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THE VOLUMETRIC AND THERMODYNAMIC PROPERTIES OF FLUIDS.

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ABSTRACT

The acentric factor theory of volumetric behavior of pure fluids is applied to mixed gases. The pseudo-critical temperature and pressure and the acentric factor are evaluated for 12 binary systems each at several compositions. It is found that a linear equation in the mole fraction and the properties of the components is adequate for the acentric factor in all cases and for the pseudo-critical constants in some systems. In other systems small quadratic terms are required for the pseudo-critical temperature and pressure. The relationship of these quadratic terms to the intermolecular forces is considered. It is believed that useful predictions of fugacities as well as of volumetric data can be made on the basis of these results.

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Corresponding states theory has been extensively used in the treatment of solutions. Particularly notable contributions were the introduction of the pseudo-critical concept by Kay¹ and of the method of conformal solutions

(1) W. B. Kay, Ind. Eng. Chem. 28, 1014 (1936).

by Longuet-Higgins.² Recent important work includes that of Prigogine and

(2) H. C. Longuet-Higgins, Proc. Roy. Soc. A205, 247 (1951).

collaborators,³ and of Scott.⁴

(3) I. Prigogine, A. Bellemans, and A. Englert-Chwoles, J. Chem. Phys. 24, 518 (1956) and earlier papers there cited.

(4) R. L. Scott, J. Chem. Phys. 25, 193 (1956).

Salsburg⁵ and Prigogine⁶ have presented excellent reviews which give

(5) Z. W. Salsburg, Annual Reviews of Physical Chemistry 8, 55 (1957).

(6) I. Prigogine, "The Molecular Theory of Solutions," North-Holland Pub. Co., Amsterdam (1957).

further references.

One limitation on all corresponding states theories of solutions is the fact that the pure components seldom follow the law of corresponding states strictly. Brown⁷ showed that the deviations of the CO-CH₄ system from solution

(7) W. B. Brown, Phil. Trans. Roy. Soc. (London) A250, 175 (1957).

theory of this type differed substantially depending on the choice of CO or

or CH_4 as the reference substance. In this paper we apply to solutions the extended theory based upon the acentric factor which has been applied to pure fluids in a recent series of papers.⁸

(8) These papers are summarized in UCRL-8093 which gives individual references.

This removes the contradiction which is inherent in a corresponding states treatment of a solution of two components which do not themselves follow the principle of corresponding states. The acentric factor theory is not exact either, but it was found to reduce the magnitude of deviation in pure substances by about a factor of ten from that of simple corresponding states theory. At the present level of accuracy of solution studies, this residual uncertainty in treatment of pure substance properties is unimportant.

In this investigation the volumetric properties of several solution systems in the single phase region are compared with the functions for pure substances. Best values of the pseudo-critical temperature and pressure and of the acentric factor are obtained as well as an estimate of the accuracy of agreement throughout the region of available data. Then the pseudo-critical constants and acentric factors for the solutions are compared with those for the pure components and methods of relating one with the other are discussed. Possible thermodynamic applications are illustrated by fugacity calculations.

Determination of Pseudo-critical Constants. In the acentric factor theory the compressibility factor is given by the equation

$$(PV/RT) = z = z^{(0)} + \omega z^{(1)} \quad (1)$$

where $z^{(0)}$ and $z^{(1)}$ are functions of the reduced temperature T_r and the reduced pressure P_r which are tabulated in UCRL-8093. The acentric factor ω is defined by the equation

$$\omega = -\log (P/P_c)_{\text{sat}} - 1.000 \text{ at } T_r = 0.700 \quad (2)$$

where $(P/P_c)_{\text{sat}}$ is the reduced vapor pressure at $T_r = 0.700$. It was explained in earlier papers that the acentric factor may be determined from vapor pressure data at any temperature well removed from the critical point.

In our present work, we seek to determine an acentric factor and pseudo-critical constants for a solution such that its volumetric behavior is given

by Eq. (1). Since solutions cannot be expected to conform exactly with even the acentric factor extension of the corresponding states theory for pure substances, there is necessarily some arbitrariness in the selection of pseudo-critical constants. The most characteristic and sensitive single phase region is that just above the critical point in both temperature and pressure. The two phase region is expanded for solutions, as compared to pure substances, consequently the range available for comparison of single phase properties begins somewhat above the point $T_r = 1$, $P_r = 1$. For typical systems the isotherms from $T_r = 1.15$ to 1.4 were most useful. These isotherms have minima in the compressibility factor at reduced pressures between 2.3 and 3.3, and data over a pressure range of about a factor of two each way from the minimum were usually available.

The precise procedure comprised first the construction of a tracing paper graph of the compressibility factor z vs $\log P$ for the region mentioned above. The values of the minima in z of the isotherms are then plotted vs $\log T$ on a second graph. The slope of this second graph was found to be relatively sensitive to the acentric factor. These plots were made for the solution systems and in addition from the tables of UCRL-8093 for pure substance behavior. Comparison of graphs of the second type with translation along the $\log T$ axis seemed to determine both the acentric factor ω (from the fit in slope) and the pseudo-critical temperature (from the relative scales of $\log T$). Then comparison of graphs of the first type allowed determination of the pseudo-critical pressure (from the relative scales of $\log P$) and of the accuracy of fit away from the minima in the isotherms.

The resulting constants are presented in Table I. The deviation in z between the observed and theoretical values was less than 1% in most regions. Comparisons were made at temperatures and pressures well outside the region used in determining the pseudo-critical constants. In an extreme comparison of this type the second virial coefficient of 40% n-butane, 60% methane was predicted from the pseudo-critical constants fitted in the high pressure region and the empirical second virial coefficient equation (A-6 of UCRL-8093). The calculated result differed from experiment by not over 6 cc/mole in the range 378-510°K. The resulting error compressibility factor at atmospheric pressure would be 0.02%.

The precision of determination of the pseudo-critical constants depends, of course, on the precision of agreement with the theoretical curves. The uncertainty in ω for the systems in Table I ranges from 0.02 to 0.1, while that in T_c or P_c ranges from 0.2 to 1%.

Table I

Pseudo-Critical Constants of Solutions (Values for 50 mole %)				
System	Ref.	T _{cm} °K	P _{cm} atm	ω _m
CH ₄ - C ₂ H ₆	a	254	48.5	0.05
CH ₄ - C ₃ H ₈	b	287	37.9	.12
CH ₄ - iso C ₄ H ₁₀	c	309	40.3	.10
CH ₄ - n - C ₄ H ₁₀	d	324	42.2	.17
C ₃ H ₈ - iso C ₅ H ₁₂	e	415	37.3	.20
C ₃ H ₈ - C ₆ H ₆	f	464	45.2	.20
N ₂ - C ₂ H ₆	g	213	41.4	.05
CH ₄ - CO ₂	h	242	57.6	.15
CO ₂ - C ₂ H ₆	i	292	55.3	.10
CO ₂ - C ₃ H ₈	j	322	49.5	.14
CO ₂ - n - C ₄ H ₁₀	k	352	46.1	.20
CH ₄ - H ₂ S	l	269	63.2	.05

(a) B. H. Sage and W. N. Lacey, Ind. Eng. Chem. 31, 1497 (1939); the 70°F isotherms appear to be inaccurate; constants in Table I are based on higher temperature data.

(b) H. H. Reamer, B. H. Sage, and W. N. Lacey, *ibid.*, 42, 534 (1950).

(c) R. H. Olds, B. H. Sage, and W. N. Lacey, *ibid.*, 34, 1008 (1942).

(d) H. H. Reamer, K. J. Kaapi, B. H. Sage, and W. N. Lacey, *ibid.*, 39, 206 (1947).

(e) W. E. Vaughan and F. C. Collins, *ibid.*, 34, 885 (1942).

(f) J. W. Glanville, B. H. Sage, and W. N. Lacey, *ibid.*, 42, 508 (1950).

(g) H. H. Reamer, F. T. Selleck, B. H. Sage, and W. N. Lacey, *ibid.*, 44, 198 (1952).

(h) H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey, *ibid.*, 36, 88 (1944).

(i) H. H. Reamer, R. H. Olds, B. H. Sage, and W. N. Lacey, *ibid.*, 37, 688 (1945).

(j) H. H. Reamer, B. H. Sage, and W. N. Lacey, *ibid.*, 43, 2515 (1951).

(k) R. H. Olds, H. H. Reamer, B. H. Sage, and W. N. Lacey, *ibid.*, 41, 475 (1949).

(l) H. H. Reamer, B. H. Sage, and W. N. Lacey, *ibid.*, 43, 976 (1951).

It is remarkable that pairs of components with such different volatility as methane and n-butane or nitrogen and ethane yield solutions which behave nearly like pure substances in the single phase region. These systems appear to be near the boundary, however, because the system methane - n - pentane deviates significantly. Experimental isotherms fitted near their minima in z fall about 2% below the theoretical curves at a pressure one-half or twice that of the minimum.

Composition Dependence of Pseudo-Critical Constants. The prima facie extension of Kay's postulates to the acentric factor system is the assumption that ω as well as T_c and P_c are linear functions of the mole fraction. Table II presents the tests of this assumption. The fourth, sixth, and eighth columns contain the quantities which are zero if the critical temperature, the critical pressure, and the acentric factor, respectively, are linear functions of the mole fraction. Three systems, propane-isopentane, propane-benzene, and nitrogen-ethane, appear to fit since none of their deviations exceed the limit of uncertainty. The remaining systems deviate by significant amounts and in a few cases by large amounts.

In cases where there is deviation from linear dependence on the mole fraction, a quadratic term suffices to yield agreement. Thus the following equations are obtained for the pseudo-critical constants of a solution of mole fraction x_1 and x_2 .

$$T_{cx} = x_1 T_{c1} + x_2 T_{c2} + 2x_1 x_2 (2T_{cm} - T_{c1} - T_{c2}) \quad (3)$$

$$P_{cx} = x_1 P_{c1} + x_2 P_{c2} + 2x_1 x_2 (2P_{cm} - P_{c1} - P_{c2}) \quad (4)$$

$$\omega_x = x_1 \omega_1 + x_2 \omega_2 + 2x_1 x_2 (2\omega_m - \omega_1 - \omega_2) \quad (5)$$

The T_c 's and P_c 's refer to the critical temperature and pressure throughout. The quantities with subscript 1 or 2 pertain to the pure components; those with subscript x to the mixture of composition x_1 , x_2 , while those with subscript m apply to the equimolal mixtures. The relationship of the quantities in parentheses to those in Table II is self-evident.

Two conclusions may be drawn from the results in Table II. First, the acentric factor of the solution is, within the limits of uncertainty, a linear function of the acentric factors of the components. Second, the deviation from

linear dependence of the pseudo-critical temperature and pressure exceeds the limit of uncertainty in many cases but does not appear to follow any simple formula based on differences of properties of pure components. We shall return later to a discussion of these conclusions in terms of molecular properties.

Calculation of Fugacities. The system defined by Eqs. (1), (3), (4), (5) provides a basis for the calculation of various thermodynamic properties of solutions. The last term in Eq. (5) is dropped in view of the results already discussed. The fugacity is probably of greatest interest because it determines both phase equilibria and chemical reaction equilibria. The derivation of fugacities from a pseudo-critical corresponding states system of equations has been given by Gamson and Watson.⁹ The method is straightforward and we shall

(9) B. W. Gamson and K. M. Watson, Nat'l Petroleum News 36, R623 (1944); see also J. Jaffe, Ind. Eng. Chem. 40, 738 (1948).

merely give the resulting equations for two components.

$$\log \left(\frac{f_1}{x_1 P} \right) = \left[\log \left(\frac{f}{P} \right) \right]_x + x_2 Y \quad (6a)$$

$$\log \left(\frac{f_2}{x_2 P} \right) = \left[\log \left(\frac{f}{P} \right) \right]_x - x_1 Y \quad (6b)$$

$$Y = \left(\frac{H^* - H}{RT_c} \right)_x \frac{[T_{c2} - T_{c1} + 2(1 - 2x_2)(2T_{cm} - T_{c1} - T_{c2})]}{2.303 T} \\ + \frac{(z_x - 1) [P_{c2} - P_{c1} + 2(1 - 2x_2)(2P_{cm} - P_{c1} - P_{c2})]}{2.303 P_c} \\ - \left[\log \left(\frac{f}{P} \right) \right]^{(1)} (\omega_2 - \omega_1) \quad (6c)$$

All of the quantities appearing in Eq. (6) have been defined or tabulated before. The subscript x indicates that the quantity is to be calculated for the reduced temperature, pressure and the acentric factor of the solution of mole fraction x_1, x_2 . The compressibility factor functions were given in Tables A-2 through A-7 of UCRL-8093 while the fugacity and enthalpy functions were

Table II

Relationship of Pseudo-Critical Constants of 50 Mole % Solutions to Properties of Components							
System		Critical T		Critical P		Acentric Factor	
Comp. 1	Comp. 2	$\frac{T_{c2}}{T_{c1}} \left[\frac{2T_{cm}}{T_{c1}+T_{c2}} - 1 \right]$		$\frac{P_{c2}}{P_{c1}} \left[\frac{2P_{cm}}{P_{c1}+P_{c2}} - 1 \right]$		$(\omega_2 - \omega_1) \left[\omega_m - \frac{\omega_1 + \omega_2}{2} \right]$	
CH ₄	C ₂ H ₆	1.60	.02	1.07	.02	.09	-.01
CH ₄	C ₃ H ₈	1.94	.02	.92	.03	.14	+.04
CH ₄	isoC ₄ H ₁₀	2.14	.03	.79	-.01	.17	.00
CH ₄	n-C ₄ H ₁₀	2.23	.05	.82	+.01	.19	.06
C ₃ H ₈	isoC ₅ H ₁₂	1.25	.00	.78	.00	.06	.02
C ₃ H ₈	C ₆ H ₆	1.52	.00	1.16	.00	.06	.02
N ₂	C ₂ H ₆	2.42	-.01	1.39	.00	.06	-.02
CH ₄	CO ₂	1.60	-.02	1.59	-.03	.21	+.03
CO ₂	C ₂ H ₆	1.00	-.04	.67	-.09	-.12	-.06
CO ₂	C ₃ H ₈	1.21	-.05	.58	-.14	-.07	-.05
CO ₂	n-C ₄ H ₁₀	1.40	-.03	.52	-.16	-.01	-.02
CH ₄	H ₂ S	1.96	-.05	1.94	-.06	.09	-.01

given in Tables A-8 through A-13 of UCRL-8093. In the low pressure region the equations of A-6, A-7, and A-8 (of UCRL-8093) give values for all the functions.

In the two phase region the fugacity of each component must be the same for each phase. The calculated fugacities for four sets of experimental equilibrium compositions in the propane-isopentane system¹⁰ are presented in Table III as an

(10) W. E. Vaughan and F. C. Collins, Ind. Eng. Chem. 34, 885 (1942).

example and test of this method.

Table III

Fugacities in the Propane-Isopentane System							
(Component 1 is propane, 2 is isopentane; fugacities are in atm)							
T, °K	P, atm	Liquid			Vapor		
		x_1	f_1	f_2	x_1	f_1	f_2
348.2	15.0	.509	10.6	2.0	.822	10.6	1.8
373.2	20.0	.414	12.1	4.0	.713	12.2	3.7
373.2	39.0	.909	25.8	0.87	.951	25.9	0.74
398.2	37.0	.577	20.9	5.0	.735	21.6	4.7

The agreement for propane fugacity is good and that for isopentane is reasonably satisfactory in view of the fact that no experimental data in or near the two phase region were used in evaluating the pseudo-critical constants.

The extension of this method to other thermodynamic functions or to more than two components is quite straightforward. The principal limitation for predictive purposes is the need for the coefficients of the quadratic terms in Eqs. (3) and (4) for the pseudo-critical temperature and pressure. We turn now to a discussion of this topic.

Discussion. Molecular solution theories^{5,6} commonly assume that the interaction energy between unlike molecules is given by the geometric mean of the interaction energies between like molecules. While the transfer of this postulate

to a pseudo-critical constant theory is not simple, it would be expected to yield a solution critical temperature less than the arithmetic mean of those of the components. Table II, however, shows a zero or positive deviation for all of the hydrocarbon systems. Also for the systems with non-hydrocarbon components, the magnitude of the negative deviation has little or no correlation with the deviation of T_2/T_1 from unity. Tentatively, we conclude that difference in molecular size tends to yield a positive deviation in the pseudo-critical temperature. This is observed in the hydrocarbon systems where the principal intermolecular attractive force is the London force between C-H bonding electrons and is essentially the same regardless of the particular hydrocarbon molecules. The deviation in pseudo-critical temperature for the other systems in Table II is decreased and is usually negative because one component of the attractive force between unlike molecules is smaller than that for like molecules. For example permanent dipole-dipole interaction must contribute to the attractive force between two H_2S molecules but is absent in $CH_4 - H_2S$ force. Quadrupole forces are probably significant for interaction of CO_2 molecules but unimportant for the hydrocarbons. The more subtle differences in London forces which arise from differences in effective polarizability per electron or effective frequency of electronic motion also affect various systems containing non-hydrocarbon components.

The pseudo-critical pressures of the hydrocarbon solutions deviate little from the arithmetic means of the values for the components. In the systems involving H_2S or CO_2 , however, the deviations are substantial and always negative. The largest values arise when (T_2/T_1) and (P_2/P_1) deviate from unity in opposite directions, i.e., when the molal volumes of the two components differ substantially.

The number of systems studied is not large enough to justify broad conclusions on an empirical basis. It would be desirable to have these quadratic term coefficients for additional systems. Nevertheless, consideration of the various factors affecting intermolecular forces should allow the experienced scientist to estimate values of $(2T_{cm} - T_{c1} - T_{c2})$ and $(2P_{cm} - P_{c1} - P_{c2})$ for systems similar to those listed in Table II with sufficient accuracy for many purposes.

It should be noted that in this study the maximum ratio of critical temperatures of components is 2.4, that of critical pressures is 2.0, and the maximum ratio of critical volumes implied is about 3. We have reason to believe that the behavior of mixed gases may become more complex when the components differ from one another to a greater degree. Thus the present methods should be used with caution outside the range defined above. Nevertheless the present method should yield useful predictions of considerable accuracy for a large variety of solution systems.

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