Table 1 includes the values of the diffusion ratio calculated in this way from flow rate vs. mean total pressure plots. The agreement is well within the probable experimental error.

DISCUSSION

The form of Equations (9) and (13) indicate a rather slow convergence to the asymptotic values at high and low pressures. Therefore a mixed mode of diffusion does occur to an appreciable degree over a wide range of values of the ratio r/λ. On the basis of the results for the porous solids this would appear to be a somewhat greater range than the hundredfold value given earlier. The convergence of Equations (9) or (13) is intermediate between the simple form of Equation (17) and the more rapidly converging intuitive equation proposed by Wheeler (2), given as

$$D_N = D_{AB}\,(1 - e^{-D_{AB}/D_{KA}}) \qquad (23)$$

A more rigorous test of Equation (9) would require experiments of the same kind as those performed on the porous solids but with true capillaries of known dimensions. Such work is currently under way.

However it would appear that the diffusion equation presented here gives an adequate description of the transition zone of diffusion for binary gas mixtures and can be applied with good accuracy to porous solids.

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NOTATION

A_s, L_s = geometric area and length of porous sample
D_{AB} = binary mutual diffusion coefficient for gases A and B, sq. cm./sec.
D_{KA} = Knudsen diffusion coefficient for gas A, sq. cm./sec.
D_N = mean diffusion coefficient
G = molecular transport rate, molecules/(sec.) (sq. cm.)
k = Boltzmann constant
L,x, = length of diffusional path, cm.
m = mass of a molecule
M = molecular weight
n = molecular concentration, molecules/cc.
N = molar transport rate, moles/(sec.) (sq. cm.)
p = partial pressure
P = absolute pressure
r = radius
$\bar{r}$ = equivalent pore radius
R = gas constant
T = absolute temperature
u = diffusional velocity in the axial direction, cm./sec., referred to a fixed set of coordinates
$\bar{v}$ = average molecular speed
y = mole fraction
λ = mean free path
η = gas viscosity
Δp = pressure differential causing flow

Subscripts

A,B = gas A and gas B, respectively

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Thermodynamic Properties of Polar Gases in the Dilute Phase

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A procedure is proposed, based in part on theory and in part on experimental data, for predicting the effect of polarity on the thermodynamic properties of polar, organic gases in the dilute phase. This correlation was used to predict compressibility factors *Z*, and the change of enthalpy with pressure, in the vapor phase.

By use of this correlation the computed compressibilities indicated an average absolute deviation of 1.0% from available experimental data, which includes reduced pressures up to 0.9 and temperatures to 1.0. Similar comparisons were made for the effect of pressure on enthalpy.

Reasonable progress has been made in developing prediction methods for thermodynamic properties of nonpolar gases, particularly pure components. However progress has been slight for polar substances where electrical properties may exert a significant effect. The objective of this paper is to present a prediction method for classes of organic, polar compounds.

PREVIOUS CORRELATIONS

The original method of Hougen and Watson (5) assumed that volume and energy were the two parameters characterizing a gas. Thus the reduced volume V/V_c or the reduced pressure P/P_c was used with the reduced temperature T/T_c to provide the two variables which determined the compressibility factor:

$$Z = PV/RT \qquad (1)$$

Experimental compressibility factor data have shown that Z is not the same function of the reduced pressure and reduced temperature for every compound. Thus more parameters are needed; these parameters must represent the forces which are present in some compounds but not in others at the same conditions of reduced pressure and temperature.

These forces are usually due to one of the following causes: deviation from spherical molecular shape, or the degree of acentricity; high electrical forces such as manifested by the dipole moment and the existence of hydrogen bonding; and quantum forces which are important in hydrogen and helium.

This latter effect will not be considered here, since it is important in only the compounds mentioned. All compounds are effected by the first effect with the exception of the inert gases, which are spherical. For this

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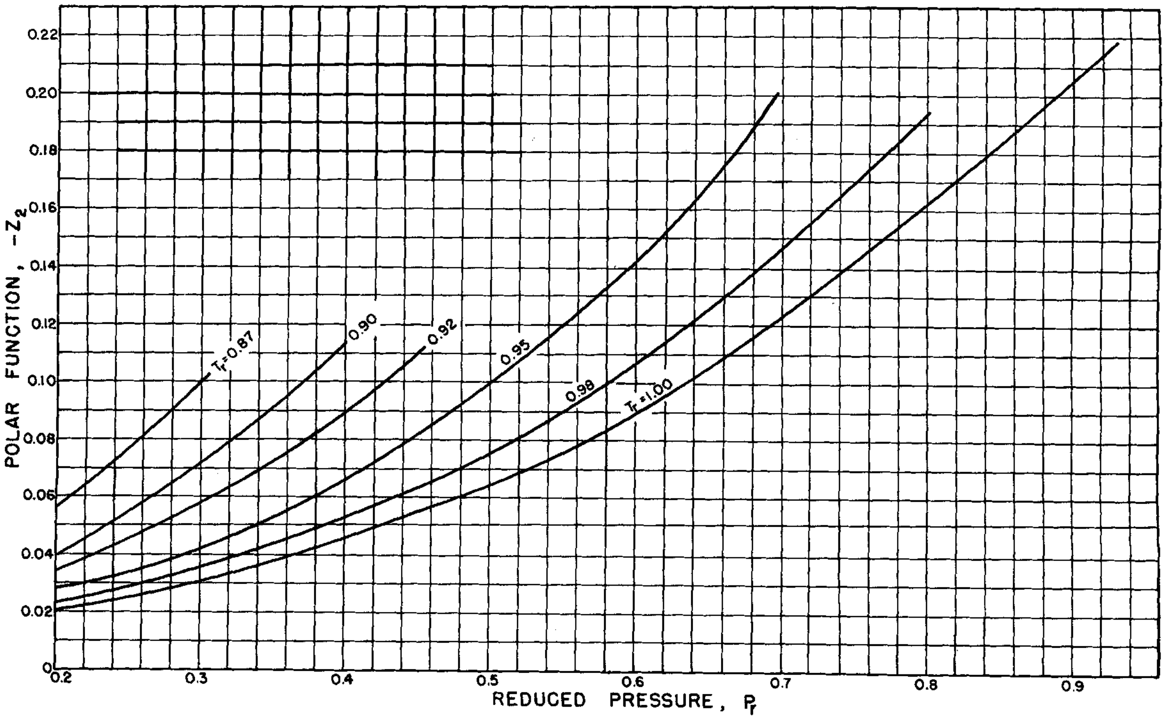

Fig. 1. The compressibility factor polar correction function, $Z_2(P_r,T_r)$.

reason Pitzer (*11*) has computed values of the compressibility factor Z_0 as a function of P_r and T_r from experimental data on the inert gases. Because none of the listed conditions are present in inert gases Z_0 is the same function of P_r and T_r for all inert gases.

It is desirable to add contributions due to acentricity and electrical forces to the value of Z_0. Pitzer has used a factor ω which is a measure of the acentricity of a molecule. When this factor is multiplied by a function Z_1 (P_r, T_r), the result is the contribution to the compressibility factor due to the acentricity. The acentric factor is defined as

$$\omega = -\log P_r - 1.000, \text{ at } T_r = 0.7 \qquad (2)$$

Thus the acentric factor, which is zero for inert gases, can be computed for each compound from vapor pressure data. Since

$$Z = Z_0 + \omega Z_1 \qquad (3)$$

Pitzer was able to calculate values of $Z_1(P_r, T_r)$ knowing $Z_0(P_r, T_r)$ and ω plus experimental values of Z for each compound. The values of $Z_1(P_r, T_r)$ were found to be quite consistent for a large number of compounds which were labeled simple fluids. Compounds with high electrical and quantum effects are excluded from the class of simple fluids.

Lydersen, Greenkorn, and Hougen (*7*) have used the compressibility factor at the critical point, Z_c, as a third parameter to predict compressibilities for nonpolar and polar compounds alike. McCracken (*7*) found that average absolute errors of 28 and 18% resulted when comparing their experimental deviations in enthalpies from the ideal gas state for methanol against correlations (*5*) and (*7*), respectively. Storvick (*19*) made a similar comparison with his experimental enthanol data and found the corresponding errors of 32 and 31%.

McCracken (*7*) and Storvick (*18*) have added polar correction terms, based on association, to the Lydersen and Pitzer correlations, respectively. These made it possible to predict enthalpy deviations from the ideal gas state within 4 to 6% error of the experimental values for methanol and ethanol. While all compounds exhibiting hydrogen bonding and the resulting association are polar, not all polar compounds show hydrogen bonding. Because the dipole is well buried in some molecules, it is blocked from the dipole of neighboring molecules by the more external atoms of its own molecule. These atoms do not allow the dipoles to become close enough together to make the dipole-dipole interaction strong enough to hold the molecules together in a hydrogen bond. Thus molecules with the more external dipoles tend to form hydrogen bonds and associate. Even though the association approach has been used with success for the alcohols, the correction term of this investigation was based on the dipole moment because it can be used for all polar compounds.

DERIVATION OF POLAR CORRELATION

The purpose of this investigation was to obtain a parameter which when multiplied by a universal function of P_r and T_r would give the polar contribution to the compressibility factor. Pitzer's method was used to isolate the nonpolar contribution because this is probably the most accurate procedure available. The required expression is of the form

$$Z = Z_0(P_r', T_r') + \omega Z(P_r', T_r') + P^* Z_2(P_r, T_r) \qquad (4)$$

where Z_2 is a function of P_r and T_r. The first two terms on the right-hand side of Equation (4) were computed in all cases from Pitzer's work.

It is important to isolate the polar and acentric effects for both theoretical and empirical reasons. Thus the first two terms of the right-hand side of Equation (4) cannot be evaluated with the critical constants and the ω factor of the polar compound without introducing constants that are themselves a function of the polarity of the molecule. What is needed is the value of these constants for a molecule which is identical to the polar one except that it is nonpolar, that is a homomorph. When the polar compound is an alcohol, ketone, or ether, the homomorph has the same structure except that oxygen is replaced by a CH_3 or CH_2 group. For example the homomorph of *n*-propanol is *n*-butane. Difficulties in choosing homomorphs exclude most inorganic substances from this type of correlation. By using the critical constants and the ω factor for the homomorph the first two terms of Equation (4) can be evaluated with Pitzer's values. Subtracting this result from the experimental compressibility

TABLE 1. PHYSICAL PROPERTIES OF POLAR COMPOUNDS

Polar compound	ϵ/k, °K.	σ, °A.	μ^*	P^*	Homomorph Compound	ω
Methanol	630	2.40	1.55	2.09	Ethane	0.115
Ethanol	748	2.53	1.32	1.58	Propane	0.164
n-Propanol	1,120	2.55	1.05	1.08	*n*-Butane	0.177
Ether	1,204	2.30	0.81	0.21	*n*-Pentane	0.262
IPE	1,655	2.12	0.76	0.19	2, 4 dimethyl pentane	0.363
Acetone	342	3.84	1.76	1.81	Isobutane	0.206
MEK	490	3.73	1.52	1.41	Isopentane	0.198
Methyl fluoride	207	3.36	1.75	0.31	Ethane	0.115
*Freon 12	—	—	—	—	—	0.172
*Sulfur dioxide	—	—	—	—	—	0.268
*Water	380	2.65	1.85	0.08†	—	0.348
*Ammonia	320	2.60	1.66	0.25†	—	0.261

* No homomorph was used for these compounds.

† P^* values were calculated from c values obtained without the use of a homomorph and are not to be compared with other values of P^* in the table.

for the polar compound one gets the polar contribution P^*Z_2 as a function of P_r and T_r. Evaluated in this way the true acentric effect for the polar compound has been determined by means of the homomorph, so that the remaining polar contribution is due to polar effects and the interaction between polar and acentric effects. Such cross effects were considered negligible in this work.

The parameter P^* was chosen to be of the form $c(u^*)^n$. The reasons for this choice were both theoretical and empirical. The reduced dipole moment is known to be the most powerful electrical parameter. It is defined by the expression

$$\mu^* = \mu/(\epsilon\,\sigma^3)^{\frac{1}{2}} \tag{5}$$

where ϵ/k and σ are the Stockmayer force constants. The value of μ^* alone cannot be used as a fourth parameter, since the dipole moment location and direction with respect to the entire molecule has an important influence on the compressibility. For the aliphatic, normal alcohols the dipole moment is centered around the oxygen atom which is not shielded from other molecules by the atoms of its own molecule. Compounds such as ethyl ether also have the dipole moment centered around the oxygen atom, but here the oxygen atom is well-buried in the molecule and will have little influence on surrounding molecules. Thus for the same value of μ^* an ether would be expected to deviate from the behavior of a simple fluid less than an alcohol. Sulfur dioxide is another molecule with a high value of μ^* which follows the simple-fluid behavior well, as shown in Table 2.

Eucken and Meyer (3) have analyzed the dipole moment of a number of compounds and found that various linkages could be assigned a partial contribution to the total dipole moment. The H-C linkage for example was given the value of 0.3 with this component vector pointing toward the hydrogen atom along the linkage. By writing the structural formula and adding the various vector components the magnitude and direction of the total dipole moment can be obtained. If this procedure is followed, then the aliphatic, normal alcohols will all have the same magnitude and direction of their dipole moments. The same is true for ketones and ethers. Experimental measurements show the magnitudes to be quite close in these cases. Because the position of the dipole moment is centered around the oxygen atom, the degree of exposure of the dipole moment to surrounding molecules should be about the same within each group and decrease in magnitude in proceeding from alcohols to ketones to ethers. Thus the molecular direction and position of the dipole moment are thought to be the same for each group. Thus the magnitude of c attempts to measure the effectiveness of the dipole moment due to its position and direction. It will be nearly zero for groups which have the dipole moment well-buried in the molecular structure. The c values given in this investigation are based on c equal to unity for the alcohols. Since the alcohols were found to have the highest polar contribution, the maximum value of c encountered in this work was unity.

TABLE 2. A COMPARISON OF CORRELATION FOR THE COMPRESSIBILITY FACTOR

All experimental compressibility factors were computed from experimental PVT data.

	Average % error between experimental and predicted values	
Compound	Pitzer	Calc. from Equation (4)
Methanol	4.20	1.30
Ethanol	3.30	1.23
n-Propanol	3.82	0.96
Methyl fluoride	6.03	0.81
Freon 12	0.41	—
Sulfur dioxide	0.91	—
Water	1.76	1.00
Ammonia	2.21	0.58

While the dipole-dipole interaction is best represented by a power series of even powers of the dipole moment, the reduced dipole moment was raised to the nth power to simplify the equation.

By assuming that the dipole-dipole interaction is the only electrical interaction of importance between molecules, many electrical interactions have been neglected. One of these, the dipole-induced dipole, arises when the permanent dipole of a polar molecule induces a dipole moment onto a neighboring molecule and these interact. Rowlinson (*15*) states that this effect is always small compared with the dipole-dipole interaction, and there is no reason why higher ordered induced interactions should not be neglected safely.

Most polar compounds also have an electric quadrupole moment, which is a second-order tensor. Buckingham and Pople (*1*) have proposed a molecular model which adds a quadrupole-quadrupole interaction term and a quadrupole-dipole interaction term to the Stockmayer potential. It is difficult to determine the magnitude of these effects, since the quadrupole moment has been measured for only a few compounds. Rowlinson (*15*) has found that the quadrupole-dipole interaction contributes about 24% to the value of the second virial coefficient for water, but this is thought to be a severe case. The quadrupole moment, like the dipole, suffers loss of effectiveness when it is well buried in the molecular structure. On this basis Rowlinson (*16*) suggests that quadrupole effects are probably not appreciable for ethers and ketones but may have a significant effect for the alcohols. Because there is no experimental data on the quadru-

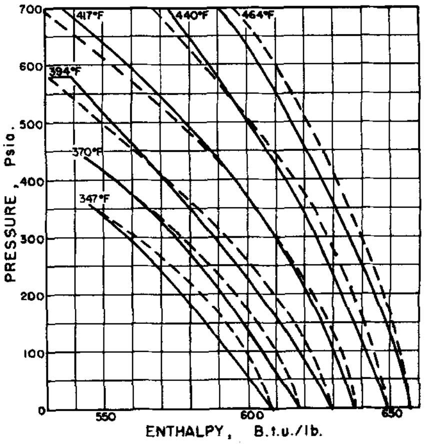

Fig. 2. Comparison of experimental and predicted enthalpy values of methanol, c = 1.0. ———— experimental, — — — — — — predicted.

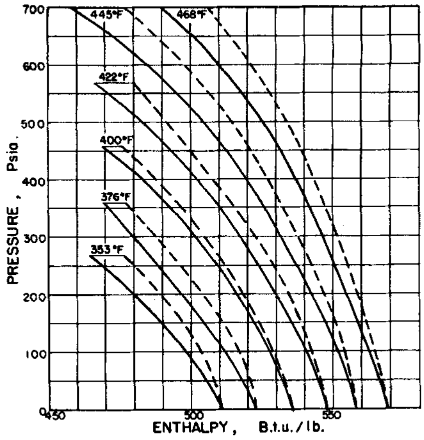

Fig. 3. Comparison of experimental and predicted enthalpy values of ethanol, c = 1.0. ———— experimental, — — — — — predicted.

poles of alcohols, these effects had to be neglected.

In order to calculate the reduced dipole moment for each compound by Equation (5) the values of the Stockmayer force constants, ϵ/k and σ must be known. These constants can be computed by the method of Hirschfelder, Curtiss, and Bird (*4*) if the second virial coefficient as defined in Equation (6), $B(T)$, is known as a function of temperature over the region to be considered:

$$PV/RT = 1 + B(T)/V + C(T)/V^2 + \ldots\ldots \quad (6)$$

Lambert and associates (*6*) have shown that the Berthelot equation for $B(T)$, Equation (7), gives accurate values for $B(T)$ for polar compounds, including alcohols and ketones if the temperature is above 300°F:

$$B(T) = (9/128)\,(RT_c/P_c)\,(1 - 6T_c^2/T^2) \quad (7)$$

where B is in units of ml./gram-mole, P in atm., and T in °K.

Since the minimum temperature used in the polar theory of this work was $T_r = 0.85$, most of the temperatures considered were above 300°F and the Berthelot equation was applicable. Rowlinson's values (*15*) were used for the force constants of methanol, acetone, and methyl fluoride. Values for ethanol, n-propanol, ethyl ether, isopropyl ether, and methyl ethyl ketone were calculated with the Berthelot equation. Rowlinson's values of ϵ/k and σ for methanol and acetone agree well with the results calculated with Equation (7). Table 1 shows the critical properties of the polar compounds and their homomorphs along with the calculated force constants used in Equation (5).

POLAR CORRELATION APPLIED TO PVT DATA

Experimental PVT data were used in order to evaluate the polar contribution to the compressibility factor as a function of P_r and T_r. First, values of $Z_2(P_r, T_r)$ were calculated from the alcohol data of Ramsay and Young (*12, 13, 14*) for methanol, ethanol, and n-propanol. Their work covers the range of temperature and pressure that was used throughout this study; that is $P_r = 0.2 - 0.9$ and $T_r = 0.85 - 1.05$. This range covers most of the area in the gas phase of the standard pressure-enthalpy diagram.

TABLE 3. c-VALUES OBTAINED FROM EXPERIMENTAL DATA

For water or ammonia no homomorph was used. Hence the results for these two substances should not be compared with other c values.

Compound	c value PVT data	Enthalpy data
Methanol	1.00	1.00
Ethanol	1.00	1.00
n-Propanol	1.00	1.00
Methyl fluoride	0.12	—
Water	0.027	—
Ammonia	0.10	—
Acetone	—	0.70
MEK	—	0.70
Ethyl ether	—	0.30
IPE	—	0.30

Since $Z_2(P_r, T_r)$ was assumed to be the same function of P_r and T_r for all polar compounds, a ratio of P^*/Z_2 for one alcohol to that of another alcohol at the same conditions will give the ratio of P^* for the first alcohol to that of the second. Since these ratios were found to be roughly constant for all values of P_r and T_r, it then could be assumed that P^* was a constant for each alcohol. Although there was a great deal of scatter in the values of these ratios, there were no trends with P_r and T_r, and hence average values of the ratios were computed.

Because c was a constant within a chemical group, the value of n which best fit the data was obtained from the alcohol ratios. Let R_1 be the ratio of methanol to n-propanol and R_2 be the ratio of ethanol to n-propanol. Then

$$R_1 = P^*Z_2(M)/P^*Z_2(P) = P^*(M)/P^*(P) = (\mu^*_M/\mu^*_P)^n \quad (8)$$

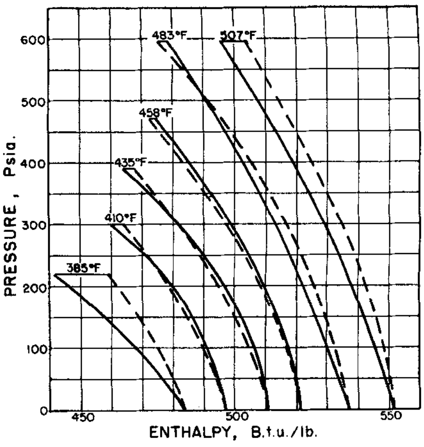

Fig. 4. Comparison of experimental and predicted enthalpy values of n-propanol, c = 1.0. ———— experimental, — — — — — — predicted.

The average value of R_1 from the alcohol ratios was 1.92. From Equation (8) $1.92 = (1.55/1.05)^n$ or $n = 1.67$.

The values of n obtained from R_1, R_2, and $R_3 = R_1/R_2$ were average to obtain the value of 5/3. The average absolute deviation of the three calculated values on n from 5/3 was found to be 2.5%.

Using $n = 5/3$ and arbitrarily setting c equal to unity for the alcohols one can compute values of Z_2 as a function of P_r and T_r. A generalized graph of Z_2 is shown in Figure 1.

The generalized graph of $Z_2\,(P_r, T_r)$, while obtained from alcohol data, might be expected to be valid for all polar compounds. All values of Z_2 are negative as was to be expected, since P^* is positive, and the effect of polarity is to lower the compressibility factor. Figure 1 shows $-Z_2$ to be an increasing function of P_r and a decreasing function of T_r. This was expected since an increase in pressure decreases the mean distance between molecules, increasing the polar effect. An increase in temperature gives the molecules more energy with which to oppose the polar effect. As the pressure approaches zero, the polar contribution P^*Z_2 must go to zero. By extrapolating Figure 1, Z_2 does appear to be nearly zero at

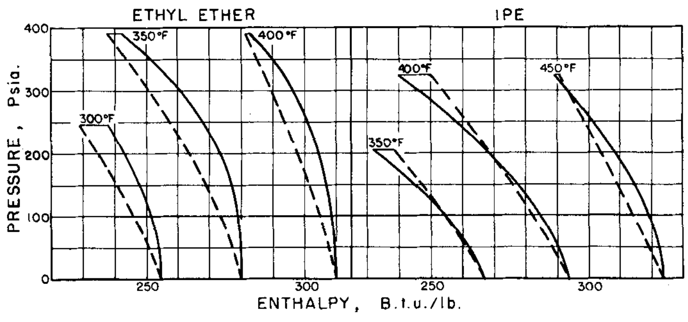

Fig. 5. Comparison of experimental and predicted enthalpy values of ethyl ether and isopropyl ether, c = 0.3. ———— experimental, — — — — predicted.

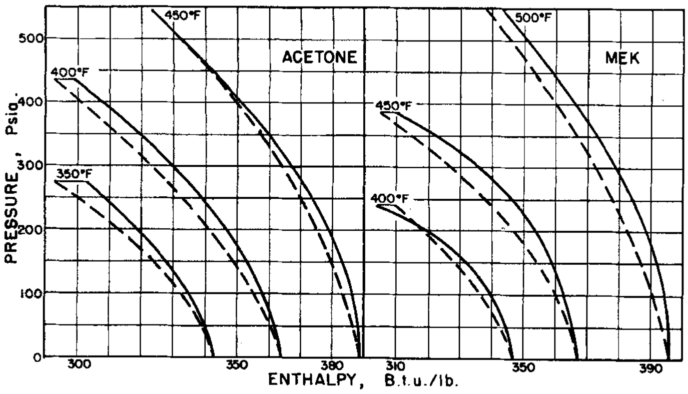

Fig. 6. Comparison of experimental and predicted enthalpy values of acetone and methyl ethyl ketone, c = 0.7. ———— experimental, — — — — — predicted.

zero pressure. As the temperature increases, P^* remains finite. In order for the polar contribution to be zero $Z_2(P_r, \infty)$ must be zero. This agrees with the trend, shown in Figure 1, of $-Z_2$ to approach zero as T_r increases.

The reliability of Equation (4) for predicting compressibilities of polar substances is summarized in Table 2. The results of utilizing Pitzer's method, which does not include the polar contribution, is also shown for comparison. For the three alcohols Pitzer's method gives an average absolute error of 3.82%, and the polar correlation yields 1.17%.

The polar correlation was next compared with PVT data for compounds other than alcohols with the generalized graph of Z_2 used. PVT data has been taken over wide ranges of temperature and pressure by Michel (*9*) for methyl fluoride. The homomorph of methyl fluoride is ethane. Pitzer's method was found to give an average absolute error of 6.03% for the compressibility factor as compared with Michel's data. With the value of *n* of 5/3, as was found from the alcohol correlations, and $c = 0.12$, the polar correlation showed a 0.81% error for the same points. The value of $c = 0.12$ was determined to give the best agreement with the observed data. Similarly calculated values of *c* for other polar substances are presented in Table 3.

While PVT information is available for a number of Freons, the only data taken at pressure above $P_r = 0.2$ was that for Freon 12 (*10*). Since the C-Cl and C-F linkages have roughly the same dipole moment contribution, Freon 12 has a relatively small dipole moment ($\mu = 0.51$). Pitzer's method was found to give an excellent fit of the experimental PVT data; the average absolute error was 0.41%. Such behavior indicates that Freon 12, like CH_3F, has a low *c* value. This suggests that the dipole moment is centralized in the molecule and blocked from neighboring molecules by the chlorine and fluorine atoms.

Sulfur dioxide, which has a reduced dipole moment only slightly less than that of *n*-propanol, illustrates that the magnitude of the dipole moment alone cannot be used as a fourth parameter. Ryhning and Hurd (*17*) have published PVT data for sulfur dioxide which was compared with values obtained from Pitzer's correlation. An average absolute error of 0.91% (see Table 2) was obtained showing that the polar effect was much less than it was for *n*-propanol.

Table 2 also includes comparisons for water and ammonia which have relatively high dipole moments. Suitable homomorphs are not available for these inorganic substances, so the properties of the compound itself were used to evaluate the first two (nonpolar) terms of Equation (4). While the correlation should not be used in this manner when homomorphs can be postulated, it is interesting to note from Table 2 that improved agreement with experimental PVT data is obtained also for water and ammonia.

APPLICATION TO ENTHALPY DATA

The change of enthalpy with pressure can be computed from compressibility data by

$$(\partial H/\partial P)_T = (-T^2R/P)(\partial Z/\partial T)_P \qquad (9)$$

Differentiating Equation (4) one gets

$$(\partial Z/\partial T)_P = (\partial Z_0/\partial T)_P$$
$$= \omega(\partial Z_1/\partial T)_P + P^*(\partial Z_2/\partial T)_P \qquad (10)$$

Each of the effects represented by the three terms on the right-hand side of Equation (10) will be considered separately. Let $H°$ be the ideal gas state enthalpy of some compound at a temperature *T* and let *H* be the enthalpy at this same temperature and an elevated pressure. Then by integrating Equation (9)

$$[(H° - H)/RT_c]_i$$
$$= T_r^2 \int_0^{P_r} (\partial Z_i/\partial T_r)_P \, d\,(\ln P_r) \qquad (11)$$

The equation for the total change of enthalpy with pressure is

$$[(H° - H)/RT_c] = [(H° - H)/RT_c]_0 + [(H° - H)/RT_c]_1$$
$$+ P^*[(H° - H)/RT_c]_2 \qquad (12)$$

where each of the terms on the right side are evaluated by Equation (11).

Values of $[(H° - H)/RT_c]_0$ and $[(H° - H)/RT_c]_1$ have been calculated by Pitzer (*10*) as a function of reduced pressure and temperature.

From Figure 1 $(\partial Z_2/\partial T_r)_P$ was determined as a function of P_r and T_r. The results are given in Table 4. With Equation (11) values of $[(H° - H)/RT_c]_2$ were computed and are presented as Table 5.

Equation (12) can be used to predict the total enthalpy change for a polar compound for which P^* is known. The quantities in the first two terms of the right-hand side apply to

Table 4. $(\partial Z_2/\partial T_r)$ as a Function of P_r and T_r

	Reduced temperature					
P_r	0.87	0.90	0.92	0.95	0.98	1.00
0.2	0.50	0.40	0.33	0.23	0.15	0.12
0.3	1.15	0.80	0.60	0.42	0.22	0.20
0.4	—	1.36	1.00	0.70	0.50	0.35
0.5	—	—	1.50	1.20	0.70	0.45
0.6	—	—	—	1.55	1.00	0.80
0.7	—	—	—	2.30	1.65	1.20
0.8	—	—	—	3.70	2.55	1.70

Table 5. $[(H° - H)/RT_c]_2$ as a Function of P_r and T_r

P_r	0.87	0.90	0.92	0.95	0.98	1.00
0.0	0.000	0.000	0.000	0.000	0.000	0.000
0.2	0.188	0.146	0.113	0.090	0.064	0.048
0.3	0.433	0.324	0.254	0.203	0.146	0.105
0.4	—	0.591	0.449	0.361	0.254	0.190
0.5	—	—	0.700	0.561	0.397	0.295
0.6	—	—	—	0.799	0.561	0.420
0.7	—	—	—	1.09	0.763	0.588
0.8	—	—	—	1.42	0.999	0.752

the homomorph of the polar compound; the values of n and c must also be known. In the following comparisons the values of n and c used for the polar contribution were those determined from the previous analysis of the PVT data (see Table 3).

Experimental enthalpy measurements for methanol and ethanol have been reported by McCracken (*8*) and Storvick (*19*). The authors have measured enthalpy data for *n*-propanol (*2*). The comparison of experimental enthalpy deviations and those computed from Equation (12) are shown for the three alcohols in Figures 2 to 4. The average difference for the alcohols was 7.8 B.t.u./lb. Neither the experimental or computed values were consistently greater, as shown by Figures 2 to 4. Hence it was concluded that the value of $c = 1.0$, as determined from PVT data, best fits the alcohol enthalpy data.

Experimental enthalpy data for ethyl ether, isopropyl ether, acetone, and methyl ethyl ketone were also available (*2*) to evaluate the validity of Equation (12). For these substances c values were not known from PVT data. However P^* and hence c could be obtained which agreed best with the experimental enthalpy data. The results are given in the last column of Table 3.

Figure 5 shows the comparison of the experimental and computed enthalpy values for ethyl ether and isopropyl ether with $c = 0.3$. In similar fashion the values of c for the acetone and methyl ethyl ketone were found to be 0.7. The experimental and computed enthalpy values for acetone and methyl ethyl ketone are compared in Figure 6.

While the calculated and experimental enthalpy deviations are near the experimental accuracy, the calculated values are inherently not of high accuracy. This is due to the differentiation of the compressibility factor with respect to temperature in Equation (10) which magnifies the error in the compressibility factor, perhaps five to seven times. Thus the polar theory may predict values of Z to within 1%, yet the predicted results for $(H^\circ - H)$ may be in error by 5 to 7% or about 4 B.t.u./lb. If to this is added the possible error in the experimental enthalpy data of a few British thermal units, the expected difference between computed and experimental enthalpy deviations is of the order of 5 to 8 B.t.u./lb. The average deviation was about 7 B.t.u./lb. for the alcohols, ketones, and ethers over the entire pressure range, as indicated in Figures 2 to 6.

Because of these experimental and computational errors the values of the c factors in Table 3 obtained from enthalpy data must be regarded as approximations. Nevertheless, they are consistent with the idea that the dipole moment becomes more shielded from neighboring molecules as one goes from the alcohols to ketones to ethers.

CONCLUSIONS

A correlation [Equation (4)] has been proposed for predicting the PVT behavior of polar gases. The method predicts compressibilities for normal alcohols and methyl fluoride which deviate about 1.0% from experimental data. This error is less than 1/3 of that obtained from previous methods.

From the correlation developed it is possible to predict the change in enthalpy with pressure for polar compounds. The average deviation between predicted and experimental enthalpy data for methanol, ethanol, *n*-propanol, ethyl ether, isopropyl ether, acetone, and methyl ethyl ketone was about 7 B.t.u./lb. This is about the same as the deviation expected from experimental errors and errors from differentiating the PVT correlation.

It has been shown that a parameter such as the reduced dipole moment cannot alone be used to obtain contributions to the compressibility factor or enthalpy of polar gases. A compound with a large dipole moment well-buried in the molecular structure will show little deviation from the behavior of Pitzer's normal fluids because the dipole is not able to interact with its neighboring molecules. Thus the significance of the dipole moment decreases in proceeding from alcohols to ethers to ketones. Additional PVT data, particularly for highly polar substances, are needed to extend and further evaluate the correlation proposed.

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NOTATION

$B(T)$ = second virial coefficient
$C(T)$ = third virial coefficient
c = multiplication factor in the form of P^*
H = enthalpy
n = power of the reduced dipole moment
P = pressure
P^* = polar parameter
R = gas constant
R_i = ratios of P^*Z_2 of one alcohol to another
T = absolute temperature
V = specific volume
Z = compressibility factor
$\epsilon/k, \sigma$ = Stockmayer force constants
μ = dipole moment
ω = acentric factor

Superscripts

$*$ = reduced or dimensionless, quantity
$\circ$ = ideal gas state
$'$ = prime designates homomorph

Subscripts

0 = contribution of an inert gas
1 = contribution due to acentricity
2 = polar contribution
r = reduced quantity
c = critical value
i = any of the contributions to the compressibility factor in Equation (10)

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