Use of the Redlich and Kwong Equation of State in Calculating Thermodynamic Properties of Gases from Experimental Compressibility Data

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Convenient and accurate methods of calculating the thermodynamic properties of gases from experimental compressibility-factor data through the use of the Redlich and Kwong equation of state are presented. Analytical and graphical methods are combined. As an example, fugacity and activity coefficients are calculated for the nitrogen-ethylene system at 50°C. for pressures up to 500 atm.

There are two problems in the determination of thermodynamic properties of gases; one is the experimental problem of getting accurate data, and the other is the problem of calculating properties from these data. This paper deals with the latter problem and assumes that adequate compressibility-factor data are available. The general equations relating thermodynamic properties to pressure by use of compressibility factors (defined by the equation $pV = CnRT$) are well known *(10)*:

$$H - H^* = \Delta H = - RT^2 \int_{p^*}^{p} (\partial C/\partial T) \frac{dp}{p} \qquad (1)$$

$$\ln (f/p = \int_{p^*}^{p} (C-1) \frac{dp}{p} \qquad (2)$$

$$S - S^* = \Delta S = - R \int_{p^*}^{p} \left[C + T\ (\partial C/\partial T) \right] \frac{dp}{p} \qquad (3)$$

Equation (3) does not need to be solved independently, for it can readily be put in a form involving the integrals of Equations (1) and (2). Making the logical substitutions reduces it to

$$S - S^* = \Delta S = - R \ln (f/p) + \Delta H/T - R \ln (p/p^*) \qquad (4)$$

It should be noted that an asterisk is used to denote the zero-pressure state, where all gases are assumed to obey the ideal-gas law. This state is a satisfactory reference for enthalpy and fugacity, but it is inconvenient in the case of entropy because S^* is infinite. In this case the reference state is taken as the ideal-gas state at 1 atm. The entropy in this state is designated as $S°$, and Equation (4) becomes

$$S - S^\circ = - R \ln (f/p) + \Delta H/T - R \ln (p) \qquad (5)$$

This reference state for entropy is particularly convenient, because absolute values of entropy can be calculated for it by statistical methods. In the case of enthalpy, absolute values are not known, and an arbitrary value must be assigned at a selected temperature in the reference state. By definition, fugacity and pressure are taken as equal in the zero-pressure reference state. The influence of temperature on thermodynamic properties is not considered in this paper, for this cannot be determined from compressibility data alone; moreover, it does not present a calculational problem comparable to that of determining the effect of pressure.

The application of Equation (5) is obvious once Equations (1) and (2) have been solved. The problem reduces then to one of evaluating the integrals in these two equations. There are two straightforward methods for doing this. The first is to perform the required operations of differentiation and integration directly by graphical methods based on the experimental compressibility-factor data. To obtain accurate results by this method, one must make exceedingly large graphs. Furthermore, graphical differentiation is inherently inaccurate, and the subsequent integration accumulates the errors.

The other method is to represent the compressibility-factor data by a very accurate equation, essentially an equation of state, and to perform the required operations entirely analytically. This is a highly desirable method, but at the present time no equation of state sufficiently accurate over wide ranges of temperature and pressure is known; moreover, such an equation would probably be highly complex and difficult to use.

A less straightforward method, but one which combines the advantages of both the foregoing methods, is the use of an approximate but simple equation of state for the calculation of approximate results, plus the use of residuals for the graphical calculation of correction factors. This general method is by no means new. It allows the analytical calculation of the major part of the result and restricts the graphical part to the determination of small numbers which can be plotted with the required accuracy on a normal-size sheet of graph paper.

CALCULATIONS

To carry out this method, one defines the residual, $\triangle C$, as the difference between the experimental value of the compressibility factor and the value predicted by the equation of state at the same temperature and pressure, i.e.,

$$\Delta C = C - C' \qquad (6)$$

Substitution for C by Equation (6) in Equations (1) and (2) gives

$$\Delta H = -RT^2\int_{p^*}^{p}(\partial C'/\partial T)\frac{dp}{p} - RT^2\int_{p^*}^{p}(\partial \Delta C/\partial T)\frac{dp}{p} \qquad (7)$$

$$\ln(f/p) = \int_{p^*}^{p}(C'-1)\frac{dp}{p} + \int_{p^*}^{p}(\Delta C)\frac{dp}{p} \qquad (8)$$

The first terms of these equations are determined analytically using an equation of state since C' is the "equation" value of the compressibility factor. The second terms are small correction factors and are usually determined graphically. The ease of the analytical calculations will of course depend on the simplicity of the equation of state; on the other hand, the size of the graphical correction factors will depend on the success with which the equation of state approximates the experimental data. Simplicity and high accuracy have not yet been combined in an equation of state. An excellent compromise however has been attained for gases by the Redlich and Kwong equation (*9*):

$$C' = 1/(1-h) - (A^2/B)(h/1+h) \qquad (9)$$

and

$$h = Bp/C' \qquad (10)$$

For a given gas or gas mixture, A and B are constants which depend on temperature only, i.e.,

$$B = k/T \qquad (11)$$

and

$$A^2/B = k'/T^{1.5} \qquad (12)$$

By use of Equations (9) to (12), Equation (7) may be reduced to the form

$$\Delta H = -1.5RT(A^2/B)\ln(1+h) + RT(C'-1) - RT^2\int_{p^*}^{p}(\partial\Delta C/\partial T)\frac{dp}{p} \qquad (13)$$

Although this equation was not presented by Redlich and Kwong (*9*), they did develop the analytical expression for the first integral of Equation (8). Using their result reduces Equation (8) to

$$\ln(f/p) = (C'-1) - \ln(C'-C'h) - (A^2/B)\ln(1+h) + \int_{p^*}^{p}(\Delta C)\frac{dp}{p} \qquad (14)$$

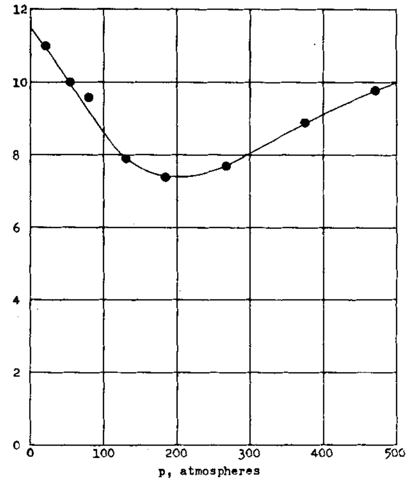

FIG. 1. CURVE FOR GRAPHICAL INTEGRATION; 59.7% N_2; NITROGEN-ETHYLENE MIXTURE, 50°C.

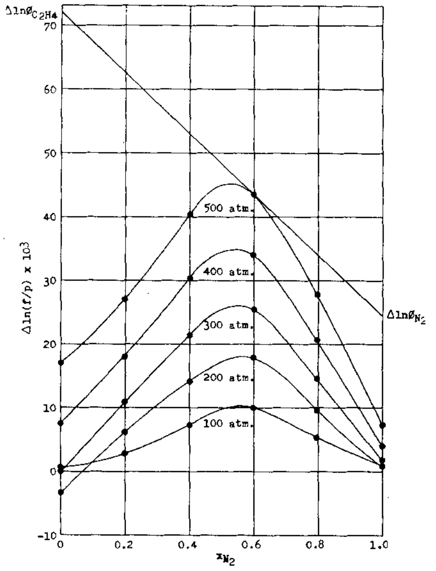

FIG. 2. CURVES FOR GRAPHICAL DIFFERENTIATIONS; NITROGEN-ETHYLENE MIXTURES, 50°C.

For the application of Equations (9), (10), (13), and (14), values of the constants B and A^2/B must be selected. This should be done with care. Probably the most satisfactory method involves a trial procedure: first, an arbitrary value of B is selected; as a starting approximation a value may be calculated from the equation given by Redlich and Kwong (*9*):

$$B = 0.0867T_c/p_cT \qquad (15)$$

Then for a given temperature a series of values of pressure covering the range being considered is used together with the corresponding experimental values of C for substitution in Equation (10) for the calculation of a series of values of h. Equation (9) is then used with these results and the corresponding experimental values of C to calculate a series of values of A^2/B. The optimum result would be values of A^2/B, which are nearly constant; one might repeat the foregoing procedure with different values of B until one was found that led to the lowest deviation of the values of A^2/B from the mean. A better procedure however is to find by trial the value of B which leads to a very nearly constant value of A^2/B at low pressure with increasing deviations at high pressures, and it is this constant low-pressure value of A^2/B which should be used together with the value of B which leads to it in Equations (9) and (10) and those which follow. The reason for this is that the integral in Equation (14) is evaluated graphically by plotting $\Delta C/p$ vs. p and determining the area under the curve. By having ΔC small at low pressures and increasing with p, values of $\Delta C/p$ will always be reasonably small, and the graphical integration will be facilitated. It should be mentioned that although ΔC and p both approach zero at zero pressure, $\Delta C/p$ remains finite, and its value is the slope of the curve of ΔC vs. p at the origin. Once the values of B and A^2/B have been selected, they are used in Equations (9) and (10) to calculate values of C' at pressures for which experimental values of C are available. Values of C' must of course be calculated (a trial procedure) with the same precision as that for which C is known. Equation (6) is then used to calculate the required values of ΔC. From this point the applications of Equations (13), (14), and (5) are obvious and do not need to be illustrated here.

Much more difficult than the foregoing calculations are the determinations of fugacity coefficients and activity coefficients of the components of gaseous mixtures. The former are defined (*9*) by the equation

$$\phi_i = \bar{f}_i/x_ip \qquad (16)$$

where $\bar{f}_i$ is the fugacity of component i in a mixture whose mole fraction in i is x_i. It may be shown that (*3*):

TABLE 1.—CONSTANTS FOR THE REDLICH AND KWONG EQUATION AT 50°C.

	A	B	A^2/B
Pure C_2H_4	0.076850	0.0014300	4.1300
19.8% N_2	0.068083	0.0013508	3.4315
40.1% N_2	0.059094	0.0012696	2.7506
59.7% N_2	0.050416	0.0011912	2.1338
79.6% N_2	0.041604	0.0011116	1.5571
Pure N_2	0.032571	0.0010300	1.0300

TABLE 2.—CALCULATED VALUES

x_{N_2}	$\Delta\ln \frac{f}{p}$	Approx. $\ln\phi_{N_2}$	$\Delta\ln\phi_{N_2}$	ϕ_{N_2}	γ_{N_2}	Approx. $\ln\phi_{C_2H_4}$	$\Delta\ln\phi_{C_2H_4}$	$\phi_{C_2H_4}$	$\gamma_{C_2H_4}$	$\ln\frac{\gamma_{N_2}}{\gamma_{C_2H_4}}$
100 atm.										
0	0.0006	0.5859	0.0064	1.808	1.793	—0.5099	0.0007	0.6010	1.000	0.584
0.198	0.0028	0.2437	0.0163	1.297	1.287	—0.4772	—0.0007	0.6202	1.032	0.222
0.401	0.0073	0.1085	0.0230	1.141	1.132	—0.4226	—0.0032	0.6533	1.088	0.038
0.597	0.0101	0.0465	0.0053	1.053	1.044	—0.3616	0.0166	0.7083	1.178	—0.120
0.796	0.0054	0.0164	0.0005	1.017	1.008	—0.2941	0.0244	0.7637	1.270	—0.229
1.000	0.0008	0.0074	0.0007	1.008	1.000	—0.2172	0.0226	0.8232	1.370	—0.316
200 atm.										
0	—0.0034	0.6854	0.0465	2.079	2.007	—0.8516	—0.0035	0.4253	1.000	0.696
0.198	0.0062	0.4221	0.0419	1.590	1.534	—0.8189	—0.0028	0.4397	1.034	0.394
0.401	0.0142	0.2204	0.0343	1.290	1.247	—0.7379	0.0005	0.4784	1.125	0.103
0.597	0.0179	0.1073	0.0122	1.127	1.088	—0.6262	0.0260	0.5488	1.292	—0.170
0.796	0.0097	0.0511	—0.0007	1.052	1.016	—0.4998	0.0497	0.6377	1.500	—0.390
1.000	0.0007	0.0345	0.0007	1.036	1.000	—0.3597	0.0382	0.7251	1.705	—0.533
300 atm.										
0	0.0001	0.6713	0.0553	2.068	1.910	—0.9832	0.0000	0.3742	1.000	0.647
0.198	0.0108	0.4629	0.0534	1.676	1.547	—0.9590	0.0002	0.3834	1.024	0.412
0.401	0.0214	0.2844	0.0523	1.400	1.292	—0.8837	0.0005	0.4135	1.104	0.156
0.597	0.0255	0.1654	0.0161	1.199	1.108	—0.7660	0.0394	0.4836	1.292	—0.152
0.796	0.0145	0.0990	0.0016	1.106	1.021	—0.6140	0.0645	0.5773	1.543	—0.412
1.000	0.0016	0.0778	0.0016	1.083	1.000	—0.4362	0.0645	0.6896	1.843	—0.611
400 atm.										
0	0.0075	0.6842	0.0578	2.100	1.831	—1.0237	0.0076	0.3621	1.000	0.604
0.198	0.0180	0.5011	0.0633	1.758	1.532	—1.0041	0.0067	0.3689	1.019	0.407
0.401	0.0303	0.3406	0.0682	1.505	1.312	—0.9346	0.0046	0.3946	1.089	0.186
0.597	0.0341	0.2257	0.0202	1.279	1.116	—0.8194	0.0541	0.4653	1.285	—0.140
0.796	0.0206	0.1561	0.0044	1.174	1.025	—0.6612	0.0829	0.5609	1.550	—0.412
1.000	0.0040	0.1333	0.0039	1.147	1.000	—0.4615	0.0857	0.6868	1.898	—0.640
500 atm.										
0	0.0169	0.7181	0.0594	2.176	1.773	—1.0154	0.0168	0.3685	1.000	0.572
0.198	0.0270	0.5506	0.0737	1.867	1.522	—0.9965	0.0152	0.3749	1.017	0.404
0.401	0.0404	0.4012	0.0815	1.620	1.321	—0.9329	0.0129	0.3986	1.081	0.200
0.597	0.0437	0.2911	0.0242	1.371	1.117	—0.8222	0.0719	0.4723	1.281	—0.136
0.796	0.0278	0.2213	0.0081	1.258	1.026	—0.6621	0.1041	0.5724	1.552	—0.415
1.000	0.0072	0.1976	0.0071	1.227	1.000	—0.4518	0.1087	0.7076	1.925	—0.653

$$\ln (f/p) = x_a \ln \phi_a + x_b \ln \phi_b + x_c \ln \phi_c + \ldots \quad (17)$$

where f is the fugacity of the mixture, defined exactly as the fugacity of a pure gas. When Equation (17) is compared with the general equation for a property of a mixture (*2*):

$$G = x_a\overline{G}_a + x_b\overline{G}_b + x_c\overline{G}_c + \ldots \quad (18)$$

we see that $\ln\phi_a$, $\ln\phi_b$, $\ln\phi_c$, etc., are related to ln (f/p) exactly as partial molal properties are related to the total property. Thus the usual equations for partial molal properties may be used to calculate values of the terms $\ln\phi_i$. Thus (*2*)

$$\ln \phi_i = \ln (f/p) - x_a \frac{\partial \ln (f/p)}{\partial x_a} - x_b \frac{\partial \ln (f/p)}{\partial x_b} - x_c \frac{\partial \ln (f/p)}{\partial x_c} \quad (19)$$

In this equation the *i*th term is omitted, and the differentiations are carried out with all x's constant except x_i and the x with respect to which the term is differentiated.

The values of ln (f/p) determined from Equation (14) can be divided into two parts: the part calculated analytically and the part calculated by graphical integration. This latter part is represented by the integral in Equation (14), and it will be defined equal to

$\Delta \ln (f/p)$, i.e.,

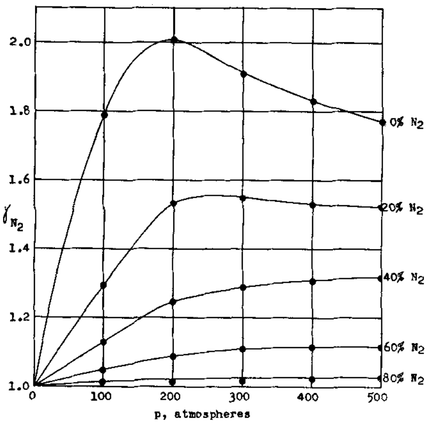

FIG. 3. ACTIVITY COEFFICIENTS FOR NITROGEN; NITROGEN-ETHYLENE MIXTURES, 50°C.

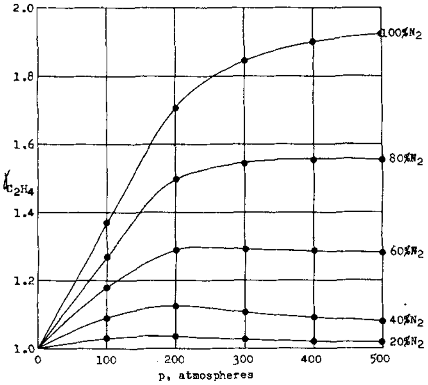

FIG. 4. ACTIVITY COEFFICIENTS FOR ETHYLENE; NITROGEN-ETHYLENE MIXTURES, 50°C.

$$\Delta \ln (f/p) = \int_{p^*}^{p} (\Delta C) \frac{dp}{p} \quad (20)$$

Substitution of the two parts of Equation (14) into Equation (19) divides it also into two parts, one of which may be evaluated analytically and the other graphically. The analytical solution was given by Redlich and Kwong(*9*), and their equation therefore gives approximate values of ln ϕ_i:

$$\text{approximate } \ln \phi_i = (B_i/B)(C'-1) - \ln(C'-C'h) - (A^2/B)\left[\frac{2A_i}{A} - \frac{B_i}{B}\right]\ln(1+h) \quad (21)$$

All quantities in this equation are for the mixture except those bearing the subscript i. A and B for the mixture are calculated by(*9*):

$$A = x_aA_a + x_bA_b + x_cA_c + \ldots$$

and

$$B = x_aB_a + x_bB_b + x_cB_c + \ldots \quad (22)$$

The corrections to be added to Equation (21) are determined according to the following equation, which comes directly from Equation (19):

$$\Delta \ln\phi_i = \Delta\ln(f/p) - x_a\frac{\partial\Delta \ln(f/p)}{\partial xa} - x_b\frac{\partial\Delta \ln(f/p)}{\partial x_b} - x_c\frac{\partial\Delta \ln(f/p)}{\partial x_c}\ldots \quad (23)$$

Again $\Delta\ln\phi_i$ corresponds to a partial molal quantity and again in this equation the ith term is omitted and the differentiations are carried out with all x's constant except x_i and the x with respect to which the term is differentiated. These differentiations are ordinarily performed graphically.

For the final calculation of the logarithm of the fugacity coefficient:

$$\ln\phi_i = \text{approximate } \ln\phi_i + \Delta\ln\phi_i \quad (24)$$

Activity coefficients are readily calculated from fugacity coefficients by the following equation:

$$\gamma_i = \frac{\bar{f}_i}{x_i f_i} = \frac{\bar{f}_i/x_i p}{f_i/p} = \frac{\phi_i}{f_i/p} \quad (25)$$

APPLICATION TO THE NITROGEN-ETHYLENE SYSTEM

Since these calculations are somewhat involved, they will be illustrated by applying them to the binary system, nitrogen-ethylene. The calculations can be checked against the values reported by Bennett(*1*), who calculated activity coefficients for this system from the same data by an entirely graphical method. It should be noted however that the method illustrated here is inherently more accurate than a purely graphical method; hence exact agreement between the results cannot be expected.

Data for four nitrogen-ethylene mixtures were reported by Hagenbach and Comings(*5*). Data for pure nitrogen and pure ethylene were taken from Michels, Michels, and Wouters(*7*) and Michels and Geldermans(*6*). The pressure range covered is from 0 to 500 atm. at a temperature of 50°C.

The constants for use in the Redlich and Kwong equation for the pure components were selected according to the method already described. Constants for the mixtures, calculated by Equation (22), are listed in Table 1.

For each composition a series of values of ΔC covering the pressure range was calculated using Equations (6), (9), and (10). It is to be noted that no value of ΔC exceeded 0.053. Graphs of $\Delta C/p$ vs. p were then prepared for each composition as illustrated in Figure 1 for the mixture containing 59.7% N_2. Values of Δln (f/p)

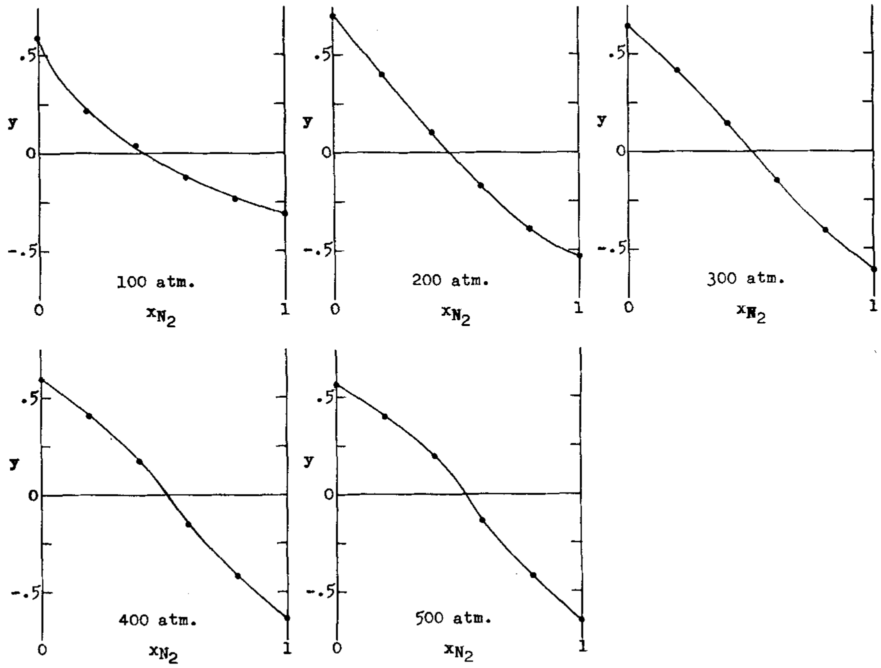

FIG. 5. NITROGEN-ETHYLENE MIXTURES, 50°C.; TESTS FOR THERMODYNAMIC CONSISTENCY. $y = \ln(\gamma_{N_2}/\gamma_{C_2H_4})$.

TABLE 3.—COMPARISON OF RESULTS WITH THOSE OF BENNETT (*1*).

p, atm.	$x_{N_2} = 0.0$		$x_{N_2} = 0.2$		$x_{N_2} = 0.4$		$x_{N_2} = 0.6$		$x_{N_2} = 0.8$		$x_{N_2} = 1.0$	
	γ_c	γ_b	γ_c	γ_b	γ_c	γ_b	γ_c	γ_b	γ_c	γ_b	γ_c	γ_b
Nitrogen												
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
100	1.79	1.45	1.30	1.27	1.13	1.14	1.05	1.06	1.01	1.01	1.00	1.00
200	2.01	1.85	1.53	1.48	1.25	1.25	1.09	1.10	1.02	1.02	1.00	1.00
300	1.91	1.99	1.55	1.55	1.29	1.28	1.10	1.11	1.02	1.03	1.00	1.00
400	1.83	1.99	1.53	1.55	1.31	1.28	1.20	1.11	1.02	1.03	1.00	1.00
500	1.77	1.99	1.52	1.55	1.32	1.28	1.20	1.11	1.02	1.03	1.00	1.00
Ethylene												
0	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
100	1.00	1.00	1.03	1.01	1.09	1.06	1.18	1.14	1.27	1.27	1.37	1.45
200	1.00	1.00	1.04	1.02	1.12	1.10	1.29	1.25	1.50	1.48	1.71	1.85
300	1.00	1.00	1.03	1.03	1.11	1.11	1.29	1.28	1.55	1.55	1.84	1.99
400	1.00	1.00	1.02	1.03	1.09	1.11	1.29	1.28	1.56	1.55	1.90	1.99
500	1.00	1.00	1.02	1.03	1.08	1.11	1.28	1.28	1.56	1.55	1.92	1.99

γ_c = activity coefficients calculated in this paper; γ_b = smoothed activity coefficients reported by Bennett.

were then determined by graphical integration [see Equation (20)] at pressures of 100, 200, 300, 400, and 500 atm. These values are listed in Table 2 and are shown on Figure 2, which is a plot of $\triangle \ln (f/p)$ vs. x_{N2} with pressure as parameter. The graphical determination of values of $\triangle \ln \phi_i$ by Equation (23) is particularly convenient for a binary mixture because the method of intercepts (*4*) can be used, as is illustrated in Figure 2 for the 59.7% N_2 mixture at 500 atm. Values of $\triangle \ln \phi_i$ determined in this way are listed in Table 2. The analytical part of the calculation was carried out by use of Equations (9) and (10) to calculate values of C' and h at even pressures of 100, 200, 300, 400, and 500 atm. for each composition. These values were then used in Equation (21) to calculate values of approximate $\ln \phi_i$ which are also listed in Table 2. The true values of $\ln \phi_i$ were then found by Equation (24). Activity coefficients were calculated by Equation (25).

RESULTS

Values of ϕ_i and γ_i are listed in Table 2, and Figures 3 and 4 show the activity coefficients plotted as a function of pressure with composition as parameter.

These results may be checked for thermodynamic consistency by the method of Redlich and Kister (*8*), which requires that a plot of $\ln (\gamma_{N2}/\gamma_{C2H4})$ vs. x_{N2} cut off equal areas on both sides of the zero ordinate. That this requirement is satisfied by the results presented in this paper is evident from the graphs shown in Figure 5. The data are from Table 2.

A comparison of these results with those of Bennett (*1*) is given in Table 3. The agreement is not perfect, but this is probably largely accounted for by the inherent inaccuracies of the straight graphical method.

CONCLUSIONS

A convenient and accurate method of calculating thermodynamic properties of gases from experimental compressibility measurements through the use of the Redlich and Kwong equation of state has been presented. The method was demonstrated for the usually troublesome calculation of fugacity and activity coefficients of the components of a gaseous mixture. The calculated activity coefficients are believed to be correct in the second decimal place, indicating an error of less than ±0.5%.

NOTATION

A = a constant
B = a constant
C = experimental value of compressibility factor
C' = equation value of compressibility factor
f = fugacity of a gaseous mixture
f_i = fugacity of pure i
$\bar{f}_i$ = fugacity of component i in a gaseous mixture
G = general property
$\bar{G}$ = general partial molal property
h = defined as being equal to Bp/C'
H = enthalpy
k, k' = constants
n = number of moles
p = pressure, atm.
p_c = critical pressure, atm.
R = universal gas-law constant
S = entropy
$S°$ = entropy in the ideal-gas state at 1 atm.
T = absolute temperature
T_c = absolute critical temperature
V = volume
x_i = mole fraction of component i
γ_i = activity coefficient of component i
ϕ_i = fugacity coefficient of component i
* = the zero-pressure state

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