Corresponding States Correlations for Liquid Compressibility and Partial Molal Volumes of Gases at Infinite Dilution in Liquids

A statistical mechanical solution theory is used as the basis for corresponding states formulations. Universal functions relate the compressibility to the reduced density and the partial molar volume to reduced solvent density only. Correlations are in good agreement with data for all types of nonelectrolytes over wide ranges of temperatures including saturated and compressed systems. The correlations provide simple methods for describing the isothermal pressure dependence of liquid volumes and the pressure dependence of the ideal-solution solubility of gases in liquids.

S. W. BRELVI and
J. P. O'CONNELL

Department of Chemical Engineering
University of Florida
Gainesville, Florida 32601

SCOPE

The pressure dependence of the volumetric properties of pure and mixed liquids are usually difficult to measure even though necessary to have for sizing and other design purposes in high pressure systems. Although Prausnitz and co-workers (1965, 1969) have developed correlations for compressibility and partial molal volume of gases at infinite dilution, both suffer from limitations on the type of substances and range of applicable conditions. The objective of the present work was to determine the applicability of statistical mechanical solution theories in correlating these properties with the additional hope that the results could be part of a more complete description of the thermodynamic properties of liquids.

CONCLUSIONS AND SIGNIFICANCE

For all liquids the product of compressibility times temperature can be expressed to a high degree of accuracy as a simple function of reduced density only, Equation (10).

The single reducing volume is the critical volume for nonpolar substances but is empirically fitted for polar substances. The form of this relation allows a simple expression for the change in volume with an isothermal change in pressure and the entire liquid state can be described from the saturation volumes and the present correlation.

The partial molal volume of gases at infinite dilution in liquids can be obtained to within a few % from a simple function of reduced density of the solvent and the reducing volumes of the gas and solvent, Equations (9) to (11). This generalized expression provides the means to correct for the effect of pressure on Henry's constant as used to predict solubilities of gases. However, the present equation does not describe the partial molal volume of liquids in liquids; apparently the liquid volumetric behavior is different when a substance is above its critical temperature. The expressions for both compressibility and partial molal volume arise from use of a statistical mechanical solution theory involving integrals of the molecular direct correlation function. Their universality can be attributed to the lack of importance of nonspherical forces in the integral of the correlation function. However, it is not clear why the integrals are independent of temperature in the liquid region since essentially complete cancellation of the effects of temperature must occur in the (positive) long range and (negative) short range values of the correlation functions and there is no molecular theory which would predict this.

THERMODYNAMIC PROPERTIES

A knowledge of the compressibility of the liquid

$$K = \frac{1}{\rho}\left.\frac{\partial \rho}{\partial P}\right]_{T,x} \tag{1}$$

can be used to generate the equation of state for the liquid along an isotherm since the change of pressure which occurs with a change in density is

$$(P_2 - P_1)_{T,x} = \int_{\rho_1}^{\rho_2} \frac{1}{\rho K}\, d\rho \tag{2}$$

For mixtures the partial molal volume is useful to describe the volumetric behavior

$$v = \Sigma\, x_i \bar{v}_i \tag{3}$$

and to correct for the pressure dependence of liquid fugacity f

$$\left.\frac{\partial \ln f_i}{\partial P}\right]_{T,x} = \frac{\bar{v}_i}{RT} \qquad (4)$$

One of the most important applications of the latter equation is in the effect of pressure on the solubility of a gas in a solvent when the vapor and liquid phases are assumed ideal and the partial molal volume is that at infinite dilution

$$\frac{1}{x_i} = \frac{H_i}{p} \exp\left[\frac{\bar{v}_i^0 P}{RT}\right] \qquad (5)$$

Here H_i is Henry's constant referred to zero pressure (Prausnitz and Chueh, 1969), and p is the partial pressure of i in the (ideal) gas phase. (The partial pressure is replaced by the fugacity if a real gas equation of state is used). Equation (5) is useful for predictive purposes when the solubility is of the order of a few % or less since nonideality in the liquid phase can then be neglected.

STATISTICAL THERMODYNAMIC BASIS FOR CORRESPONDING STATES CORRELATION

Distribution functions have recently become of considerable interest and use in theories of fluids (Rowlinson, 1969). The radial distribution function g which is the probability of finding a molecular center at a distance r from a center at the origin (averaging of the orientation dependence has been performed), and the direct correlation function c which is a measure of the short-range molecular correlations, are commonly used for modeling and correlational purposes.

Recently, the relation of these functions to solution thermodynamic properties has been discussed by O'Connell (1971a). For the properties of interest here, the appropriate relations for an M-component solution are

$$\frac{1}{\rho KRT} = 1 - \sum_{n=1}^{M} \sum_{m=1}^{M} x_n x_m C_{nm} \qquad (6)$$

$$\frac{\bar{v}_i}{KRT} = 1 - \sum_{j=1}^{m} x_j C_{ij} \qquad (7)$$

The mole fractions are x and the C_{ij} are spatial integrals of the direct correlation function between species i and j. These are functions of all conditions of state (T, ρ, x).

For a solute (1) at infinite dilution in a solvent (2), Equations (6) and (7) become

$$\frac{1}{\rho K_2{}^0 RT} = 1 - C^0{}_{22} = 1 - \rho \int c^0{}_{22}(r)dr \qquad (8)$$

$$\frac{\bar{v}_1{}^0}{K_2{}^0 RT} = 1 - C^0{}_{12} = 1 - \rho \int c^0{}_{12}(r)dr \qquad (9)$$

CORRESPONDING STATES RELATION FOR ISOTHERMAL COMPRESSIBILITY

The equation of state of liquids is generally determined by fitting the results of compression experiments (density versus pressure) to analytical expressions such as the Huddleston or Tait equation (Rowlinson, 1969). The compressibility is determined from the derivative of the equation and is a function of density and temperature. Further, statistical mechanical perturbation theory indicates that nonspherical forces do not appear in the first-order approximation for the isothermal compressibility (Gubbins and O'Connell, 1972). This suggests that the integral $C^0{}_{22}$ [Equation (8)] when properly reduced is expressible as a generalized function of reduced temperature and pressure. Experimental results indicate that the variation of $(1 + 1/\rho KRT)$ with ρ for both saturated and compressed liquids is similar for a wide variety of substances and is temperature independent. There does not appear to be any simple explanation for the temperature independence. Experimental compressibility data for Ar, O_2, N_2, CH_4, CCl_4, $nC_{10}H_{22}$, $nC_{12}H_{26}$, $nC_{14}H_{30}$ and $nC_{16}H_{34}$ were used to derive an empirical correlation for $[1 + 1/\rho K_2{}^0 RT]$ as a function of the reduced density $\tilde{\rho}$, $(= V^*/V)$; V^* is a characteristic parameter for each substance. The first five of the above substances were chosen as the primary set because they are composed of simple molecules and v^* was set equal to the critical volume. The long chain hydrocarbons were included to extend the reduced density range of the correlation, and the data chosen were reported to have a very low experimental error. The characteristic volumes were obtained from matching the hydrocarbon data to the simple substance curve in the region of overlap. This form $(1 + 1/\rho K_2{}^0 RT)$ was chosen to obtain the limit of unity when V^*/V equals unity as for the simple substances. This was done even though the correlation is uncertain at reduced densities less than 1.5 where data are sparse and temperature dependence appears to become important. An analytical expression for the correlation from which K may be found at a given value of temperature T and density ρ when its characteristic volume has been determined is

$$\ln\left[1 + \frac{1}{\rho KRT}\right] = -0.42704(\tilde{\rho} - 1) + 2.089(\tilde{\rho} - 1)^2 - 0.42367(\tilde{\rho} - 1)^3 \qquad (10)$$

Figure 1 shows a plot of this correlation along with some representative data over the reduced density range $1.5 \leq \tilde{\rho} \leq 3.7$. For all substances other than those mentioned above the characteristic parameter was determined by fitting experimental compressibility data to Equation (10). The fitted characteristic parameters are probably within the errors of experiment or those of predictive correlations for the critical molar volumes of nonpolar substances. Thus, for nonpolar substances where compressibility data do not exist, v_c, as measured or predicted, may be used for v^*. For polar substances, we have found v^* to be less

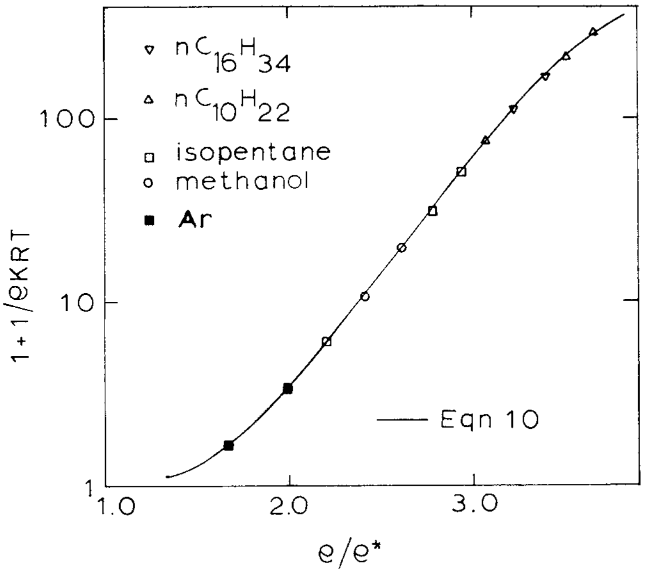

Fig. 1. Generalized correlation for liquid compressibility.

TABLE 1. GENERALIZED CORRELATION FOR LIQUID COMPRESSIBILITY

Substance	Temp. range, °K	# data points	v^* cc/g-mole	v^*/v_c	Root mean square dev., %	Data ref.
Argon	81-140	9	74.57	1.0	4.4	*a*
CH_4	90.66-100	11	99.5	1.0	5.8	*a*
N_2	63.18-120	7	90.1	1.0	3.1	*a*
O_2	60-150	9	73.4	.986	6.4	*a*
$C_{10}H_{22}$	298-358	10	602.0	1.0	3.5	*b*
$C_{40}H_{82}$	423-573	4	2,575.0	1.016†	2.6	*c*
Benzene	278-473	7	255.0	.981	4.8	*a*
PSU 88‡	311-408	3	1,530.0	—	3.8	*d*
Water	273-573	10	46.4	.828	6.9	*a*

† Critical volume estimated by Lyderson's method. See Reid and Sherwood (1966).
‡ Complex hydrocarbon. See reference *d* for formula.
[a] J. S. Rowlinson, *Liquids and Liquid Mixtures*, p. 11-65, Plenum Press, New York (1969).
[b] P. S. Snyder and J. Winnick, "The Pressure, Volume and Temperature Properties of Liquid *n*-Alkanes at Elevated Pressures," 5th Symp. Thermophys. Properties, ASME (1970).
[c] A. K. Doolittle and B. Doolittle, *AIChE J.*, **6**, 157 (1960).
[d] W. G. Cutler et al., *J. Chem. Phys.*, **29**, 727 (1959).

than v_c. Since v^* is apparently related to the size parameter in the spherical force field (Gubbins and O'Connell, 1972) and there is no way of getting this from any other macroscopic data, it must be fitted to at least one piece of compressibility data.

Table 1 shows results of calculation with Equation (10) for nine representative substances. The fractional root mean square deviation in $(1 + 1/\rho KRT)$, δ, is always less than 0.08; the largest error in $(1 + 1/\rho KRT)$ encountered over the aggregate of the 70 state points shown in Table 1 was 0.11. Table A1* lists characteristic volumes for other substances. In general, for substances with known characteristic parameters, both polar and nonpolar, Equation (10) provides a means of calculating K to an accuracy of at least 6 to 8% at all values of T and reduced densities greater than 1.5.

The magnitude of the errors reported in Table A1 may appear to be large in some instances. However, since considerable manipulation of the usual compression data (v versus P at constant T) has occurred and errors may be magnified, the actual effect on reproducing the experimental densities can be quite small. For example, the data are often fitted to the Tait equation which then is differentiated to obtain the compressibility. If the data are not fitted extremely well, the compressibility can be in serious error. Since we have fitted compressibility data to obtain v^*, and the results are quite sensitive to this parameter, the values may not be the best possible ones for predicting densities. On the other hand, when the integrated form of Equation (10) is used along with the fitted value of v^*, the predictions of density can still be extremely good. An example is that of ammonia shown in Table 2. The volume change V_1 to V_2 corresponding to a change in pressure P_1 to P_2 is calculated using the correlation of Equation (10) in Equation (2).

$$\frac{(P_2 - P_1)V^*}{RT} = \int_{\rho_1}^{\tilde{\rho}_2} \{\exp[-.42704(\tilde{\rho} - 1) + 2.089(\tilde{\rho} - 1)^2 - .42367(\tilde{\rho} - 1)^3] - 1\}\, \tilde{d\rho} \quad (11)$$

Although the root-mean-square deviation in fitting the function $(1 + 1/\rho KRT)$ for ammonia is 8.8%, the root-mean-square deviation between calculated and experimental volumes for twelve pressures covering the range of volumetric data available was 0.34% and the largest error was 0.66%. This error is of the order of magnitude obtained by predictive methods for saturation volumes which have several parameters, for example, the modified Rackett equation (Spencer and Danner, 1972). Together with such equations, the present work gives a two-parameter method for describing the entire dense liquid region for all substances to an accuracy of the order of 1%. (It even may be possible that for polar substances the two parameters of these methods can be correlated). Equation (10) seems simpler and more generally applicable than the correlation of Chueh and Prausnitz (1969) which is limited to substances which follow Pitzer's 3-parameter corresponding states theory; the errors in calculating the compressibility from the two correlations are of the same order.

TABLE 2. ISOTHERMAL COMPRESSIBILITIES AND VOLUMES OF LIQUID AMMONIA

Temp., °K	Pressure, atm	Volume cc/gm mole Calculated†	Volume cc/gm mole Experimental*	Isothermal compressibility $\times 10^4$, (atm)$^{-1}$ Calculated†	Isothermal compressibility $\times 10^4$, (atm)$^{-1}$ Experimental*
253	2.0	—	25.5629	0.82	0.82
	283.1	25.0557	25.0818	0.69	0.69
	654.9	24.4792	24.4307	0.54	0.58
	1,400.0	23.6506	23.5263	0.38	0.44
273	4.5	—	26.622	1.09	1.06
	283.1	25.9159	25.9556	0.87	0.86
	654.9	25.1468	25.1804	0.66	0.69
	1,400.0	24.1973	24.1200	0.44	0.50
298	10.0	—	28.1996	1.65	1.52
	283.1	27.1516	27.2068	1.21	1.14
	654.9	26.1575	26.2008	0.87	0.87
	1,400.0	24.8781	24.8081	0.53	0.59
313	16.0	—	29.3369	2.19	1.89
	283.1	27.9708	28.1554	1.55	1.35
	654.9	26.7504	26.8957	1.04	0.98
	1,400.0	25.2760	25.3487	0.61	0.65

† Equation (2); from saturation pressure to given pressure.
‡ Equation (10).
* Reference *p*, Table A1.

---

* Tabular material has been deposited as Document No. 01922 with the National Auxiliary Publications Service (NAPS), c/o CCM Information Corp., 866 Third Ave., New York 10022 and may be obtained for $2.00 for microfiche or $5.00 for photocopies.

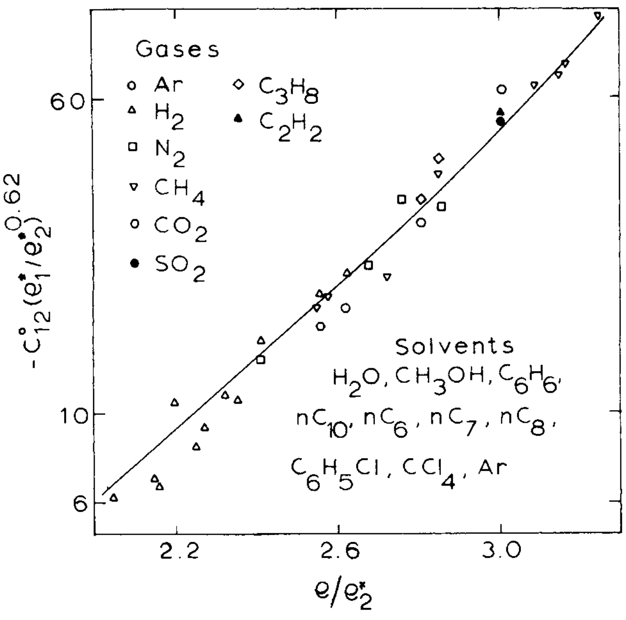

Fig. 2. Generalized correlation for partial molar volumes of gases at infinite dilution in liquids ——— line is Equation (12).

CORRESPONDING STATES CORRELATION FOR PARTIAL MOLAL VOLUME

The partial molal volume of a solute at infinite dilution in a solvent is generally determined by observing the change in volume of the mixture with a change in component composition but may be obtained from data on solubility versus pressure using Equation (5). (However, see Orentlicher and Prausnitz, 1964).

Values of C^0_{12} were calculated using Equations (9) and (10) and experimental values of partial molar volumes for a wide variety of solute (1) — solvent (2) pairs. In cases where the total pressure of the system was unknown but expected to be low, the volume of the pure solvent was taken to be that at its saturation pressure. In the spirit of the preceding correlation, the variation of C^0_{12} with reduced solvent density was investigated and found to be similar for all solute-solvent pairs. This suggested a generalized correlation consisting of two factors, one a function of the reduced solvent density, and the other a function of the relative molecular sizes of the solute and solvent, as expressed by the reducing volumes. The empirical correlation for C^0_{12} is shown in Figure 2 and is similar to that for C^0_{22}. We have developed an analytical expression for calculating C^0_{12} for use in Equation (9) to obtain $\bar{v}_1{}^0$ when Equation (10) is used for $K_2{}^0$. It is

$$\ln - C^0_{12}\left[\frac{v_2{}^*}{v_1{}^*}\right]^{0.62} = -2.4467 + 2.12074\tilde{\rho} \;\ldots\; 2.0 \leq \tilde{\rho} \leq 2.785$$

$$= 3.02214 - 1.87085\tilde{\rho} + .71955(\tilde{\rho})^2 \;\ldots\; 2.785 \leq \tilde{\rho} \leq 3.2 \quad (12)$$

Here $\tilde{\rho} = \rho v_2{}^*$, the density of the pure solvent reduced by its characteristic volume; and it is used in both Equations (10) and (12). The form of the correlation was determined using characteristic parameters from compressibility data or critical volumes only [the effective critical volume was used for hydrogen (Prausnitz and Chueh, 1969)]. The experimental systems represent a great variety of gas-solvent systems, including some systems under high pressures. The partial molar volumes calculated from (12) agree with experimental volumes to within 5% in most cases, and 15% in all cases. In Table A3* calculations are compared both with experimental values and the results of the generalized correlation of Lyckman et al. (1965). The accuracy of the correlations is similar for solvents saturated at low temperatures. However, the present correlation relates the change in partial molar volume with respect to pressure and is accurate for solvents near their critical points. This is clearly seen in the calculations for the hydrogen-benzene system where changes of 30% in the partial molar volume with pressure are well predicted, and the high temperature behavior is correlated closely.

Equation (11) was determined from partial molal volume data of five gases whose characteristic volumes were determined from liquid compressibility data (Ar, N_2, O_2, CH_4, NH_3) and three gases whose characteristics were assumed to be their critical volume (CO, C_2H_2, H_2) as shown in Table A2. Table A2 shows values of v^* obtained for seven other gaseous substances where no liquid compressibility are available. Since each of these values was obtained from experiment using several solvents, it would appear that these values are as valid for both correlations as are those for the five substances that data of both kinds are available. [An exception to this may be CO_2 where sketchy liquid data (Amagat, 1913) are not fitted well.]

It should be noted that partial molal volumes of liquid-liquid systems do not follow the present correlation. As with the activity coefficients (O'Connell, 1971b), apparently the volumetric behavior of gases in liquids is different from that of liquids in liquids. On the other hand, it seems likely that a correlation of the present form could be developed for liquids in liquids.

The similar variations of C^0_{22} and C^0_{12} with reduced density may indicate that all direct correlations on the molecular scale are affected in the same manner by changes in the system density.

ACKNOWLEDGMENT

The authors are grateful to the donors of the Petroleum Research Fund for financial support and to the University of Florida Computing Center for use of its facilities.

NOTATION

c_{ij} = molecular direct correlation function between molecules of species i and j
C_{ij} = reduced volume integral of molecular direct correlation function
f_i = fugacity of component i, atm
H_i = Henry's constant for solute i in solvent, atm
K = isothermal compressibility, atm^{-1}
P = pressure, atm
R = gas constant
T = temperature, °K
x_i = mole fraction component i
v = molar volume, cc/g-mole
ρ = density, g-mole/cc

Superscripts

0 = pure solvent or infinitely dilute solution
~ = reduced property

---

* See footnote on page 1241.

* = characteristic property
$\bar{}$ = partial molar property

Subscripts

1 = solute
2 = solvent or pure component
c = critical property

LITERATURE CITED

Amagat, E. H., "Internal Pressure of Fluids," *Annals de chem. phys.*, **28**, 5 (1913).

Chueh, P. L., and J. M. Prausnitz, "A Generalized Correlation for the Compressibilities of Normal Liquids," *AIChE J.*, **16**, 471 (1969).

Gubbins, K. E., and J. P. O'Connell, "Liquid Compressibilities and Angle Dependent Correlation Functions," in preparation.

Lyckman, E. C., C. A. Eckert and J. M. Prausnitz, "Generalized Reference Fugacities for Phase Equilibrium Thermodynamics," *Chem. Eng. Sci.*, **20**, 685, 703 (1965).

O'Connell, J. P., "Thermodynamic Properties of Solutions from Correlation Functions," *Mol. Phys.*, **20**, 27 (1971a).

———., "Molecular Thermodynamics of Gases in Mixed Solvents," *AIChE J.*, **17**, 653 (1971b).

Orentlicher, M., and J. M. Prausnitz, "Thermodynamics of Hydrogen Solubility in Cryogenic Solvents at High Pressures," *Chem. Eng. Sci.*, **19**, 775 (1964).

Prausnitz, J. M., "Thermodynamic Representation of High Pressure Vapor-Liquid Equilibria," *ibid.*, **18**, 613 (1963).

———., and P. L. Chueh, *Computer Calculations for High Pressure Vapor-Liquid Equilibria*, p. 27, Prentice-Hall, Englewood Cliffs, N. J. (1968).

Reid, R. C., and T. K. Sherwood, *The Properties of Gases and Liquids*, pp. 6-42, 571-636, McGraw Hill, New York (1966).

Rowlinson, J. S., *Liquids and Liquid Mixtures*, pp. 26-36, 249-307, Plenum Press, New York (1969).

Spencer, C. F., and R. P. Danner, "Improved Equation for Prediction of Saturated Liquid Density," *J. Chem. Eng. Data*, **17**, 236 (1972).

Manuscript received March 28, 1972; revision received May 26, 1972; paper accepted July 20, 1972.

Calculation Method for the Response Time to Step Inputs for Approximate Dynamic Models of Distillation Columns

A calculation method to determine the response time to be used for approximate mathematical models is developed for the dynamic behavior of distillation columns. Previous work has shown that the concept of *Inventory time* can be successfully used to approximate the response time, that is, the 60% point of the step response, of distillation columns operating at a high degree of separation. A modified version of the inventory time method, based on the minimum change of storage, has been developed to predict the response time for other ranges of separation within reasonable bounds of error, ± 10%. Only steady state and design data were used. A rigorous nonlinear simulation generates the steady state and transient data upon which the approximate models are based.

While the modified inventory time method developed cannot handle every possible operating condition with the desired degree of accuracy, it has been shown to apply over a much wider range of operating conditions than the original inventory time method.

W. A. WEIGAND
A. K. JHAWAR and
T. J. WILLIAMS

School of Chemical Engineering
Purdue University
Lafayette, Indiana 47907

SCOPE

Distillation, the most widely used separation technique in the processes industries, is a nonlinear dynamic process. The extent of the nonlinear behavior is highly dependent on the range of operation of the column. In addition, disturbances in column operation can cause product quality to be upset for considerable periods of time. Since many columns operate at very high rates of production, a decrease in the product which is off specification could potentially lead to great economic savings. A means of substantially reducing this period is to use a combination