

ON THE THERMODYNAMICS OF SOLUTIONS. V
AN EQUATION OF STATE. FUGACITIES OF GASEOUS SOLUTIONS¹

OTTO REDLICH AND J. N. S. KWONG
Shell Development Company, Emeryville, California

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The calculation of fugacities from P - V - T data necessarily involves a differentiation with respect to the mole fraction. The fugacity rule of Lewis, which in effect would eliminate this differentiation, does not furnish a sufficient approximation. Algebraic representation of P - V - T data is desirable in view of the difficulty of numerical or graphical differentiation. An equation of state containing two individual coefficients is proposed which furnishes satisfactory results above the critical temperature for any pressure. The dependence of the coefficients on the composition of the gas is discussed. Relations and methods for the calculation of fugacities are derived which make full use of whatever data may be available. Abbreviated methods for moderate pressure are discussed.

The old problem of the equation of state has a practical aspect which has become increasingly important in recent times. The systematic description of gas reactions under high pressure requires information about the fugacities, derived sometimes from extensive data but frequently from nothing more than the critical pressure and temperature.

For practical purposes a representation of the relation between pressure, volume, and temperature based on two or three individual coefficients is desirable, although a representation of this type satisfies the theorem of corresponding states and therefore cannot be accurate. Since the calculation of fugacities involves a differentiation with respect to the mole fraction, an *algebraic* representation by means of an equation of state appears to be desirable. After this paper had been written, Joffe (12) showed that fugacities can be correctly derived also from generalized charts. An algebraic method, however, if based on a suitable equation of state, appears to be more convenient. It is free from the arbitrariness necessarily involved in the drawing of generalized charts. In addition, an approximate equation of state can be used for the precise representation of experimental data with the aid of approximate deviation functions.

I. AN EQUATION OF STATE

Several theoretical and practical considerations lead to the following equation of state. We omit a detailed discussion because the reasoning is circumstantial and by no means rigorous. The equation is therefore essentially empirical. Its justification rests mainly on the degree of approximation obtained by comparatively simple means.

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The proposed equation is represented by

$$P = RT/(V - b) - a/T^{1/2}V(V + b) \quad (1)$$

It will be used in the form:

$$Z = 1/(1 - h) - (A^2/B)h/(1 + h) \quad (2)$$

$$Z = PV/RT \quad (3)$$

$$A^2 = a/R^2T^{2.5} = 0.4278T_c^{2.5}/P_cT^{2.5} \quad (4)$$

$$B = b/RT = 0.0867T_c/P_cT \quad (5)$$

$$h = BP/Z = b/V \quad (6)$$

The relations between the coefficients a and b or A^2 and B and the critical tem-

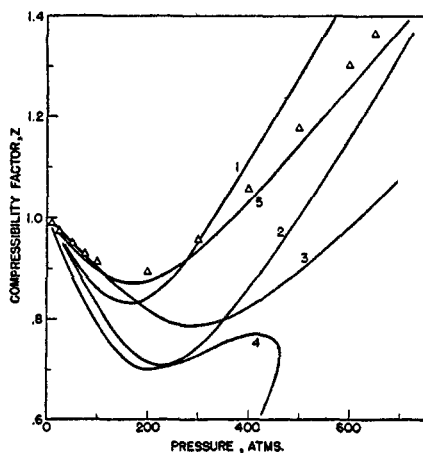


FIG. 1

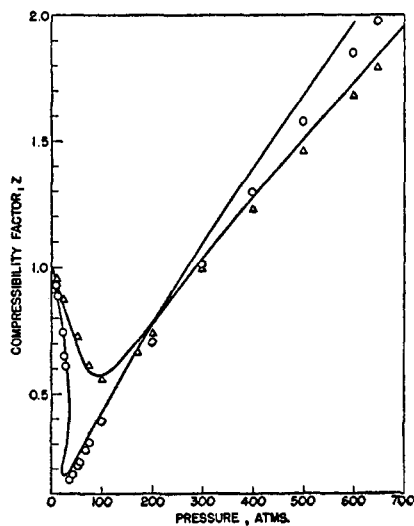


FIG. 2

FIG. 1. Compressibility factor of ethane (237.8°C.). Curve 1, van der Waals; curve 2, Dieterici; curve 3, Berthelot; curve 4, Wohl; curve 5, equation 2; Δ , experimental data (26).

FIG. 2. Compressibility factor of *n*-butane. Experimental data (23): O, 137.8°C.; Δ , 237.8°C. Curves: equation 2.

perature T_c and pressure P_c follow from the critical conditions. The quantities A^2 and B are expressed in atm.^{-1}

The results obtained from equation 2 have been compared with experimental data for various gases in a wide pressure range. A few examples are shown in figures 1-3. The temperature, the pressure range, and the data for the maximum deviation are given in table 1 for all gases examined. A comparison with similarly simple equations of state is shown in figure 1 for the arbitrarily chosen example of ethane. Considering the limitation imposed on any equation containing but two or three individual coefficients by the failure of the correspondence theorem, the approximation obtained by equation 2 is satisfactory.

At high pressures the volume of all gases approaches a limiting value (13)

which is practically independent of the temperature and close to $0.26V_c$ ($V_c =$ critical volume). In equation 1 this limiting volume is represented by the coefficient b . The equation has been constructed to satisfy the condition

$$b = 0.26V_c \quad (7)$$

in order to furnish good approximation at high pressure.

For low pressures Berthelot's equation is known to furnish a very good approximation. The second virial coefficient derived from equation 2

$$\beta = b - a/RT^{1.5} = 0.0867(RT_c/P_c)[1 - 4.93(T_c/T)^{1.5}] \quad (8)$$

agrees quite well with the value derived from Berthelot's equation

$$\beta = 0.0703(RT_c/P_c)[1 - 6(T_c/T)^2] \quad (9)$$

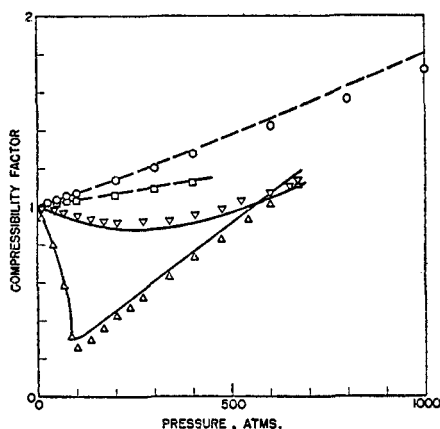


FIG. 3. Compressibility factor of hydrogen and carbon dioxide. Experimental data: hydrogen (17), \circ , 0°C .; (2), \square , 399.3°C . Carbon dioxide (25), ∇ , 33.8°C .; \triangle , 237.8°C . Curves: equation 2.

for the critical and higher temperatures. Below the critical temperature, the deviations of both equations from experimental data increase with decreasing temperature. Here Berthelot's equation furnishes a better approximation for low pressures.

Sometimes it is useful to know the limiting tangents in a diagram of Z against P . If we transform equation 2 into

$$Z = 1 + BP - A^2P(Z - BP)/Z(Z + BP) \quad (10)$$

we find that the tangents are represented by

$$1 + (B - A^2)P = 1 + \beta P/RT \quad \text{for } P = 0 \quad (11)$$

$$1 + BP \quad \text{for } P = \infty \quad (12)$$

Although equations 2 and 6 represent Z only implicitly as a function of P , numerical calculations are not laborious: Calculate B and A^2/B according to

TABLE 1
Maximum deviations

SUBSTANCE	TEMPERATURE	PRESSURE RANGE	DATA REFERENCE	MAXIMUM DEVIATION			
				At pressure	Z (observed)	Z (calculated)	
	°C.	atm.		atm.			
Hydrogen.....	0	2542	(17)	2542	2.706	3.067	
	150	2970	(17)	2970	2.267	2.564	
Nitrogen.....	399.3	400	(2)	300	1.089	1.098	
	0	1000	(2)	1000	2.064	1.977	
Oxygen.....	399.3	1000	(2)	1000	1.511	1.416	
	0	1000	(11)	1000	1.736	1.664	
Carbon dioxide.....	199.5	900	(11)	900	1.413	1.362	
	37.8	680	(25)	680.5	1.116	1.168	
Methane.....	237.8	680	(25)	680.5	0.916	0.878	
	37.8	680	(22)	680.5	1.447	1.415	
Ethane.....	237.8	680	(22)	680.5	1.330	1.289	
	37.8	680	(26)	61.24	0.248	0.292	
Ethylene.....	237.8	680	(26)	680.5	1.405	1.353	
	150	3000	(15, 18)	2473	3.653	3.584	
Propane.....	104.4	204	(27)	40.84	0.525	0.584	
	100	181	(5)	45	0.245	0.430*	
<i>n</i> -Butane.....	275	303	(5)	130	0.808	0.787	
	137.8	680	(23)	680.5	2.060	2.187	
Isobutane.....	237.8	680	(23)	680.5	1.858	1.913	
	137.8	340	(19)	34.02	0.216	0.269	
	237.8	340	(19)	340.2	1.117	1.094	
MIXTURES	MOLE FRACTION METHANE						
Methane-ethane.....	0.4006	50	60	(16)	60	0.759	0.780
Methane-isobutane.....	0.4681	137.8	340	(21)	170.1	0.690	0.714
Methane-carbon dioxide....	0.4055	37.8	680	(25)	51.0	0.641	0.613

* The value of Z changes rapidly in the vicinity of the critical point. The experimental value $Z = 0.430$ corresponds to a pressure of 43 atm.

TABLE 2
Auxiliary functions

h	$1/(1-h)$	$h/(1+h)$	h	$1/(1-h)$	$h/(1+h)$
0.02	1.0204	0.01961	0.3	1.4286	0.23077
0.04	1.0417	0.03846	0.4	1.6667	0.28571
0.06	1.0638	0.05660	0.5	2.0000	0.33333
0.08	1.0870	0.07407	0.6	2.5000	0.37500
0.1	1.1111	0.09091	0.7	3.3333	0.41176
0.15	1.1765	0.13043	0.8	5.0000	0.44444
0.2	1.2500	0.16667	0.9	10.0000	0.47369
0.25	1.3333	0.20000			

equations 4 and 5, estimate the required range of the auxiliary variable h from equation 6, calculate Z according to equation 2 with the aid of table 2 for a suitable set of values of h , and calculate $P = hZ/B$ for the values of h chosen in the preceding step. Graphical interpolation furnishes Z for any value of P .

Equation 2 can be advantageously used for the presentation of experimental data and for subsequent thermodynamic calculations. The deviation function

$$W = Z_E - Z_S \quad (13)$$

(Z_E = experimental value of Z ; Z_S = value calculated from the equation of state) is restricted to a small range and varies only slowly with P . It can be easily interpolated and represented graphically or by means of a short table. Thermodynamic calculations can be carried out algebraically in Z_S so that graphical or numerical differentiations and integrations are required only for the small deviation W . The advantage is considerable, especially in differentiations.

It is convenient to call the quotient of the fugacity and the pressure "fugacity coefficient."² The relationship between fugacity, volume, and pressure (*cf.* 9) together with equation 2 furnishes for the fugacity coefficient φ the equation:

$$\ln \varphi = \int_0^P (Z - 1) dP/P = Z - 1 - \ln(Z - BP) - (A^2/B) \ln(1 + BP/Z) \quad (14)$$

II. GASEOUS MIXTURES

It will be expected that equation 2 holds about equally well for gaseous mixtures. The question is only in which way the coefficients A and B of the mixture depend on the corresponding coefficients A_i and B_i and the mole fractions y_i of the components.

Since the coefficient b has been introduced as the limiting volume, it is quite obvious that it depends linearly on the mole fractions. Therefore,

$$b = \sum_i y_i b_i; \quad B = \sum_i y_i B_i \quad (15)$$

This relation deviates from the original theory of van der Waals and from the general theory of the second virial coefficient (8). But the theory is valid only for moderate pressures where the influence of b is small. The linear relation 15 follows from our interpretation of b for high pressures, where the influence of b is decisive. This relation is well supported by experimental data (20).

The situation is different for the attraction coefficient a . Molecular theory leads to the result that the second virial coefficient is a function of second degree of the mole fractions. This result is also experimentally well established (8). Since the coefficient a is important at moderate pressures, a reasonable approximation can be achieved only by assuming a similar relationship for a : namely,

$$a = a_1 y_1^2 + a_2 y_2^2 + \cdots + 2a_{12} y_1 y_2 + \cdots \quad (16)$$

² Prigogine and Defay (24) recently introduced this term by means of a slightly different definition which appears to be less convenient.

The coefficients $a_{12} \dots$ of the cross terms can be related to the properties of the pure components by the usual though somewhat arbitrary assumption that

$$a_{12} = (a_1 a_2)^{1/2} \quad (17)$$

Equations 4, 16, and 17 furnish

$$A = \sum_i y_i A_i \quad (18)$$

Equations 15 and 18 are in accord with the conclusions of several authors, especially Gillespie (9a, 14) and Beattie (4), and are for moderate pressures well supported by their discussions of experimental data.

The second virial coefficient

$$\beta = RT(B - A^2) = RT[\sum y_i B_i - (\sum y_i A_i)^2] \quad (19)$$

is a linear function of the mole fractions only in the exceptional case that all coefficients A_i are equal. In first approximation for low pressures we have

$$Z = 1 + \beta P/RT \quad (20)$$

Since the attraction coefficient A^2 is in general far more important here than B , we arrive at the conclusion that the deviations from the perfect law cannot even in first approximation be represented by a linear function of the mole fractions. In general, the volume of a gaseous mixture ceases to be additive as soon as the gas ceases to be perfect or, a gaseous mixture is a perfect *solution* only as long as it is a perfect *gas*. In other words, no legitimate pressure range exists for the application of the rule of Amagat (1). Since the fugacity rule of Lewis and Randall is thermodynamically connected with Amagat's rule, this fugacity rule, too, does not furnish a correct first approximation. This conclusion does not depend on the assumption of a particular equation of state. It is in accord with experimental data (*cf.* 10).

The difference in the dependence of B and A^2 on the composition and the difference in the influence of these coefficients on Z in different pressure ranges accounts for a fact which at first is very surprising: volume-composition curves approach straight lines at high pressure but in general deviate widely from straight lines at moderate pressures.

III. THE FUGACITY COEFFICIENT

The replacement of the fugacity by the fugacity coefficient is especially useful in calculations pertaining to solutions. We define the fugacity coefficient φ_r of the component r of a solution by means of

$$\varphi_r = f_r/y_r P \quad (21)$$

where f_r denotes the fugacity of the component r .

For gaseous mixtures the fugacity coefficient is given, therefore, by the relation

$$\ln \varphi_r = \int_0^P (Z_r - 1) dP/P \quad (22)$$

where the partial molal compressibility factor \bar{Z}_r is to be derived from Z according to

$$\bar{Z}_r = Z + \partial Z / \partial y_r - \sum_i y_i \partial Z / \partial y_i \quad (23)$$

The summation is to be extended over all components. The partial differentiation is to be carried out, of course, at constant values of all mole fractions except that one with respect to which Z is differentiated.³

The derivation of the fugacity coefficients from equations 2, 6, 15, 18, 22, and 23 is possible but tedious. Much more convenient is a calculation in which the order of the differentiation with respect to the mole fraction (equation 23) and the integration with respect to the pressure (equation 22) is reversed. We define the molal quantity U by

$$U = \sum y_i \log \varphi_i \quad (24)$$

According to equations 22 and 23, and 2 and 6, we find

$$\begin{aligned} 2.303U &= \int_0^P (Z - 1) dP/P \\ &= Z - 1 - \ln(Z - BP) - (A^2/B) \ln(1 + BP/Z) \end{aligned} \quad (25)$$

$$\log \varphi_r = U + \partial U / \partial y_r - \sum_i y_i \partial U / \partial y_i \quad (26)$$

The dependence of Z on A and B is given by equations 2 and 6, and that of A and B on the mole fractions by equations 15 and 18. The calculation leads without difficulty to

$$\begin{aligned} \log \varphi_r &= 0.4343(Z - 1)B_r/B - \log(Z - BP) \\ &\quad - \frac{A^2}{B} \left[\frac{2A_r}{A} - \frac{B_r}{B} \right] \log(1 + BP/Z) \end{aligned} \quad (27)$$

Properly arranged, the computation of fugacity coefficients according to equation 27 does not require an undue amount of time. For each temperature and composition of the gaseous mixture the fugacity coefficients of all components and for all desired pressures are calculated in one set. The required steps are:

- I. A_i and B_i for all components (equations 4 and 5)
- II. A and B for the mixture (equations 15 and 18)
- III. Z for the mixture as a function of P (equations 2 and 6)
- IV. $\log \varphi_r$ (equation 27)

Sometimes a sufficient approximation, at least for first information, is obtained by calculating the case in which one of the components is present in large excess, $y_s = 1$. In this case the quantities A , B , and Z assume the values

³ Equation 23 applies to any molal quantity Z and the corresponding partial molal quantities \bar{Z}_r . It is derived from the usual definition of partial molal quantities by replacing mole numbers by mole fractions. The derivation of equation 23 is *not* based on an assumption that the y_i 's are independent. It is therefore not necessary, though of course it is permissible, to eliminate one of the y_i 's in Z before applying equation 23.

A , B , and Z , of the pure solvent gas, so that the calculation is considerably shorter.

TABLE 3
Hydrogen-nitrogen

TEMPERATURE	MOLE FRACTION H_2	0		0.5		1	
		600	1000	600	1000	600	1000
0°C.	Pressure (atm.).....	600	1000	600	1000	600	1000
	Fugacity of components (calculated).....	689	1636			927	2159
	Same (Bolshakov).....	737	1811			899	1992
	φ_1/φ_1^0 (calculated).....	1.27	1.26	1.09	1.08	1	1
	φ_1/φ_1^0 (Bolshakov).....	1.20	1.20	1.07	1.07	1	1
	φ_2/φ_2^0 (calculated).....	1	1	1.03	1.07	1.28	1.32
	φ_2/φ_2^0 (Bolshakov).....	1	1	1.04	1.05	1.23	1.27
200°C.	Fugacity of components (calculated).....	758	1569			783	1565
	Same (Bolshakov).....	831	1806			769	1513
	φ_1/φ_1^0 (calculated).....	1.08	1.09	1.03	1.04	1	1
	φ_1/φ_1^0 (Bolshakov).....	1.03	1.04	1.02	1.02	1	1
	φ_2/φ_2^0 (calculated).....	1	1	1.01	1.01	1.08	1.11
	φ_2/φ_2^0 (Bolshakov).....	1	1	1.00	1.00	1.04	1.04

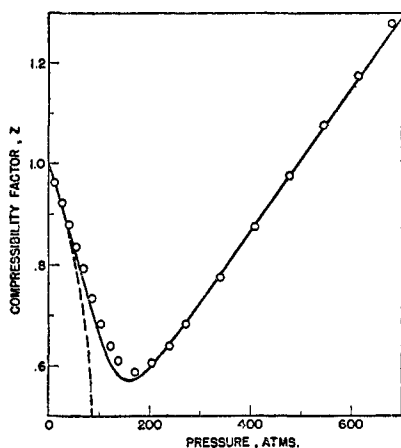


FIG. 4

FIG. 4. Compressibility factor of methane-carbon dioxide (mole fraction of methane = 0.4055). Experimental data (25): \circ , 37.8°C. Full line: equations 2, 15, 18. Broken line: Berthelot's equation.

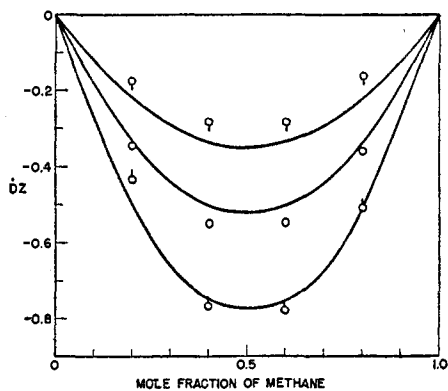


FIG. 5

FIG. 5. Methane-ethane (50°C.). Deviation function ΔZ (cf. equation 35). Experimental data (16): \diamond , 13.61 atm.; \square , 40.83 atm.; \circ , 68.04 atm. Curves: equation 36.

A test of equations 14 and 27 is shown in table 3. The fugacities of hydrogen and nitrogen and the activity coefficients φ_1/φ_1^0 and φ_2/φ_2^0 of their mixtures have

been computed from experimental data by Bolshakov (7). His results for 200°C. cannot be quite accurate, since they are not in complete accord with the Duhem-Margules equation. For other gases, especially hydrocarbons, smaller deviations may be expected according to the results reported in table 1.

Since equation 27 is strictly derived from the assumed equation of state and equations 15 and 18, its validity depends only on the validity of these relations. Figure 4 is presented as an example for Z . The maximum deviations for three mixtures are given in table 1.

Experimental P - V - T data for the pure components, if available, can be used for improving the results obtained by means of equation 27. As in equation 13, we represent the difference between the experimental and calculated values of Z_j for the component j by the function W_j . If no data for the mixtures are available the best assumption for the deviation function W of the mixture is

$$W = y_j W_j \quad (28)$$

The improved value of $\ln \varphi_r$ is then obtained by adding

$$\int_0^P W_r dP/P \quad (29)$$

to the value obtained by means of equation 27.

If data are available also for mixtures, equation 28 can be replaced by a better interpolation function. The calculation of the additional term in $\ln \varphi_r$ according to equations 25 and 26 will not present any difficulty.

IV. APPROXIMATIONS FOR MODERATE PRESSURE

In the pressure range which is sufficiently well represented by the second virial coefficient (equations 19 and 20), equations 22 and 23 furnish

$$\ln \varphi_r = [B_r - A_r^2 + (A_r - A)^2]P \quad (30)$$

This relation is useful in the calculation of the correction for the imperfection of the vapor in liquid-vapor equilibria. The equilibrium between a liquid (mole fraction x_r , molal volume V_r' and activity coefficient γ_r' of the component r) and its vapor is determined by the condition

$$\ln k_r x_r \gamma_r + V_r' P / RT = \ln y_r \varphi_r P \quad (31)$$

The proportionality factor k_r is eliminated by means of the condition for the equilibrium of the pure component under the vapor pressure p_r^0 .

$$\ln k_r + V_r' p_r^0 / RT = \ln \varphi_r^0 p_r^0 \quad (32)$$

The equilibrium condition, therefore, is

$$\ln (x_r \gamma_r p_r^0 / y_r P) = (B_r - A_r^2 - V_r' / RT)(P - p_r^0) + (A_r - A)^2 P \quad (33)$$

For binary solutions, the last term becomes $(A_1 - A_2)^2 (1 - y_r)^2 P$. A relation of this type has been previously proposed by Scatchard and Raymond (28).

The fugacity rule of Lewis leads to omission of the last term. But this term

has in principle the same order of magnitude as the preceding one. However, it is small if the values of the critical constants of the components do not differ appreciably.

In equation 30 the term $(B_r - A_r^2)P$ represents the logarithm of the fugacity coefficient of the pure gas, while $(A_r - A)^2P$ indicates its dependence on the composition. Thus if Z_r for the pure gas is known, we obtain a better approximation by means of the relation

$$\ln \varphi_r = \int_0^P (Z_r - 1) dP/P + (A_r - A)^2 P \quad (34)$$

in which the equation of state is used only for determining the dependence on the composition.

Another approximation furnishes appreciably better results. We discuss only binary systems, although the method can be extended to the general case without difficulty. We define

$$\dot{D}Z = Z - y_1 \dot{Z}_1 - y_2 \dot{Z}_2 \quad (35)$$

where \dot{Z}_1 and \dot{Z}_2 denote the values of Z_1 and Z_2 of the pure components at the pressures $y_1 P$ and $y_2 P$, respectively. By means of equations 2 and 6 we can develop the quantity $\dot{D}Z$ in terms of powers of P . The first-order term is

$$\dot{D}Z = y_1 y_2 P (B_1 + B_2 - 2A_1 A_2) \quad (36)$$

This approximation holds quite well up to pressures of about 50 atm. (see figure 5). From equation 36 we derive the corresponding approximation for the fugacity coefficient:

$$\ln \varphi_1 = \int_0^{y_1 P} (Z_1 - 1) dP/P + y_2 (\dot{Z}_1 - \dot{Z}_2) + y_2^2 P (B_1 + B_2 - 2A_1 A_2) \quad (37)$$

This quite convenient approximation has an important practical advantage. Sometimes we want to know the fugacity coefficient of a substance in a gaseous mixture below its critical temperature under a total pressure which is higher than its vapor pressure. A relation such as equation 34 cannot be used in this case, because Z_r cannot be measured up to the total pressure P . But equation 37 requires the knowledge of the compressibility factor of the pure gas only up to its partial pressure and therefore is always applicable.

V. CONCLUSION

A variety of problems arise in the calculation of fugacities of gaseous mixtures for two reasons: First, the available experimental data are widely different. Sometimes only the critical temperature and pressure are known, sometimes P - V - T data for some or all of the components, sometimes a complete set of data for the mixtures. In each case, full use should be made of the data. Second, short methods are desirable for moderate pressures. It is believed that the relations discussed in the preceding sections cover the whole range and that the methods proposed do not require an unreasonable amount of time.

Whenever a complete set of data is not available, some assumptions must be introduced which can be only imperfect approximations.

The methods proposed contain only two assumptions: the equation of state (equation 1) and the dependence of the coefficients A and B on the composition (equations 15 and 18).

The equation of state furnishes a second virial coefficient which is in good accord with experimental data at the critical temperature and above. Similarly, the ratio between the limiting volume at high pressure and the critical volume is equal to the average of experimental data which vary within fairly close limits. The equation of state is therefore in accord with general experimental experience to the extent to be expected of an equation containing only two coefficients.

The assumed dependence of the coefficients A and B on the composition of the gaseous mixture takes into account the relative importance of these coefficients at low and high pressures, the theoretical interpretation of these coefficients, and experimental tests of this interpretation.

The degree of approximation obtained by the two assumptions, as ascertained in a number of test examples, is believed to be satisfactory in view of the fact that no experimental data are used except the critical pressure and temperature.

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