = Tait equation constant for pure compound 2, dimensionless
$\overline{J'}_m$ = best fit value for Tait constant [Equation (14)], dimensionless
J'_{cs_2} = constant defined in Equation (7), for pure carbon disulfide, dimensionless
$(J_r)_{cs_2}$ = constant as defined by Equation (8), for pure carbon disulfide, ohms
J'_i = Tait equation constant for sample i, dimensionless
j = subscript indicating either pure component 1 or 2
K = bellows constant, defined by Equation (5)
K_{12} = constant defined by Equation (2)
L = Tait equation constant, lb. sq. in.
L_{cs_2} = Tait equation constant for pure carbon disulfide, lb./sq. in.
L_1 = Tait equation constant for pure component 1, lb./sq. in.
L_2 = Tait equation constant for pure component 2, lb./sq. in.
$\overline{L}_m$ = best fit value for Tait constant [Equation (15)], lb./sq. in.
L_i = Tait equation constant for sample i, lb./sq. in.
$(MW)_1$ = molecular weight of acetone
$(MW)_2$ = molecular weight of carbon disulfide
P = pressure, lb./sq. in.
P_o = initial pressure, lb./sq. in.
R_o = resistance of Karma wire at atmospheric pressure, ohms
R_1, R_2, R_3, R_n = components in measuring bridge (Figure 2), ohms
R_S = resistance of Karma wire segment as measured, ohms
$R_w - R'_w$ = slide wire rheostat, ohms
T = temperature
V = volume of bellows at pressure P, cc.
V^o = volume of bellows at 1 atm., cc.
V_1, V_2 = components in measuring bridge (Figure 2)
$V^o{}_1$ = molal volume of pure component 1 at 1 atm., cc.
$V^o{}_2$ = molal volume of pure component 2 at 1 atm., cc.
V_m = molal volume of mixture at pressure P, cc.
$V^o{}_m$ = molal volume of mixture at 1 atm., cc.
$(V^o)_{cs_2}$ = volume of bellows at 1 atm. containing pure carbon disulfide, cc.
$(V^o{}_m)_{raw}$ = molal volume of mixture at 1 atm. as obtained directly from the density data at 0°C., cc.
$(V^o{}_m)_{calc.}$ = molal volume of mixture at 1 atm. as calculated using Equations (2), (12), and (13), cc.
ΔV^m = molal change in volume on mixing at pressure P, cc.
$(\Delta V^m)^o$ = molal change in volume on mixing at 1 atm., cc.
X = mole fraction
X_1 = mole fraction component 1 (acetone)
X_2 = mole fraction component 2 (carbon disulfide)
ρ^o = density at 1 atm., g./cc.

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Liquid-Liquid Phase Behavior of Binary Solutions at Elevated Pressures

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Isothermal pressure elevation can sometimes cause liquid-liquid phase separation of binary liquid mixtures. A quantitative thermodynamic analysis of this effect is made and applied to the system acetone—carbon disulfide at 0°C. with the use of available P-V-T-X data and vapor pressure data at low pressure. Visual observations of the phase separations at pressures up to 80,000 lb./sq.in. were used to compare with the results of the thermodynamic analysis.

The separation of two liquid phases in equilibrium has been the subject of much study (*1*), and thus the phase behavior of a large number of binary liquid systems has been examined. While both temperature and pressure affect the phase behavior of such systems, few of the investigations have been concerned with the pressure effect (*2*). Correspondingly, the prediction of the effect of pressure on liquid-liquid phase behavior has received almost no attention whatever (*3*).

Timmermans (*4*) was among the first to investigate experimentally the effect of pressure on the mutual solubility of binary liquid mixtures. Subsequent studies of this type have been recently catalogued by Timmermans in a rather comprehensive fashion (*2*).

The general techniques for the use of thermodynamics in the prediction of the effect of pressure on phase equilibria were elucidated over 30 yr. ago by Adams (*5*), and have been used to predict isothermal phase diagrams of solid eutectic forming systems (*5, 6*) and the isothermal solid-liquid phase behavior of binary systems which form solid solutions (*7*). There has, however, been no attempt to use these techniques for the prediction of the pressure effect on the mutual solubilities of liquid pairs.

The thermodynamic prediction of the pressure effect on phase equilibria is invariably dependent on knowledge of solution behavior data for the system in question at some reference pressure as well as the volumetric properties of the phases as functions of pressure (*5*). Solution behavior data, usually expressed in terms of activities, have been the object of a large amount of research, especially for binary mixtures of nonelectrolytes (*2*). The volumetric properties of condensed phases under pressure have not been nearly as well investigated (*8*).

It was decided to develop a method for predicting the effect of pressure on the liquid-liquid phase behavior of a binary mixture of nonelectrolytes. Such a method would be based on thermodynamic relations similar to those developed by Adams (*5, 6*) and by Winnick and Powers (*7*) for solid-liquid behavior. The visual observation of phase separation would also be attempted for comparison with the predicted results.

THERMODYNAMIC DEVELOPMENT

At constant pressure and temperature the criterion for equilibrium in any system is that the Gibbs free energy must be at a minimum (*9*). Thus, a binary liquid system will separate into two liquid phases only if such a configuration will provide the system with a lower free energy than would be available if the system remained as a single phase. It remains only to provide a relationship which will allow the calculation of the free energy of such a system in terms of thermodynamic quantities which are either available or obtainable in the laboratory.

The molal free energy of mixing ΔG^m is defined as the difference between the free energy of a mole of solution and the sum of the free energies of the unmixed components:

$$[\Delta G^m = G_m - \Sigma X_i G_i]_{T,P} \tag{1}$$

Alternatively, this expression can be written as the sum of the ideal and excess free energies of mixing. For the case of a binary mixture

$$(\Delta G^m)_{T,P} = RT\,(X_1 \ln X_1 + X_2 \ln X_2) + (\Delta G^E)_{T,P} \tag{2}$$

True Free Energy Diagram

When plotted against mole fraction, the change in free energy on mixing will appear similar to the lower curve in Figure 1 if substances 1 and 2 are completely miscible. If instead a plot such as the upper curve is obtained, a miscibility gap is indicated. Any mixture whose homogeneous* concentration lies between X_1' and X_1'', say at X_1^o,

* That concentration which would result if the mixture were a single phase.

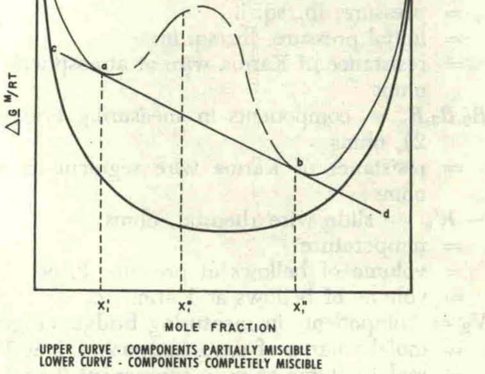

Fig. 1. Hypothetical free energy diagram.

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will be in equilibrium only when two liquid phases of compositions X_1' and X_1'' are present. Points a and b are determined from the points of tangency of a straight line cd. In this composition range the free energy of two such phases is lower than that resulting from a single phase. The portion of the curve between a and b is dotted because this is a hypothetical region.

It is easily shown that the concentrations of the phases in equilibrium are determined by a straight line drawn tangent to the curve at two points (*10*) and that the true portion of the curve between these two concentrations is this same straight line (*10*). The reasons for general use of the continuous curve are given by Rowlinson (*11*) and will not be dealt with here.

Effect of Pressure

The effect of external pressure on the free energy of mixing of a binary liquid system can be described as

$$\left(\frac{\Delta G^m}{RT}\right)_{T,P,X} = \left(\frac{\Delta G^m}{RT}\right)_{T,P_o,X} + \frac{1}{RT}\int_{P_o}^{P}\left(\frac{\partial \Delta G^m}{\partial P}\right)_{T,X} dP \quad (3)$$

From basic thermodynamics

$$\left(\frac{\partial \Delta G^m}{\partial P}\right)_{T,X} = \Delta V^m \quad (4)$$

so that

$$\left(\frac{\Delta G^m}{RT}\right)_{T,P,X} = \left(\frac{\Delta G^m}{RT}\right)_{T,P_o,X} + \frac{1}{RT}\int_{P_o}^{P} \Delta V^m\, dP \quad (5)$$

A similar form is obtained in terms of the excess free energy on mixing

$$\left(\frac{\Delta G^E}{RT}\right)_{T,P,X} = \left(\frac{\Delta G^E}{RT}\right)_{T,P_o,X} + \frac{1}{RT}\int_{P_o}^{P} \Delta V^m\, dP \quad (6)$$

By use of Equation (5), the free energy of mixing for any binary system can be evaluated at any pressure if the free energy is known at some pressure P_o and change in volume on mixing data are available from pressure P_o to the pressure desired over the entire range of composition. If the system in question is completely miscible at pressure P_o, but becomes partially immiscible upon application of pressure, this effect will be indicated by a straight line portion in the free energy diagram as explained above (see Figure 1). Equation (5) indicates this will be possible only if ΔV^m is positive.

Representation of Free Energy Diagram

The free energy curve, or excess free energy curve, at any pressure must be thermodynamically consistent across the range of mole fraction. This consistency can be assured when two sets of data are added, as suggested by Equations (5) and (6), by smoothing with respect to mole fraction using the technique reported by Myers and Scott (*12*). This method utilizes the least-square fitting of the values found from Equation (6) in the form:

$$\left(\frac{\Delta G^E}{RT}\right) = \frac{X_1X_2}{1-B(1-2X_1)}\sum_{n=0}^{m} A_n\,(1-2X_1)^n \quad (7)$$

This technique, while not "improving" the data, offers a convenient, thermodynamically consistent means of representing them.

CHOICE OF SYSTEM AND TEMPERATURE

Use of the qualitative tools presented by Prigogine (*3*) is a great aid in the selection of systems which may separate into two liquid phases under isothermally increasing pressures. Four criteria were used in selecting a system for experimental study (*10*):

1. The system must be a binary nonelectrolyte solution.
2. It must either have been noted to separate under isothermally increasing pressures, or be expected to do so as a consequence of a large positive excess free energy of mixing at 1 atm., and positive volume changes on mixing.
3. Solidification must not occur at pressures below those necessary to cause liquid-liquid phase separation.*
4. The free energy at 1 atm. must be accurately known at a temperature where phase separation can be induced with pressures within the range of the experimental equipment (90,000 lb./sq.in.).

A large number of systems was considered and on the basis of these criteria the system acetone–carbon disulfide was selected for study. The choice was made, in part, because accurate free energy data for this system can be calculated from vapor pressure data which are available at low pressure where the solutions are completely miscible (*13*). These data are reported at 35.17°C. and it was desirable to make use of these data directly by obtaining volumetric data (*8*) and by observing phase separations at this same temperature. However, preliminary experiments (*10*) revealed that separation into two liquid phases could not be achieved at pressures below the maximum safe pressure of the visual equipment unless the temperature were lowered to 0°C. Therefore volumetric data for the acetone–carbon disulfide system were obtained at 0°C. and the free energy data were adjusted from 35.17° to 0°C. by utilizing additional published data as is described in a later section.

After a complete set of volumetric data had been obtained (*8*) at 0°C., it was decided to make visual observations of phase separations at −2°C. to permit determinations to be made over a wider range of compositions than would have been possible at 0°C. The procedure

* Relations which allow the prediction of solidification of a binary system under pressure have been reported by Adams (*5*) for eutectic forming mixtures and by Winnick and Powers (*7*) for solid-solution forming mixtures. Such predictions are, however, dependent on knowledge of the behavior of the solid phase under pressure. These data are at present extremely scarce.

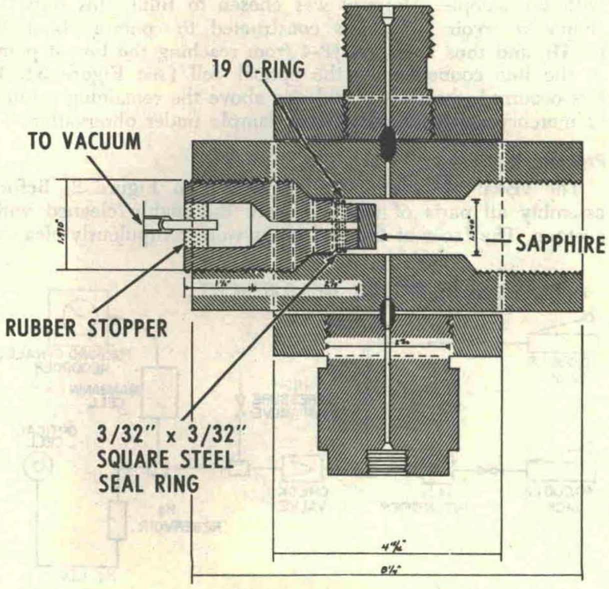

Fig. 2. Visual cell.

used to adjust the phase diagram from −2°C. to 0°C. is described in a later section.

EXPERIMENT

Equipment

Visual Cell. The visual observation cell as shown in Figure 2 is constructed of 4340 steel hardened to about 40 Rockwell C. The cell body is 10 in. long by 4 in. in diameter. The two end plugs are 3½ in. long by 2 in. in diameter. The maximum safe pressure for the cell is 90,000 lb./sq.in. Two 1/32 in. holes lying on a diameter of the cell midway along its length allow access to the cell interior. The yoke, as pictured with its driving plugs, holds two double-ended cones of 5/16 in. tubing firmly in these holes. Replacement of the top coned tubing with a solid double-ended cone resulted in a dead end seal.

The two transparent sapphire windows, which permit visual observation of the experimental mixture in the center of the cell, are 1 in. in diameter by 0.4 in. thick. The pressure seal is made similar to that reported by Poulter (*14*), where the window is sealed against the face of the end plug using the unsupported area principle of Bridgman (*15*). Sealing between the end plug and cell is made by a soft steel ring of square cross section which under an applied load, rides up the 45 deg. angle of the end plug and firmly into the cell. In order to seal securely the window to the end plug, both had to be nearly optically flat. The end plugs were first lapped flat by hand using No. 900 wet grit and then polished with No. 3/0 emery polishing paper. However, because the sapphires were found to be dish-shaped to about five wavelengths from flatness, a good seal was not obtained until some pressure was applied to the chamber. For this reason, a vacuum was applied to the rear of the windows whenever there was no pressure inside the cell. A silicone rubber O-ring, as shown in Figure 2 provided an initial seal between the end plug and cell until a pressure high enough to deform the steel ring was obtained.

The temperature of the cell was maintained by circulating water-glycol solution controlled to ±0.2 F. (8) through a copper coil soldered to the cell yoke. About 20 ft. of ¼ in. tubing was used. The coil was covered with Fiberglas insulation held down with heavy-duty cloth-backed tape.

Auxiliary Equipment. The pressure transmission apparatus, gauges, and temperature control have been described elsewhere (8). One new piece of equipment was used in this study, other than the visual cell.

To prevent contamination of the sample in the visual observation cell by the pressure transmission fluid (JP-4 jet fuel) an intermediate pressure transmitter had to be used which would act to deliver the pressure into the cell yet not mix with the sample. Mercury was chosen to fulfill this duty. A simple reservoir (*10*) was constructed to contain about 10 cc. Hg and thus keep the JP-4 from reaching the lowest point in the line connected to the optical cell (see Figure 3). If this occurred, the JP-4 would rise above the remaining column of mercury and contaminate the sample under observation.

Procedure

The visual observation cell is shown in Figure 2. Before assembly all parts of the cell were thoroughly cleaned with acetone. The faces of the end plugs were scrupulously cleaned and wiped dry with lens tissue until no dust was apparent. The sapphires were then pressed on firmly. When the interference pattern caused by the air space between sapphire and end plug ceased to change when hand pressure was removed, the sapphire was assumed to be in place. At this time, vigorous shaking would not dislodge the sapphire. A vacuum was applied behind both sapphires to assure that they remained in position. The steel rings were then set in place and the silicone rubber O rings were slipped on above them. The cell was set into position in the yoke and the bottom driving plug and cone were threaded in until the cell was firmly pressed against the top underside of the yoke. This arrangement made a temporary seal at the bottom so that the liquid sample could be inserted. The end plugs were then carefully inserted after all threads were coated with molybdenum-disulfide grease. The vacuum was maintained behind the sapphires at all times (see Figure 2). The mercury leg and reservoir were cleaned with acetone, filled with mercury, and placed in position. The first liquid sample was then injected with a hypodermic syringe and a length of 0.5 mm. I.D. stainless steel tubing. The top cone and driving plug were screwed in tightly using a 16 in. smooth-jawed wrench. Because carbon disulfide attacks all known elastomer O rings, including silicone rubber, the pressure was raised rather rapidly so as to set the steel rings before the O rings dissolved enough to fail; about 60,000 lb./sq.in. was sufficient. The pressure was then slowly released and the sample left in for 24 hr. to allow it to dissolve out as much of the O rings as possible, and thus prevent contamination of subsequent samples. The cell was then drained and the procedure repeated. Rinsing was carried out with acetone, using the hypodermic syringe and tubing, and the experimental trials begun. As long as the end plugs were not moved, the steel rings provided a seal over the entire pressure range. If, however, they had to be removed, the entire sealing procedure had to be repeated with new steel and rubber rings. On removal, the O rings were found to be ragged, soft, and rather lifeless. On immersion in carbon disulfide no further dissolution was apparent.*

Each experimental sample was prepared according to the method of Powers (*16*). The sample was inserted in the same manner as the first and the pressure raised to about 20,000 lb./sq.in. After Fiberglas insulation was wrapped around the cell, cooling was begun and about 12 hr. were allowed to assume thermal equilibrium. The vacuum was removed from behind the sapphires and a mercury-in-glass thermometer was placed into one end plug with its bulb resting against the sapphire, a rubber stopper at the outer end of the plug acting as an insulator. The temperature read on the thermometer

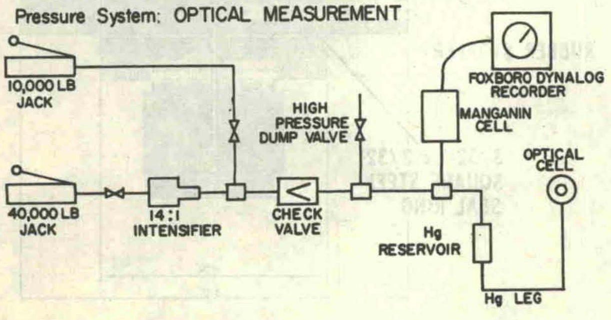

Fig. 3. Experimental equipment.

* The O rings were left in a beaker of carbon disulfide for about 1 hr. and removed, the carbon disulfide then being allowed to evaporate. At dryness, no residue was noted. When the same experiment was carried out with a new silicone O ring, a visible film of sediment was observed.

TABLE 1. OBSERVATION LIQUID-LIQUID SEPARATIONS

Acetone-carbon disulfide

X_1	T, °C.	P, lb./sq. in.
0.1479	−2.0	>82,000*
0.2022	−2.0	76,000
0.2022	−1.75	75,500
0.2494	−2.0	72,500
0.2971	−2.0	73,600
0.2971	−1.0	76,000
0.40	−7.0	64,000
0.40	−2.0	73,000
0.4717	−2.0	74,500
0.5267	−2.0	78,000
0.5267	−1.25	79,500
0.6422	−2.0	>85,000*
0.93	−2.0	>77,500*

* No separation was noted to this pressure.

was essentially the same* as that of a copper-constantan thermocouple lying between the yoke and cell. The pressure was increased until cloudiness occurred. It was held there and the temperature allowed to restabilize. The pressure was then lowered until the solution cleared, and then raised again to the translucent pressure. These two pressures, that necessary to cause cloudiness and that to cause clearing, coincided within about 500 lb./sq.in.

That no JP-4 entered the cell during the successful experimental trials was known on the basis of two observations. First, at all times there was a slight leak at the fitting at the bottom of the mercury reservoir. As long as mercury was leaking, it could be safely assumed that no JP-4 could reach the cell. If JP-4 were leaking, it was possible that the column of JP-4 had reached the low point in the mercury leg and could rise into the cell. Second, when JP-4 did enter the cell it was evidenced by streams of high viscosity having an index of refraction much different from the experimental mixtures.

Nine mixtures ranging in composition from 14.79 to 93% acetone were examined at −2°C. As mentioned earlier, this temperature was used instead of 0°C., where the P-V-X and density measurements were made (*8*) in order to obtain a more complete phase diagram. This was the case since the range of pressures where separation occurred was uncomfortably near the limit of the equipment. In order to estimate the effect of temperature on the separation pressure, three samples were allowed to warm slightly, while the pressure was raised sufficient to maintain cloudiness.

At the conclusion of each trial, the cell was warmed by pumping 30°C. water through the copper tubing to prevent any water from condensing inside the pressure chamber during the time the cell was open for rinsing and sample insertion.

Results

The results of the visual observations are listed in Table 1. The resultant curve at −2°C. is shown as Figure 4. Detailed results can be obtained from the junior author.

PREDICTION OF PHASE SEPARATION

To make a prediction of the isothermal liquid-liquid phase diagram to compare with the observed results, Equation (5) must be evaluated over the entire range of composition at every pressure deemed necessary. This requires first that the free energy of mixing curve at atmospheric pressure be established, and second that the integral term involving the change in volume on mixing be evaluated at each pressure.

Free Energy at 1 Atm.

The excellent vapor-pressure data of Zawidsky (*13*) for the system acetone–carbon disulfide at 35.17°C. were used to evaluate the excess free energy of mixing at this temperature. These values were then smoothed with Equation (*7*). A fourth-order fit was found to represent the data best. The values of the coefficients A_n of Equation (*7*) are listed as the first row in Table 2. In order to convert the data to 0°C., the enthalpy of mixing data at 16°C. of Schmidt (*17*) and specific heat data at 20°, 30°, and 40°C. of Staveley (*18*) were used in the thermodynamic relation (*10*):

$$\left[\left(\frac{\Delta G^E}{RT}\right)_{0^\circ\mathrm{C.}} - \left(\frac{\Delta G^E}{RT}\right)_{35.17^\circ\mathrm{C.}} = \int_{308.17^\circ\mathrm{K.}}^{273^\circ\mathrm{K.}} \left\{\frac{\Delta H^m{}_{289^\circ\mathrm{K.}} + (\Delta \bar{C}_P{}^m)(T-289)}{RT^2}\right\} dT\right]_X \quad (8)$$

at each 0.02 mole fraction increment. The resulting values of the difference in the excess free energy on mixing at the two temperatures were smoothed with Equation (7) once more. A third-order fit was sufficient. The resulting constants were $A_0 = -0.277$, $A_1 = -0.089$, $A_2 = -0.080$, and $A_3 = -0.196$.

* To within 0.2°C. or as accurately as the thermocouple potential was measured (*10*).

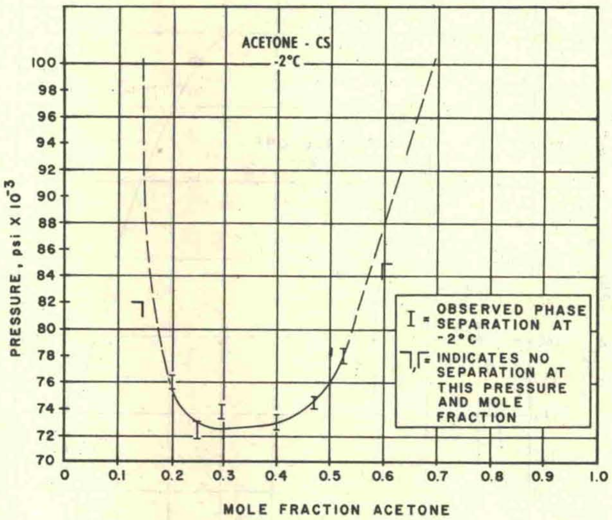

Fig. 4. Observed phase separations.

Unfortunately, two or three of the enthalpy data are inconsistent, as seen in Figure 5. Any error introduced in fitting these data is magnified enormously when used to determine the slope of the free energy curve.

The excess free energy of mixing at 0°C. and 1 atm. was also smoothed with Equation (*7*). The resultant constants are shown as row 2 of Table 2.

Change in Volume on Mixing

The results for the excess free energy at 0°C. and 1 atm. were used as the basis for calculating the free energy on mixing at each pressure by making use of results reported for the change in volume on mixing for this system at 0°C. (*8*). The change in volume on mixing is represented at any pressure to 100,000 lb./sq.in. and at any mole fraction by

$$\left[\Delta V^m = (\Delta V^m)^\circ - (V_m)^\circ \bar{J}_m{}' \ln\left(\frac{\bar{L}_m + P}{\bar{L}_m}\right) + X_1 (V_1)^\circ J_1{}' \ln\left(\frac{L_1 + P}{L_1}\right) + X_2 (V_2)^\circ J_2{}' \ln\left(\frac{L_2 + P}{L_2}\right)\right]_{T,X} \quad (9)$$

This relation results from combination of the semiempirical Tait equation for isothermal compressibility with the definition of the change in volume on mixing at any pressure (*8*). The constants $\bar{J}_m{}'$ and $\bar{L}_m$ are independent of pressure but are functions of the composition (*8*):

$$\left.\begin{aligned} \bar{J}_m{}' &= 0.09158 + 0.008499\,X_1 - 0.03482\,X_1^2 + 0.02415\,X_1^3 \\ \bar{L}_m &= 17191. - 8455.2\,X_1 - 131.52\,X_1^2 + 4291{,}7\,X_1^3 \end{aligned}\right\} \quad (10)$$

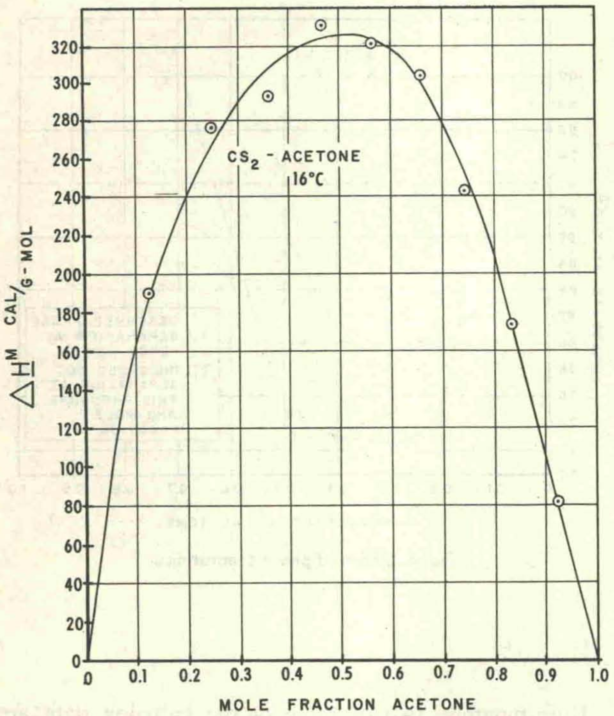

Fig. 5. Reported enthalpy of mixing data (17).

The constants J_j' and L_j are evaluated from Equations (10) with $X_1 = 1.0$ for $j = 1$ and $X_1 = 0.0$ for $j = 2$. Equation (9) is integrated to yield

$$\left[\int_{14.7}^{P} \Delta V^m \, dP = P\,(V_m)^\circ - \bar{J}_m'\,(V_m)^\circ \left[\bar{L}_m \ln\left(\frac{\bar{L}_m + P}{\bar{L}_m}\right) - P(1 + \ln \bar{L}_m)\right] - \sum_{j=1}^{2}\left\{ X_j (V_j)^\circ \left[P - J_j'\left(L_j \ln\left\{\frac{L_j + P}{L_j}\right\} + P\left\{ \ln\left(\frac{L_j+P}{L_j}\right) - 1 \right\}\right)\right]\right\}\right]_{T,X} \quad (11)$$

Table 2. Results of Smoothing $\Delta G^E/RT$

T, °C.	P, lb./sq.in.	A_0	A_1	A_2	A_3	A_4
35.17	14.7	1.600	0.896	0.158	0.127	0.439
0	14.7	1.877	0.985	0.238	0.323	0.439
0	10,000.0	1.979	1.016	0.252	0.301	0.453
0	20,000.0	2.061	1.043	0.268	0.280	0.466
0	30,000.0	2.132	1.064	0.283	0.259	0.478
0	40,000.0	2.196	1.081	0.298	0.239	0.490
0	50,000.0	2.255	1.093	0.312	0.220	0.501
0	60,000.0	2.310	1.101	0.326	0.201	0.513
0	70,000.0	2.363	1.106	0.338	0.183	0.524
0	80,000.0	2.413	1.108	0.351	0.165	0.535
0	90,000.0	2.461	1.107	0.362	0.148	0.545
0	100,000.0	2.507	1.104	0.373	0.131	0.556

Prediction of Phase Behavior

This integral was evaluated at each 5,000 lb./sq.in. increment in pressure and added to the excess free energy on mixing at 1 atm. and 0°C. as suggested by Equation (6). These results were fitted at each pressure with Equation (7). A fourth-order fit was used, as was for the curves at 1 atm. The equations were converted from excess to total molal free energy change on mixing with Equation (2). The constants representing the excess free energy at each 10,000 lb./sq.in. increment in pressure are listed in Table 2. Values of $\Delta G^m/RT$ thus calculated were plotted vs. composition with a Calcomp plotter. Some representative curves are shown in Figure 6. The straight lines in the figure were drawn by hand and their points of tangency to the curves indicate the compositions of the phases predicted to be in equilibrium. These points are shown plotted as pressure vs. composition in Figure 7.

As noted previously, phase separations were observed experimentally at −2°C., whereas the thermodynamic predictions were made at 0°C. In order to adjust the experimentally observed results (Figure 4) from −2° to 0°C., the variation in pressure of phase separation with temperature was determined for several solutions in the temperature range from −7.0° to −1.0°C. (Table 1). Values of the rate of change of pressure of phase separation with temperature $(\partial P/\partial T)_X$ were estimated from these

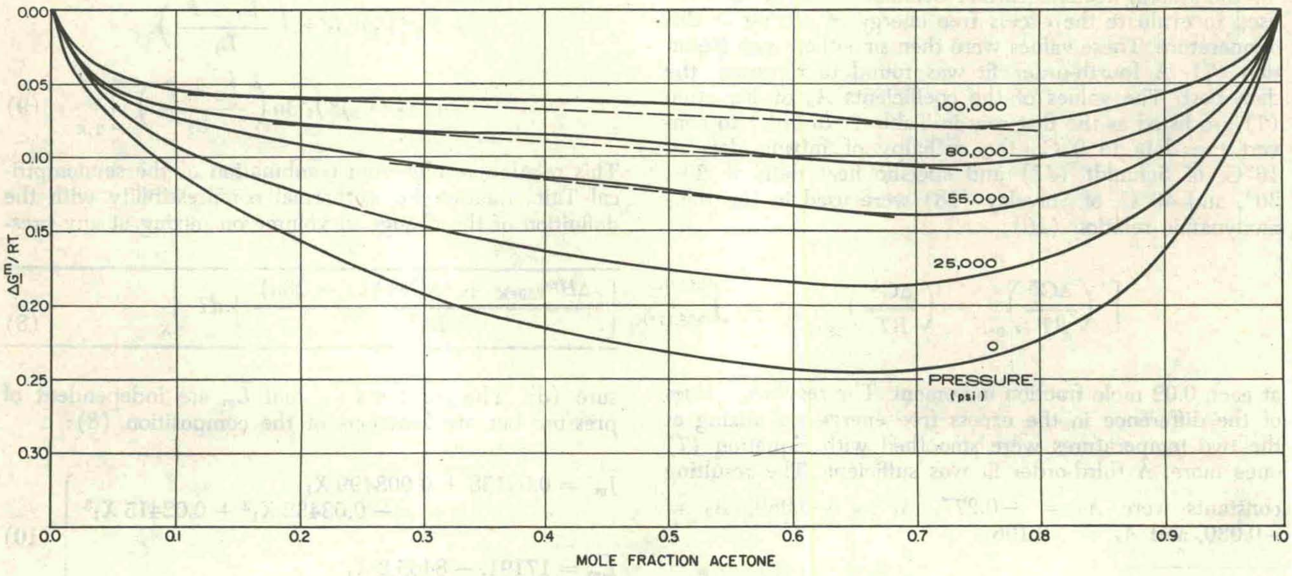

Fig. 6. Free energy of mixing at representative pressures.

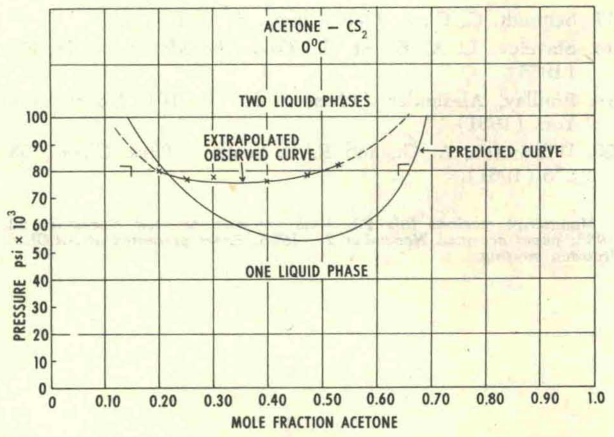

Fig. 7. Comparison of predicted and observed phase diagrams.

results and used to estimate the pressures of phase separation at 0°C. plotted in Figure 7.

CONCLUSIONS

The agreement between the predicted and extrapolated observed curves in Figure 7 is quantitatively less than desirable. There is, however, substantial qualitative agreement. Error analysis carried out on the compressibility measurements indicate the possibility of 1 to 5% error in the change in volume on mixing (*10*). Several other causes undoubtedly contributed to the lack of agreement. In order to make the prediction, the experimental data of three different investigators had to be incorporated: the vapor-pressure data of Zawidsky, the specific heat data of Staveley, and the heat of mixing data of Schmidt. Of these, the last are least reliable. The curve in Figure 5 was taken to be an accurate representation of the experimental data and no adjustment was made to improve the agreement between the predicted and observed results. However, a curve can be drawn through the data of Schmidt (Figure 5) which would yield quantitative agreement between the resulting prediction of phase separation and the results presented in Figure 7. This curve would lie within the limits of accuracy of the reported heat of mixing data.

The extrapolated observed curve is subject to unknown error of extrapolation with a minimum amount of data. In addition, the actual data may be in error due to the errors in temperature and pressure measurements and sample purity. The effect of the last is especially difficult to estimate. The critical solution pressure may be shifted either upward or downward by very small amounts of impurities (*19*).

A study analogous to this one has been reported by Williamson and Scott (*20*). They attempted to match predicted and observed liquid-liquid phase separation for two systems. However, while the present study examines the effect of pressure isothermally, Williamson and Scott examined the effect of temperature isobarically. It is interesting to note that similar relative agreement is reported. The authors mention extreme sensitivity of the prediction to small uncertainties in the excess properties.

The contributions of the present study are summarized as follows:

1. A method has been described which can be used to predict the pressure of isothermal liquid-liquid phase separation making use of free energy data at low pressure and volumetric data over the entire pressure range.

2. A calculational procedure is given that provides a means of checking the thermodynamic consistency of several diverse types of data.

3. The isothermal liquid-liquid phase diagram for the system acetone–carbon disulfide has been determined at −2°C.

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NOTATION

A_n = coefficient in series [Equation (7)]
B = skewing factor [Equation (7)]
$\Delta \overline{C}_p{}^m$ = average molal change in specific heat on mixing
G_i = molal free energy of pure component *i*
ΔG^E = excess molal change in free energy on mixing
G_m = molal free energy of mixture
ΔG^m = molal change in free energy on mixing
ΔH^m = molal change in enthalpy on mixing
J_1' = Tait equation constant for pure compound 1 [Equation (9)]
J_2' = Tait equation constant for pure compound 2 [Equation (9)]
$\overline{J}_m'$ = best fit value for Tait constant [Equation (9)]
L_1 = Tait equation constant for pure component 1 [Equation (9)]
L_2 = Tait equation constant for pure component 2 [Equation (9)]
$\overline{L}_m$ = best fit value for Tait constant [Equation (9)]
P = pressure, lb./sq. in.
P_o = initial pressure, lb./sq. in.
R = gas constant
T = temperature
$(V_1)^o$ = molal volume of pure component 1 at 1 atm.
$(V_2)^o$ = molal volume of pure component 2 at 1 atm.
$(V_j)^o$ = molal volume of pure component *j* at 1 atm.
$(V_m)^o$ = molal volume of mixture at 1 atm.
ΔV^m = molal change in volume on mixing at pressure P
$(\Delta V^m)^o$ = molal change in volume on mixing at 1 atm.
X = mole fraction
X_j = mole fraction component *j*
X_1 = mole fraction component 1 (acetone)
X_2 = mole fraction component 2 (carbon disulfide)
X_1' = mole fraction component 1 in phase 1
X_1'' = mole fraction component 1 in phase 2
X_1^o = hypothetical homogeneous composition (Figure 1)

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