9. Markovitz, Hershel, and D. R. Brown, *Trans. Soc. Rheol.*, 7, 137 (1963).
10. Slattery, J. C., *Phys. Fluids*, 7, 1913 (1964).
11. Ziabicki, Andrzej, and Krystyna Kedzierska, *Kolloid Z.*, **171**, 111 (1960).
12. Scriven, L. E., *Chem. Eng. Sci.*, **12**, 98 (1960).
13. Aris, Rutherford, "Vectors, Tensors, and the Basic Equations of Fluid Mechanics," Prentice-Hall, Englewood Cliffs, N. J. (1962).
14. Slattery, J. C., *Chem. Eng. Sci.*, **19**, 379 (1964).
15. McConnell, A. J., "Applications of Tensor Analysis," Dover, New York (1957).
16. Reiner, Markus, "Deformation, Strain and Flow," Interscience, New York (1960).

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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*):

$$(\Delta V^m)^o = \frac{-K_{12}X_1X_2V^o{}_1V^o{}_2\,[X_1(\partial V_1/\partial P)^o{}_T + X_2(\partial V_2/\partial P)^o{}_T]}{[X_1V^o{}_1 + X_2V^o{}_2]^2} \quad (2)$$

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**.

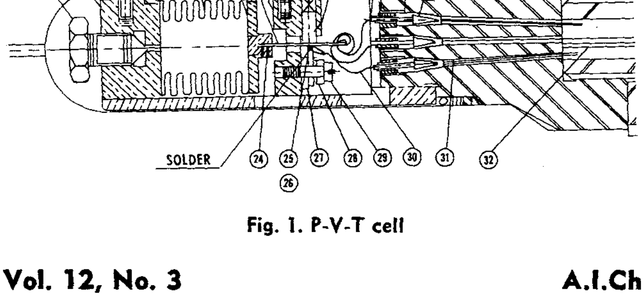


Fig. 1. P-V-T cell

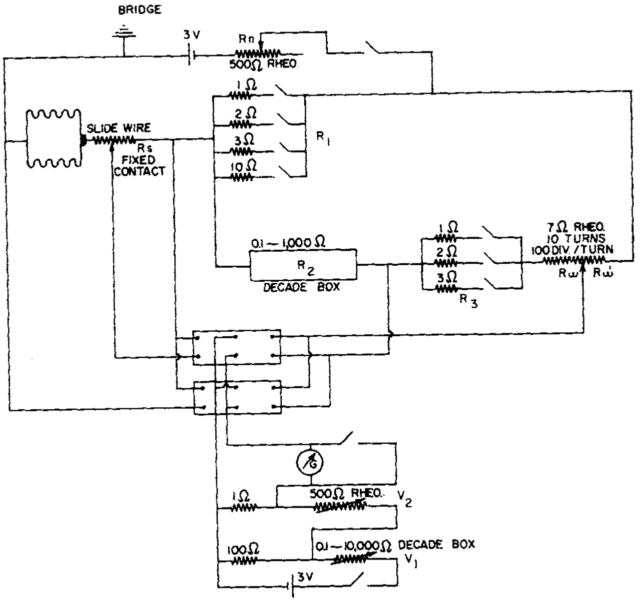


Fig. 2. Resistance measuring bridge.

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

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

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 R_O,* $(J_r)_{cs2}$, 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

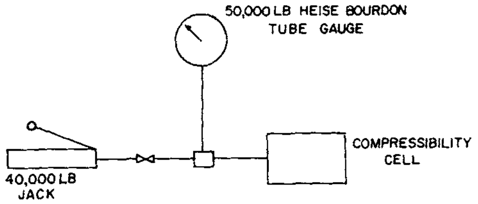
Densities at 1 Atm. The pycnometer mentioned earlier was used to determine the density-composition diagram of the system acetone–carbon disulfide at 0°C.

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.

(a) Pressure System COMPRESSIBILITY MEASUREMENT TO 25,000psi



(b) Pressure System: COMPRESSIBILITY MEASUREMENT FROM 25,000psi

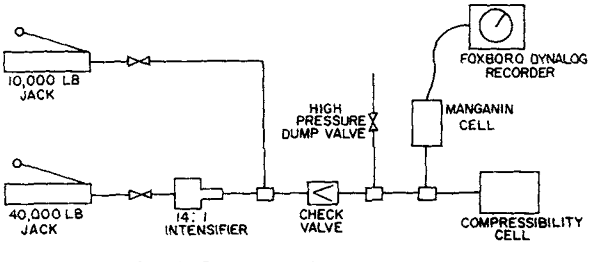


Fig. 3. Experimental equipment.

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* 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*).

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.

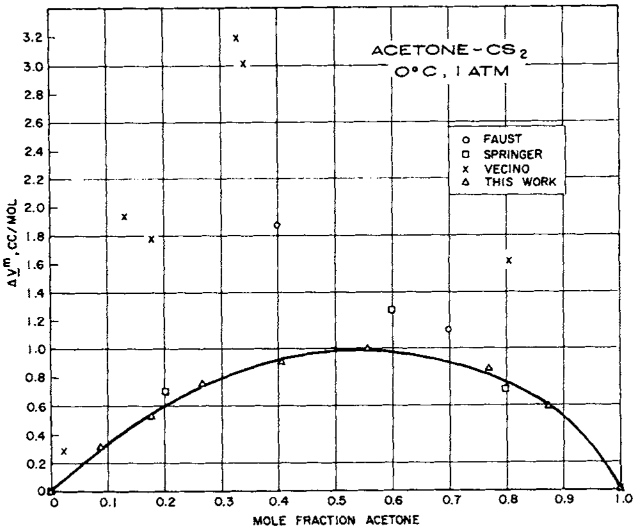

Fig. 4. Volume of mixing at 1 atm.

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:

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

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:

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

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

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):

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

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.

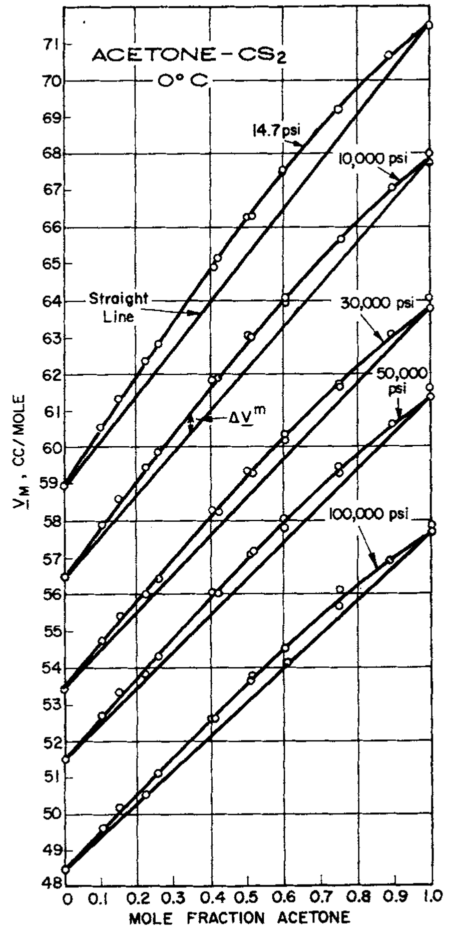

Fig. 5. Molar volume at representative pressures.

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:

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

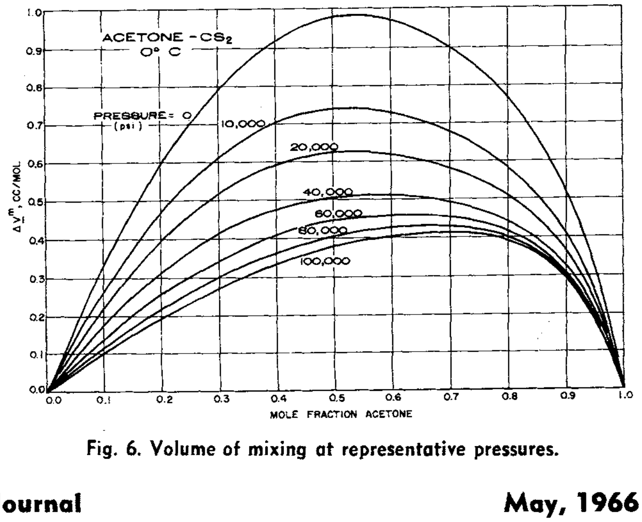

Fig. 6. Volume of mixing at representative pressures.

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.
$(V^o_m)_{\text{raw}}$ = molal volume of mixture at 1 atm. as obtained directly from the density data at 0°C., cc.
$(V^o_m)_{\text{calc.}}$ = 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.

LITERATURE CITED

1. Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, **47**, 429 (1912).
2. *Ibid.*, **49**, 1 (1913).
3. *Ibid.*, **58**, 166 (1923).
4. *Ibid.*, **67**, 1 (1931).
5. *Ibid.*, **77**, 129 (1949).
6. *Ibid.*, **74**, 21 (1940).
7. Balachandran, C. B., *J. Ind. Inst.*, **38A**, 10 (1956).
8. Singh, H., and R. S. Seth, *Ann. Phys.*, **5**, 53 (1959).
9. Van Itterbeck, A., and L. Verhaegen, *Proc. Phys. Soc.*, **62B**, 800 (1949).
10. Gibson, R. E., and O. H. Loeffler, *J. Phys. Chem.*, **43**, 207 (1939).
11. Eduljee, H. E., D. M. Newitt, and K. E. Weale, *J. Chem. Soc.*, Part IV, 3086 (1951).
12. Reamer, H. H., Virginia Berry, and B. H. Sage, *J. Chem. Eng. Data*, **6**, 184 (1961).
13. Cutler, W. G., et al, *J. Chem. Phys.*, **29**, 727 (1958).
14. Benedict, M., G. B. Webb, and L. C. Rubin, *Chem. Eng. Progr.*, 449 (1951).
15. Hougen, O. A., K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," Pt. 2, 2 ed., Wiley, New York (1959).
16. Pitzer, K. S., and G. O. Hultgren, *J. Am. Chem. Soc.*, **80**, 4793 (1958).
17. Tait, P. G., "Physics and Chemistry of the Voyage of H. M. S. Challenger," Vol. II, Part IV (1888).
18. Carl, H., *Z. Phys. Chem.*, **101**, 238 (1922).
19. Cutler, W. G., Ph.D. dissertation, Pennsylvania State Univ., University Park, Pa. (1955).
20. Gibson, R. E., *J. Am. Chem. Soc.*, **56**, 4 (1934).
21. *Ibid.*, **59**, 1521 (1937).
22. Wohl, A., *Z. Phys. Chem.*, **99**, 234 (1921).
23. Gibson, R. E., and O. H. Loeffler, *J. Am. Chem. Soc.*, **63**, 443 (1941).
24. Arons, A. B., and R. R. Halverson, *J. Chem. Phys.*, **15**, 785 (1947).
25. Ginell, R., *ibid.*, **34**, 1249 (1961).
26. Hildebrand, J. H., and R. L. Scott, "Solubility of Nonelectrolytes," p. 143, Reinhold, New York (1950).
27. Winnick, Jack, Ph.D. thesis, Univ. Oklahoma, Norman (1963).
28. Bridgman, P. W., *Proc. Am. Acad. Arts Sci.*, **66**, 185 (1931).
29. Harwood Engineering Co. publications.
30. Seitz, L., and G. Lechner, *Ann. Phys.*, **49**, 93 (1916).
31. Powers, J. E., *Chem. Anal.*, **49**, 54 (1960).
32. Kremann, R., R. Meingast, and F. Gugl, *Monatsch*, **35**, 1235 (1914).
33. Bridgman, P. W., *J. Chem. Phys.*, **9**, 794 (1941).
34. Faust, *Z. Phys. Chem.*, **90**, 97 (1912).
35. Springer, R., and H. Roth, *Monatsch.*, **56**, 1 (1930).
36. Vecino and Verona, *Anal. Soc. Espan. Fis. Quim.*, **11**, 498 (1913).
37. Washburn, E. W., "International Critical Tables," 1 ed., McGraw-Hill, New York (1928).
38. Winnick, Jack, and J. E. Powers, this issue.

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