Volumetric Properties of Nonpolar Gaseous Mixtures

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Volumetric data of nonpolar gaseous mixtures are analyzed in terms of the theory of corresponding states. Special attention is given to an analysis of the second virial coefficient and to the calculation of pseudocritical constants.

Second virial coefficients are calculated from experimental data for ten binary systems. These coefficients, with those previously published, are correlated by means of a generalized equation involving three parameters for each component: the critical volume, the reduced temperature, and the acentric factor.

Equations are derived for the pseudocritical temperature and pressure of mixtures. These equations are considerably more accurate than those given by Kay's rule. Because of the complexity of the proposed equations for the pseudocritical parameters, a simplified pseudocritical method is presented which is sufficiently accurate for most chemical engineering purposes, especially at reduced temperatures exceeding 1.3.

Methods are available for predicting with good accuracy the volumetric properties of nonpolar gases in the pure state, but no method of comparable validity has been reported for mixtures of these gases. The volumetric properties of gaseous mixtures not only are of interest for applications similar to those pertaining to pure gases, but they also are required for accurate determination of phase equilibria and for correct specification of the driving force in separation operations and chemical kinetics. In vapor-liquid equilibria, for example, departure from ideal behavior in the gaseous phase at high pressures may be at least as large as that in the liquid phase. The *P-V-T-y* behavior of a gaseous mixture uniquely determines the fugacity for each component at any particular temperature, pressure, and composition, and the fugacities in turn, determine the equilibrium curve.

Various methods for predicting the properties of gaseous mixtures have been proposed, but for the most part these have been strictly empirical. While such methods have been successful in limited cases, large errors often appear in unexpected instances, demonstrating the basic weakness of a purely empirical approach.

In view of the inadequacy of the present methods this investigation has attempted to develop equations based as much as possible on available theory while remaining within the realm of engineering utility.

The nonideality of gaseous mixtures can be conveniently regarded as consisting of two parts: one part is due to the nonideality of the pure gases and the other to the nonideality of mixing. This paper considers only the second part. The nonideality of pure gases has received much attention previously, and, with the help of corresponding-states correlations, volumetric properties of nonpolar or slightly polar gases can now be predicted accurately. The problem of computing the volumetric properties of a gaseous mixture, therefore, consists of relating the properties of the mixture to the corresponding properties of the pure components.

VIRIAL EQUATION

The volumetric properties of gases are conveniently expressed by an equation of state. The only equation of state with a sound theoretical basis is the virial equation, and, because of its theoretical origin, it is possible to extend this equation to mixtures by establishing an exact relationship between the equation for a mixture and the equations for the pure components. The virial equation is a series in the reciprocal volume

$$z = \frac{PV}{RT} = 1 + \frac{B}{V} + \frac{C}{V^2} + \cdots \qquad (1)$$

When Equation (1) is applied to a mixture, the virial coefficients are functions of composition as well as temperature. The composition dependence of the virial coefficients is given by (*2, 10*)

$$B_m = \sum_{ij} y_i y_j B_{ij} \qquad (2)$$

$$C_m = \sum_{ijk} y_i y_j y_k C_{ijk} \qquad (3)$$

For a binary mixture Equations (2) and (3) reduce to

$$B_m = y_1^2 B_{11} + 2y_1 y_2 B_{12} + y_2^2 B_{22} \qquad (2a)$$

$$C_m = y_1^3 C_{111} + 3y_1^2 y_2 C_{112} + 3y_2^2 y_1 C_{122} + y_2^3 C_{222} \text{ etc.} \qquad (3a)$$

B_{11}, C_{11}, B_{22} and C_{222} depend only on the forces acting between like molecules; the remaining coefficients, called *cross coefficients*, depend on the forces acting between unlike molecules.

The nonideality of mixing vanishes only if the following hold for the cross coefficients:

$$B_{12} = \tfrac{1}{2}(B_{11} + B_{22}) \qquad (4)$$

$$C_{112} = \tfrac{1}{3}(2C_{111} + C_{222}) - (B_{11} - B_{22})^2 \qquad (5a)$$

and

$$C_{122} = \tfrac{1}{3}(C_{111} + 2C_{222}) - (B_{11} - B_{22})^2 \qquad (5b)$$

Equations (4) and (5*a, b*) lead to the following for the virial coefficients for the mixture:

$$B_m = y_1 B_{11} + y_2 B_{22} \qquad (6)$$

$$C_m = y_1 C_{111} + y_2 C_{222} - 3y_1 y_2 (B_{11} - B_{22})^2 \qquad (7)$$

Equations (6) and (7) and similar equations for the higher virial coefficients are equivalent to Amagat's law of additive volumes or to the identical statement that the compressibility factor of a mixture at constant temperature and pressure is a straight-line function of the composition. This simplification is very rarely valid even for simple gases; to illustrate, Figure 1 shows the observed compressibility factors (*11*) for mixtures of methane and ethane at 50°C. and 60 atm. Instead of a straight line the plot is a parabola, which is to be expected from Equation (2*a*), since at this temperature and pressure virial coefficients higher than the second can be neglected.

At moderate densities, where the volumetric properties of gases are adequately described by a virial equation terminating after the second term, the key to the nonideality of mixing lies in the cross coefficient B_{ij}. Compressibility data for mixtures were therefore analyzed to determine these cross coefficients and to relate them to the properties of the pure components. This analysis is described in the next two sections. In a later section the results on second virial coefficients are used to derive formulas for the calculation of pseudocritical constants for gas mixtures.

ANALYSIS OF SECOND-VIRIAL-COEFFICIENT DATA

Volumetric data of ten binary gaseous systems have been analyzed to determine the experimental values of B_{12} at three different compositions, whenever possible, and at several different temperatures. The references and the temperature range for those systems studied are listed in Table 1.

The experimental values used were those at densities less than the pseudo critical density (d_{c_m}), which is defined here as

$$d_{c_m} = \frac{1}{V_{c_m}} = (\sum_i y_i V_{c_i})^{-1} \qquad (8)$$

Table 1. References for Experimental Data Employed

System	Temperature Range, °F.	Reference
A. Volumetric Data for Mixtures		
1. Methane-ethane	32–122	*11*
2. Methane-propane	100–460	*19*
3. Methane–*n*-butane	160–460	*21*
4. Methane-*i*-butane	160–460	*21*
5. Ethane-propylene	220–400	*20*
6. Ethane-nitrogen	40–460	*20*
7. Butane-nitrogen	310–400	*1*
8. Carbon dioxide–nitrogen	77–257	*21*
9. Carbon dioxide–propane	100–460	*20*
10. Carbon dioxide–*n*-butane	220–400	*20*
B. Volumetric Data or Virial-Coefficient Data for Pure Gases		
1. Methane	100–460	*12,22*
2. Ethane	100–460	*11,22*
3. Nitrogen	40–460	*8*
4. Propane	100–460	*19*
5. *n*-Butane	160–460	*19*
6. *i*-Butane	160–460	*19*
7. Propylene	220–460	*20*
8. Carbon dioxide	100–460	*20*
C. Published Virial-Coefficient Data		
1. Methane-neopentane	86–266	*6*
2. Methane–tetramethyl silane	122–266	*6*
3. Methane–sulfur hexafluoride	104–208	*6*
4. Methane–*n*-pentane	100–460	*23*
5. Methane–carbon dioxide	100–460	*23*
6. Ethane–carbon dioxide	100–460	*23*
7. Propylene–carbon dioxide	5–176	*7*
8. Nitrogen–carbon dioxide	77	*12*
9. Carbon monoxide–carbon dioxide	77	*12*
10. Hydrogen–carbon dioxide	77	*12*
11. Hydrogen-ethylene	77	*12*
12. Hydrogen-nitrogen	77	*12*
13. Hydrogen–carbon monoxide	77	*12*

The volumetric data were represented by the equation

$$V(z-1) = B_m + \frac{C_m}{V} \qquad (9)$$

For the range of densities mentioned it was found that the second and third virial coefficients represented the data with an accuracy comparable to the accuracy of the experimental measurements. The virial coefficients were evaluated by the method of least squares with the aid of a high-speed digital computer. After each analysis the residuals were analyzed; any experimental measurements deviating by more than three times the standard deviation were discarded, and the virial coefficients were reevaluated from the remaining data. To calculate the B_{12}'s from the second virial coefficients for the mixtures the virial coefficients for the pure components must be known. Table 1 also gives the references for the volumetric data used to evaluate the second virial coefficients of the pure components.

In addition to the systems listed in Table 1, an analysis was made of the compressibility data for the binaries methane–*n*-heptane (*17*), methane-decane (*18*), hydrogen sulfide–*n*-heptane (*19*), hydrogen sulfide–decane (*19*), propane-isopentane (*21*), propane-benzene (*19*), and *n*-butane–decane (*19*). These mixtures were of special interest, since each one consists of two species of considerably different size, the critical volume ratio ranging up to slightly over six. Unfortunately however the data for these systems were not reported at densities sufficiently moderate to use the truncated virial equation, and an indirect method of analysis was used. The compressibility data for these systems were fitted by a set of pseudocritical constants in a manner described previously (*16*). With these pseudocritical constants it was possible to predict the compressibilities at lower densities and hence to compute the second virial coefficients.

The details of the calculations as well as the complete numerical results are given elsewhere (*5*). The results obtained were analyzed in terms of the theory of corresponding states as described in the next section.

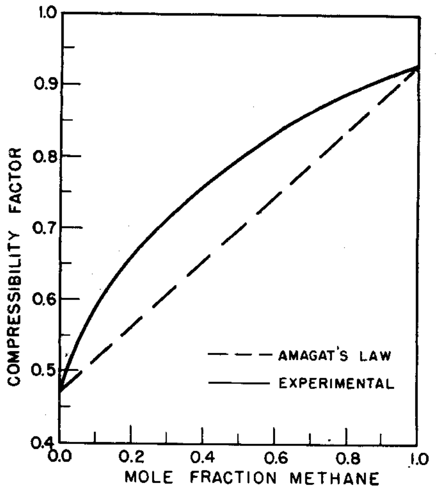

Fig. 1. Compressibility factors for the methane-ethane system at 50°C. and 60 atm.

CORRESPONDING-STATES THEORY FOR MIXTURES

The molecular basis for the theory of corresponding states for pure, simple fluids was discussed by Pitzer about twenty years ago (*13*), and Guggenheim (*4*) and others have shown that when the reduced second virial coefficient B/V_c (where V_c is the critical volume) is plotted against the reduced temperature, a universal function is obtained which, to a good approximation, represents the data for a variety of substances of low molecular weight. It was then shown by Guggenheim and McGlashan (*3*) that this universal plot could be applied to mixtures by writing

$$\frac{B_{ij}}{V_{c_{ij}}} = \theta_B\left(\frac{T}{T_{c_{ij}}}\right) \qquad (10)$$

For the special case where $i = j$ the characteristic temperature and the characteristic volume become respectively the critical temperature and the critical volume of the pure component. For the case where $i \neq j$ Guggenheim and McGlashan suggested the mixing rules

$$T_{c_{ij}} = (T_{c_{ii}} T_{c_{jj}})^{1/2} \qquad (11)$$

$$V_{c_{ij}}{}^{1/3} = \tfrac{1}{2}(V_{c_{ii}}{}^{1/3} + V_{c_{jj}}{}^{1/3}) \qquad (12)$$

This extension of the corresponding-states theory to mixtures gives good results for mixtures of light components but progressively worse results as the size of the gas molecules increases. This is not surprising in view of the limitations clearly indicated by Pitzer (*13*) as in-

Table 2. Constants r and s* for Calculating the Pseudocritical Temperature

T_r/ω	0		0.25		0.10		0.15		0.20	
	r	s	r	s	r	s	r	s	r	s
1.0	3.197	1.524	4.936	1.718	7.626	1.969	11.79	2.283	18.80	2.725
1.25	2.389	1.420	3.642	1.577	5.483	1.773	8.394	2.033	13.15	2.381
1.50	1.899	1.351	2.871	1.484	4.242	1.645	6.460	1.866	9.897	2.151
2.00	1.326	1.263	1.988	1.364	2.871	1.484	4.317	1.653	6.422	1.862
3.00	0.823	1.175	1.222	1.245	1.708	1.323	2.526	1.439	3.621	1.575

T_r/ω	0.25		0.30		0.35		0.40		0.48
	r	s	r	s	r	s	r	s	
1.0	31.11	3.333	57.07	4.310	119.47	5.988	352.51	9.901	T_{c_m} is given by $\left(\frac{\gamma}{V_{c_m}}\right)^{1/2}$
1.25	21.69	2.882	38.68	3.650	80.91	5.025	227.89	8.065	
1.50	16.26	2.577	28.27	3.205	58.81	4.367	162.66	6.897	
2.00	10.46	2.193	17.66	2.660	36.73	3.571	95.25	5.405	
3.00	5.779	1.802	9.307	2.105	20.47	2.817	46.25	3.937	

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*The lower limit of the Pitzer compressibility tables is for a reduced temperature of 0.8. Values of r and s at $T_r = 1.0$ may be used with sufficient accuracy for the range of reduced temperatures of 0.8 to 1.0.

herent in any two-parameter theory of corresponding states. To extend the corresponding-states treatment to pure, nonsimple fluids of nonpolar (or slightly polar) character, Pitzer and coworkers (*14*) recently showed that the volumetric properties of such fluids could be correlated by introducing one additional parameter. It was found that the compressibilities of a large class of substances could be expressed as functions of the reduced temperature T_r, the reduced pressure P_r, and the acentric factor ω defined by

$$\omega \equiv -\log_{10} P_r \quad (\text{saturated at } T_r = 0.7) - 1.00 \tag{13}$$

The acentric factor is a measure of the deviation from simple-fluid behavior; for simple fluids (argon, krypton, xenon, and methane) the acentric factor is zero. These ideas can also be applied to a correlation of second virial coefficient data. Pitzer and Curl (*15*) showed that for a large number of pure substances the reduced second virial coefficient BP_c/RT_c (where P_c and T_c are the critical pressure and temperature) could be expressed in the form

$$B = B^0 + \omega B' \tag{14}$$

with

$$\frac{B^0 P_c}{RT_c} = \theta_B{}^0(T_r)$$

and

$$\frac{B' P_c}{RT_c} = \theta_B{}'(T_r) \tag{15}$$

The interpretation of second virial coefficient data for mixtures as presented here is based on an extension of the method of Guggenheim and McGlashan within the framework of the three-parameter theory of corresponding states.

In the generalized equation for second virial coefficients reported by Pitzer and Curl [Equation (15)] the virial coefficients are reduced by the quantity P_c/RT_c rather than by the critical volume. For pure gases the former is preferred because critical pressures are usually more accurately known than critical volumes; however for gaseous mixtures the latter is more convenient because a characteristic critical volume is more readily calculated than a characteristic critical pressure. The characteristic critical volumes and temperatures are each proportional to one of the parameters in the intermolecular potential function for the interaction of dissimilar molecules, whereas the characteristic critical pressure is not directly related to either of these parameters. It was preferable therefore to make the following modification of the Pitzer and Curl equation. By definition the compressibility factor at the critical point is

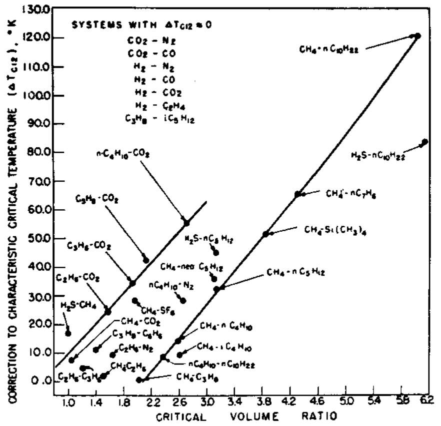

Fig. 2. Corrections to the characteristic critical temperature for several nonpolar gaseous systems.

$$z_c = \frac{P_c V_c}{RT_c} \tag{16}$$

When $B^0/V_c = B_{r_V}{}^0$; $B'/V_c = B_{r_V}{}'$, from Equations (14), (15), and (16)

$$z_c(B_{r_V}{}^0 + \omega B_{r_V}{}') = \theta_B{}^0 + \omega \theta_B{}' \tag{17}$$

The compressibility tables reported by Pitzer and coworkers (*14*) show that the critical compressibility factor is given by

$$z_c = z_c{}^0 + \omega z_c{}' = 0.291 - 0.08\omega \tag{18}$$

For simple fluids, which have zero acentric factors, Equation (17) reduces to

$$B_{r_V}{}^0 = \frac{\theta_B{}^0}{0.291} \tag{17a}$$

When one subtracts Equation (17*a*) from Equation (17) and rearranges,

$$B_{r_V}{}' = \frac{0.274\,\theta_B{}^0 + \theta_B{}'}{0.291 - 0.08\omega} \tag{19}$$

The extension of the three-parameter theory of corresponding states therefore is of the form

$$\frac{B_{ij}}{V_{c_{ij}}} = B_{r_V}{}^0\left(\frac{T}{T_{c_{ij}}}\right) + \omega_{ij} B_{r_V}{}'\left(\frac{T}{T_{c_{ij}}}\right) \tag{20}$$

where $B_{r_V}{}^0$ and $B_{r_V}{}'$ are given by Equations (17*a*) and (19) respectively.

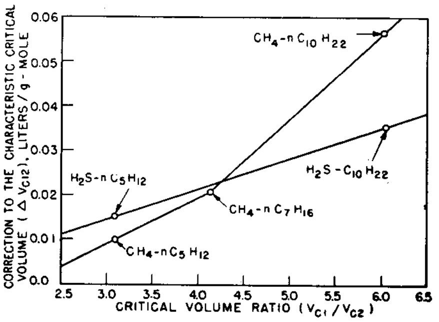

Fig. 3. Correction to the characteristic critical volume (Vc_{12}) for several systems.

The accuracy of the experimental B_{12}'s is insufficient to establish unequivocal values for the three parameters ω_{12}, $T_{c_{12}}$, and $V_{c_{12}}$; therefore simple algebraic rules were adopted for two characteristic parameters:

$$\omega_{12} = \tfrac{1}{2}(\omega_1 + \omega_2) \tag{21}$$

$$V_{c_{12}} = \tfrac{1}{2}(V_{c_1} + V_{c_2}) \tag{22}$$

The value of $T_{c_{12}}$ was then adjusted to fit the experimental data. Because the acentric-factor correction at reduced temperatures greater than unity is generally, relatively small and often not much greater than the experimental error, it is difficult empirically to obtain an unambiguous expression for the characteristic acentric factor. Of the various simple algebraic combinations Equation (21) appeared to give the best results.

Equation (22) is less conventional than the frequently employed Lorentz combination

$$V_{c_{12}}{}^{1/3} = \tfrac{1}{2}(V_{c_1}{}^{1/3} + V_{c_2}{}^{1/3}) \tag{23}$$

However, when the ratio of the critical volumes of the pure components (V_{c_1}/V_{c_2}) is close to unity, the numerical difference between the linear combination [Equation (22)] and the Lorentz combination [Equation (23)] is smaller than the experimental error, and when the ratio of the critical volumes is much larger than unity, neither equation can be expected to be very accurate. Of the five gaseous systems studied by Guggenheim and McGlashan the B_{12} values for four systems did not depend significantly on the method chosen for predicting the characteristic critical volume; the linear average and the Lorentz average give almost identical results. The remaining system, the methane–*n*-butane study, will be disregarded, since the virial coefficients used by Guggenheim and McGlashan are believed to be inaccurate.

On the basis of the mixing rules given by Equations (21) and (22) a value of the characteristic critical temperature was chosen for each system such that the experimental values of B_{12} for each temperature agreed with the values calculated by Equation (20).* Within the experimental error these characteristic critical temperatures were constant with respect to temperature. In several cases, for structurally or chemically similar gases, the experimental values of the characteristic critical temperature agreed with those predicted by the Guggenheim method [Equation (11)]. However with increasing difference in size and nature of the molecules the predicted and experimental values diverge.

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*For hydrogen fictitious critical values were used. These are T_c = 43.4°K., V_c = 50 cc./g.-mole, and ω = 0.

$$\Delta T_{c_{12}} = (T_{c_1} T_{c_2})^{1/2} - T_{c_{12}} \text{ (experimental)} \qquad (24)$$

it was found for all cases studied that $\Delta T_{c_{12}}$ was positive, becoming zero in the limit when the two components were of similar size and chemical nature. Figure 2 shows a plot of the correction $\Delta T_{c_{12}}$ against the critical volume ratio of the pure components with the critical volume of the larger component in the numerator. These data indicate that for mixtures with components of widely different critical volumes the characteristic critical temperature is always less than that given by the geometric mean of the pure-component critical temperatures.

When the ratio of critical volumes (V_{c_1}/V_{c_2}) exceeds three, the characteristic critical volume is no longer quite the arithmetic average of the critical volumes of the pure components. For these highly asymmetric systems it was found that agreement within the general framework proposed here could be improved by including a small correction term for the characteristic critical volume. Figure 3 shows a plot of this correction $(\Delta V_{c_{12}})$ defined by

$$\Delta V_{c_{12}} = \tfrac{1}{2}(V_{c_1} + V_{c_2}) - V_{c_{12}} \text{ (experimental)} \qquad (25)$$

The corrections were calculated from volumetric data for the systems methane–*n*-pentane, methane–*n*-heptane, methane-decane, hydrogen sulfide–*n*-pentane, and hydrogen sulfide–decane. Like the temperature corrections the volume corrections are always positive; however they are considerably less important.

Although it appeared impossible to obtain a unique correlation for the characteristic critical temperatures, Figure 2 shows that families of related systems obey definite trends. For example, binary mixtures containing aliphatic hydrocarbons will be considered. Experimental values for the characteristic critical temperature for the methane-ethane system and for the methane-propane system agree with those predicted by the Guggenheim method, and the correction $\Delta T_{c_{12}}$ is zero. When the ratio of critical volumes of the components exceeds two, the experimental and calculated critical temperatures diverge. For this family of systems the correction $\Delta T_{c_{12}}$ is nearly a linear function of the critical volume ratio (Figure 2). Similar behavior is observed for mixtures of aliphatic hydrocarbons with carbon dioxide.

For nonpolar gaseous systems containing very dissimilar molecules the characteristic critical temperature is consistently less than that predicted by the Guggenheim method. Since the critical temperature is proportional to the energy parameter in the intermolecular potential function, the low values for $T_{c_{12}}$ indicate that the energy parameter corresponding to the interaction between two dissimilar molecules is smaller than that predicted by the geometric mean. This behavior is to be expected for systems whenever the dominant intermolecular forces are dispersion forces. In his original paper on dispersion forces London (*9*) showed that the energy of interaction between unlike molecules of different sizes is always less than the product of the square roots of the pure-component energies, the geometric mean being an upper limit which is approached only as the sizes of the unlike molecules become identical. The experimental results shown in Figure 2 are therefore in complete qualitative agreement with London's theory.

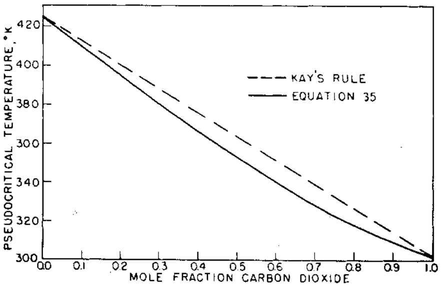

Fig. 4. Pseudocritical temperature for the carbon dioxide–*n*-butane system at a reduced temperature of 1.0.

Although the use of corresponding-states theory does not correlate the available data as completely as might be desired, it is nevertheless possible to make a very good estimate of the second virial coefficient of any binary or multicomponent gas mixture containing nonpolar (or slightly polar) components. With the help of Figure 2 corrections to the characteristic critical temperature can be estimated for most binary interactions, and in highly asymmetric systems a small, relatively unimportant correction can be estimated from Figure 3. These corrections, in conjunction with the critical temperatures, critical volumes, and acentric factors of the pure components, define the characteristic parameters by which corresponding states theory for pure gases and vapors can be extended to their mixtures.

CALCULATION OF PSEUDOCRITICAL CONSTANTS

The pseudocritical constants for a mixture are defined in such a way that, when applied to the generalized-compressibility-factor tables, they predict the correct compressibility factor for the mixture; that is, the reduced temperature and pressure for a mixture are given by

$$T_r = \frac{T}{T_{cm}} \qquad (26)$$

$$P_r = \frac{P}{P_{cm}} \qquad (27)$$

The reduced temperature and pressure in conjunction with the Pitzer compressibility tables correctly predict the volumetric behavior of the gaseous mixture at the temperature and pressure under consideration; to utilize the Pitzer tables an acentric factor is also required. For a mixture an acentric factor ω_m can be calculated by

$$\omega_m = \sum_i y_i \omega_i \qquad (28)$$

This rule has no basis in theory; however since the correction to the compressibility factor owing to the acentric factor is generally quite small, the method of averaging the acentric factors of the pure components in a mixture is relatively unimportant.

The pseudocritical temperature and pressure can be determined conveniently from volumetric data in a manner described previously (*16*). This was done for a variety of binary systems, and it was found (*16*) that these pseudocritical parameters are predicted with only low accuracy by the simple linear equations known as *Kay's Rule*.

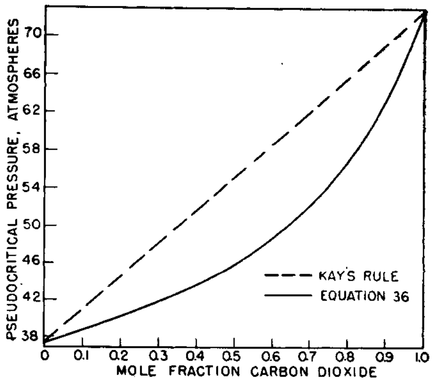

Fig. 5. Pseudocritical pressure for the carbon dioxide–*n*-butane system at a reduced temperature of 1.0.

PREDICTION OF THE PSEUDOCRITICAL CONSTANTS

Because the pseudocritical temperature is such a complicated function of the composition, it appears necessary to include some information on the nature of the interaction between unlike molecules in any successful method of prediction. The equations for the second virial coefficient of a mixture provide a convenient theoretical base from which the equation for the pseudocritical temperature can be derived. As discussed earlier the second virial coefficient for a mixture is a quadratic function of the mole fractions of the components [Equation (2)], where the virial coefficients with like subscripts are those of the pure components and the virial coefficients with unlike subscripts are those arising from the interaction of pairs of unlike molecules.

Equation (2) forms the theoretical basis on which the prediction of pseudo-

TABLE 3. SUMMARY OF CALCULATED COMPRESSIBILITY FACTORS FOR VARIOUS SYSTEMS

System	Number of mixtures	Temperature range, °K.	Pressure range, atm.	Number of points	% Deviation from experimental values			
					Maximum deviation		Average deviation	
					P.p.m.*	Kay's Rule	P.p.m.*	Kay's Rule
H_2S-CH_4	3	278-444	119-544	16	2.8	—	1.0	—
H_2S-nC_5H_{12}	3	444	41-544	10	5.5	18.8	2.0	—
H_2S-$C_{10}H_{22}$	3	380-444	27-476	13	1.4	—	0.7	—
CO_2-H_2	2	273-473	200-500	8	2.2	7.9	1.3	6.3
CO_2-nC_4H_{10}	16	344-411	34-476	19	2.2	26.1	1.0	11.3
C_3H_8-C_6H_6	2	511	34-408	7	2.6	—	0.9	—
CH_4-$C_{10}H_{22}$	3	377-511	102-306	9	2.6	—	1.3	—
CH_4-nC_5H_{12}	3	311-511	54-340	16	2.6	7.9	0.4	1.2
(CH_4-nC_4H_{10}-$C_{10}H_{22}$)	2	344-511	85-306	11	0.9	7.4	0.4	3.7
H_2-N_2-CO_2-CO-CH_4	1	278-344	136-272	4	0.4	4.3	0.2	2.8

*P.p.m. = proposed pseudocritical method.

critical constants is based. When one uses Equation (2) together with a modification of the equation of Pitzer and Curl (*15*), expressions have been derived for the pseudocritical temperature, volume, and pressure of a mixture having an arbitrary number of components. The details of the derivation are presented elsewhere;* only the results are given below.

PROCEDURE FOR COMPUTING PSEUDOCRITICAL CONSTANTS

1. After the critical temperature, critical volume, and the acentric factor for each component have been obtained, the characteristic critical temperatures and volumes for all possible different pairs of components are calculated from the following equations:

$$T_{c_{ij}} = (T_{c_i} T_{c_j})^{1/2} - \Delta T_{c_{ij}} \qquad (29)$$

$$V_{c_{ij}} = \tfrac{1}{2}(V_{c_i} + V_{c_j}) - \Delta V_{c_{ij}} \qquad (30)$$

The appropriate $\Delta T_{c_{ij}}$ and $\Delta V_{c_{ij}}$ corrections, if required, may be estimated from Figures 2 and 3. The correction $\Delta V_{c_{ij}}$ is needed only in highly asymmetric cases, and even then it is small (*7*).

2. The pseudocritical volume and the acentric factor for the mixture are computed from

$$V_{c_m} = \sum_{ij} y_i y_j V_{c_{ij}} \qquad (31)$$

$$\omega_m = \sum_i y_i \omega_i \qquad (32)$$

3. Quantities β and γ are computed:

$$\beta = \sum_{ij} y_i y_j (V_c T_c)_{ij} \qquad (33)$$

$$\gamma = \sum_{ij} y_i y_j (V_c T_c^2)_{ij} \qquad (34)$$

4. The pseudocritical temperature is calculated:

$$T_{c_m} = \frac{\beta + \sqrt{\beta^2 + r V_{c_m} \gamma}}{2 s V_{c_m}} \qquad (35)$$

Constants r and s are obtained from Table 2. To use this table a preliminary value of the reduced temperature is required. It may be approximated with sufficient accuracy by $T/(\beta/V_{c_m})$.

5. The pseudocritical pressure is

$$P_{c_m} = \frac{R T_{c_m}}{V_{c_m}} \sum_i y_i z_{c_i} \qquad (36)$$

The proposed method requires a knowledge of the critical volumes of all components in the mixture. Critical volumes are difficult to determine experimentally; whenever reliable values of the critical volume are not available, it is best to compute them from the more accurately known critical temperature, critical pressure, and acentric factor [Equations (16) and (18)]. Critical volumes computed in this way are accurate to better than 2% for almost all cases.

COMPARISON OF PREDICTED AND EXPERIMENTAL COMPRESSIBILITY FACTORS

Compressibility factors have been calculated by using Kay's Rule and the preceding equations; the calculated values are compared with the experimental ones for ten different nonpolar systems, including one ternary and one five-component system. The comparisons are made mainly at high pressures because at these pressures the discrepancies between calculated and experimental compressibility factors are greatest and the severest test is placed upon any correlation. A summary of the results for these ten systems* is presented in Table 3. With one exception the compressibility factors predicted by the proposed pseudocritical method agree within 3.0% or less of the experimental values. Kay's Rule is decidedly less accurate, although in many examples it is sufficiently accurate for engineering calculations. The results show that the proposed pseudocritical method is successful in both liquid and gaseous phases throughout the entire range of the Pitzer compressibility tables from reduced temperatures of 0.8 to 4.0 and from reduced pressures of 0.2 to 9.0.

The n-butane–carbon dioxide system was subjected to special calculations. Kay's Rule and the pseudocritical method proposed here were tested for accuracy in predicting the volumetric behavior in both liquid and gaseous phases at the two-phase boundary at pressures of 500 to 1,100 lb./sq. in. abs. Maximum deviation for the proposed pseudocritical method for both phases is 2.2%; for the liquid phase Kay's Rule gives very poor agreement with 26% error in one case. In the gas phase at moderate pressures there is a fortunate cancelation of the errors owing to the wrong pseudocritical pressure, and agreement is better than in the liquid phase; at high pressures in the gaseous phase this cancelation is not effective, and errors are again very large. The over-all average error of Kay's Rule is slightly more than 10%. Figures 4 and 5 show the composition dependence of the pseudocritical temperature and of the pseudocritical pressure according to Kay's Rule and the equations derived in this work. The large disagreement in the pseudocritical pressure as predicted by the two methods illustrates the main reason why Kay's Rule is so inaccurate for this system.

The proposed method for calculating the pseudocritical constants is considerably more accurate than Kay's Rule. Of course in all cases the $\Delta T_{c_{12}}$ correction for the characteristic critical temperature was obtained from virial coefficients or other volumetric data as explained earlier. When such data are not available, the characteristic temperature correction (and for highly asymmetric systems the volume correction) must be estimated, and the method proposed here is necessarily somewhat dependent on the accuracy of such estimates.

MIXTURES WITH HYDROGEN

Mixtures containing hydrogen must be treated with caution. At 100°C. the reduced temperature of hydrogen exceeds 8.0, twice the range of validity of the virial equations used to derive the pseudocritical method. Compressibility factors for two hydrogen-containing systems reported in Table 3 were predicted with excellent accuracy; however the mixtures were at high reduced temperatures, where the compressibility factors are relatively insensitive to errors in the pseudocritical constants. Because the reduced temperature of hydrogen at room temperatures is beyond the range of validity of the virial equations used, the predicted pseudocritical parameters for hydrogen-containing systems may be less accurate than those for other systems.

Owing to quantum effects, pseudocritical parameters instead of the experimental critical constants are used for

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*Tabular material has been deposited as document 5767 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $2.50 for photoprints or $1.75 for 35-mm. microfilm.

*Detailed results for these ten systems are given elsewhere (*5*).

hydrogen in a corresponding-states correlation. The recommended values are a pseudocritical temperature of 43.4°K., a pseudocritical volume of 50 cc./g.-mole, and an acentric factor of zero.

SIMPLIFIED PSEUDOCRITICAL METHOD

The proposed pseudocritical method is a fairly complicated procedure; therefore for calculations in which only moderate accuracy is required a method is desired for rapidly approximating the pseudocritical constants. Comparison of the pseudocritical constants predicted by Kay's Rule and those proposed here shows that, for the ten systems listed in Table 3, the linear combination of critical temperatures is more accurate than the linear combination of critical pressures. For the pseudocritical temperature the maximum deviation of Kay's linear rule from the experimental value occurs for systems containing components with extremely different critical temperatures. For the ten systems studied the greatest deviation is 7%. The linear combination of critical pressures is much worse, being more than 50% in error for the system hydrogen sulfide-decane and as much as 20% for several other systems. The linear combination of critical volumes however is accurate to within better than 4% for all ten systems. Therefore it is proposed that the following modifications of Kay's Rule will considerably increase its accuracy:

$$\omega_m = \sum_i y_i \omega_i \tag{37}$$

$$T_{c_m} = \sum_i y_i T_{c_i} \tag{38}$$

$$P_{c_m} = \frac{R T_{c_m}}{\sum_i y_i V_{c_i}} \sum_i y_i z_{c_i} \tag{39}$$

For most nonpolar mixtures the last two rules should be accurate to within 5%. The methane-decane system with a ratio of critical volumes, V_{c_1}/V_{c_2}, of 6.1 and a ratio of critical temperatures, T_{c_1}/T_{c_2}, of 3.2 represents an extreme example of a system containing components with widely different critical constants; yet Kay's Rule for the pseudocritical temperature is in error by only 7%.

As shown in Equation (39) an error of 5% in the pseudocritical temperature produces an error of 5% in the critical pressure. The Pitzer compressibility tables show that an error of about 5% in the reduced temperature and pressure result in 5 to 6% maximum error in the calculated compressibility factors for reduced temperatures of 1.3 and above. In the reduced-temperature range above 1.3 therefore the proposed modification of Kay's Rule should be quite satisfactory. The smaller the difference between the respective values of the critical temperatures and the critical volumes of the pure components, the more accurate are the predicted pseudocritical constants as predicted by any of the methods discussed here, particularly if the $T_{c_{12}}$ corrections are small. The propane-benzene system is an example of this, since the ratio of critical volumes is only 1.3 and the ratio of critical temperatures is 1.5. In spite of the great dissimilarities in the molecular structure of the two compounds the errors in the pseudocritical constants predicted by Kay's Rule are actually negligible.

The simplified pseudocritical method is satisfactory for a majority of practical cases; however near the critical region it cannot be expected to be accurate generally, and more complicated procedures are required.

PREDICTION OF PHASE BEHAVIOR

The pseudocritical method developed in this work appears to represent the volumetric properties of a variety of mixtures with good accuracy in both gas and liquid phases. It should therefore be possible to compute the fugacities of all components in the mixture. The form of Equations (29) to (36) is not very convenient for such computations, but in principle the method developed here should be useful in the prediction of phase equilibria.

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NOTATION

B, C, D = second, third, and fourth virial coefficients which are functions of temperature and composition
d = molar density
P = pressure
$P_{c_{12}}$ = characteristic critical pressure
P_{c_m} = pseudocritical pressure
P_r = reduced pressure
R = universal gas constant
r, s = parameters in pseudocritical temperature equation
T = temperature
$T_{c_{12}}$ = characteristic critical temperature
$\Delta T_{c_{12}}$ = correction to characteristic critical temperature
$T_{c_{ij}}$ = temperature characteristic of interaction between molecule of species i and molecule of species j
T_{c_m} = pseudocritical temperature
T_r = reduced temperature
V = volume
$V_{c_{12}}$ = characteristic critical volume
$\Delta V_{c_{12}}$ = correction to characteristic volume
$V_{c_{ij}}$ = volume characteristic of interaction between molecule of species i and molecule of species j
y_i = mole fraction of component i
z = compressibility factor

Greek Letters

α = $\sum_{ij} y_i y_j V_{c_{ij}}$
β = $\sum_{ij} y_i y_j (V_c T_c)_{ij}$
γ = $\sum_{ij} y_i y_j (V_c T_c^2)_{ij}$
θ_B = generalized universal function for second virial coefficient
ω = acentric factor

Subscripts

c = critical
i, j, k = components i, j, and k
1, 2 = components 1 and 2
m = property for a mixture and signifies that quantity is for mixture as whole
r = reduced, dimensionless property

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