x = dimensionless coordinate parallel to flow = $\eta / \frac{3}{2} \frac{Ua^2}{D_{ae}}$
y = dimensionless coordinate = ξ / a
z = dimensionless coordinate = ζ / b

Greek Letters

γ = aspect ratio = a/b
ζ = spatial coordinate perpendicular to the flow direction and parallel to the catalytic plate
η = spatial coordinate parallel to the flow direction
μ = viscosity
ξ = spatial coordinate perpendicular to the flow direction and the catalytic plate
ρ_a = mass concentration of species a
ρ_{ao} = mass concentration of species a at $x = 0$
Σ = summation symbol

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A Fourth Parameter for the Vapor Pressure and Entropy of Vaporization of Polar Fluids

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Pitzer's acentric factor approach has been extended to the vapor pressure and entropy of vaporization of polar fluids. Normal fluid vapor pressure functions have been determined for $0.44 \leq T_R < 0.56$. A polarity factor has been defined and polar correction terms established for the vapor pressure for $0.44 \leq T_R < 0.70$ and for the entropy of vaporization for $0.56 \leq T_R \leq 0.72$. The polar correction terms enable the accurate calculation of the vapor pressure and entropy of vaporization of a polar fluid from its normal boiling point and normal latent heat of vaporization. The results of this study also form the basis for the extension of this approach to other thermodynamic properties of polar fluids.

Accurate values of the volumetric and thermodynamic properties of pure substances and mixtures are required in many important applications. Reliable methods have been presented for the calculation of these properties for nonpolar fluids and certain nonpolar gas mixtures. Similar procedures are presently not available for polar fluids and for mixtures containing at least one polar constituent.

Pitzer (*17*) has shown that the original theorem of corresponding states which has formed the basis of many reduced state correlations for thermodynamic properties is only applicable for simple fluids such as argon, krypton, and xenon. This is because the potential energy curves of simple fluids can be adequately described by functions containing two characteristic parameters, such as the Lennard-Jones potential. Pitzer proposed an extended theorem of corresponding states for *normal fluids* in which a third parameter ω accounts for the effects of the size and shape of the molecules. The extended theory is equivalent to the use of an intermolecular potential which contains an additional shape parameter (such as the Kihara potential). The acentric factor ω is empirically defined as

$$\omega = -\log P_R\big|_{T_R=0.700} - 1.000 \qquad (1)$$

The functional dependence between the compressibility factor and the reduced temperature, reduced pressure, and acentric factor was approximated by a Taylor series truncated after the first-order term as follows:

$$z = z^{(0)} + \omega\, z^{(1)} \qquad (2)$$

where $z^{(0)}$ is the compressibility factor of a simple fluid ($\omega = 0$). Values of $z^{(0)}$ and $z^{(1)}$ have been presented for a complete range of reduced temperatures and reduced pressures (*19*), and similar tables were prepared for other thermodynamic properties (*4, 19*). Pitzer and Hultgren (*18*) and Prausnitz and Gunn (*20*) have used the values of $z^{(0)}$ and $z^{(1)}$ to develop relationships for the pseudocritical constants and acentric factors of nonpolar gas mixtures.

For polar fluids, Hall and Ibele (*9*) have proposed a similar extended theory in which the reduced dipole group is the third parameter. Pitzer (*17*) combined the first-order terms resulting from the Kihara potential and the Stockmayer potential for polar molecules and obtained the following relationship for the second virial coefficient reduced with the Boyle volume:

$$\left(\frac{B}{v_B}\right) = \left(\frac{B}{v_B}\right)^{(0)} + a\left(\frac{B}{v_B}\right)^{(1)} + b\left(\frac{B}{v_B}\right)^{(2)} \qquad (3)$$

where a is the shape parameter and b is a fourth parameter, the reduced dipole group. The terms $(B/v_B)^{(1)}$ and $(B/v_B)^{(2)}$ are functions of the reduced Boyle temperature T/T_B. Pitzer showed that the use of only a third parameter is adequate for slightly polar substances, but that for highly polar fluids a fourth parameter should be used. Curl and Pitzer (*4*) have suggested that the normal fluid approach be restricted to those fluids whose surface tension constants σ_0 can be calculated to within 5% by the following equation

$$\frac{\sigma_0 v_0^{2/3}}{T_c} = 1.86 + 1.18\omega \qquad (4)$$

As indicated by the theoretical considerations, Equation (4) does not apply for highly polar and hydrogen-bonding fluids.

The only attempt at the extension of the acentric factor approach to polar substances by the addition of a fourth parameter was the study of Eubank and Smith (*7*) for the thermodynamic properties of dilute gases. This approach requires that an appropriate homomorph (a nonpolar substance having the same size and shape) be available for the polar substance and is therefore restricted to some pure organic substances. However, the theoretical considerations indicate that Pitzer's tables for the compressibility factor can be used directly if a suitable fourth parameter is defined and polar correction terms are established.

THE VAPOR PRESSURE OF POLAR FLUIDS

Because the vapor pressure formed the basis for the definition of the acentric factor, this property was chosen as the starting point for the extension of the normal fluid approach to polar fluids. The vapor pressure of a polar fluid has been defined as follows:

$$\log P_R = (\log P_R)^{(0)} + \omega(\log P_R)^{(1)} + x(\log P_R)^{(2)} \qquad (5)$$

where x is an empirical parameter for polar substances similar to the acentric factor for normal fluids, and $(\log P_R)^{(2)}$ is the polar correction term. The parameter x is defined to be zero for normal fluids so that the $(\log P_R)^{(0)}$ and $(\log P_R)^{(1)}$ terms are the same as those obtained previously by Pitzer et al. (*19*) for reduced temperatures between 0.56 and 1.0.

In Figure 1 values of $\log P_R$ obtained from experimental data are plotted against $1/T_R$ for the normal fluid *n*-heptane and the polar fluid water. These substances have almost the same value of ω if Equation (1) for normal fluids is used. It can be seen from Figure 1 that the reduced vapor pressures of the two substances are virtually identical for $T_R \geqq 0.7$, but that below this temperature significant deviations occur. Reid and Sherwood (*21*) recommend that the Riedel reduced vapor pressure equation, which is very similar to Pitzer's normal fluid relationship, not be used for polar substances for $T_R < 0.65$. Thek and Stiel (*25*) have recently developed a reduced vapor pressure equation which produces improved results for polar substances because it effectively includes an additional parameter involving the normal latent heat of vaporization.

The normal fluid vapor pressure equation [Equation (5) with $x = 0$] was tested for a number of polar fluids for $0.7 \leqq T_R < 1.00$. It was found that there is a slight polar correction for this region, but its magnitude was found to be less than the experimental accuracy of the data. Therefore, the $(\log P_R)^{(2)}$ term in Equation (5) has been defined to be zero for $T_R \geqq 0.7$. Thus the definition of ω in Equation (1) is the same for polar fluids as for normal fluids. The value of $(\log P_R)^{(2)}$ was defined to be 1.00 at $T_R = 0.6$, so that

$$x = \log P_R\big|_{T_R=0.6} - \log P_{Rn}\big|_{T_R=0.6} \qquad (6)$$

where P_{Rn} is the reduced vapor pressure calculated from the normal fluid equation.

Experimental vapor pressure data for the polar fluids listed in Table 1 were used to establish the values of ω and x presented for these substances. The sources of the data are included in the table. Values of $(\log P_R)^{(2)}$ were established for reduced temperatures between 0.56 and 0.70 by plotting $\log P_R - \log P_{Rn}$ for each substance at a constant reduced temperature against x. The resulting line for $T_R = 0.56$ is shown in Figure 2. Straight lines were obtained for the entire region, indicating that Equation (5) is a valid representation of the vapor pressure of polar fluids and that higher-order terms and cross terms in the series expansion are not required. The values of $(\log P_R)^{(2)}$ obtained for this region are presented in Table 2.

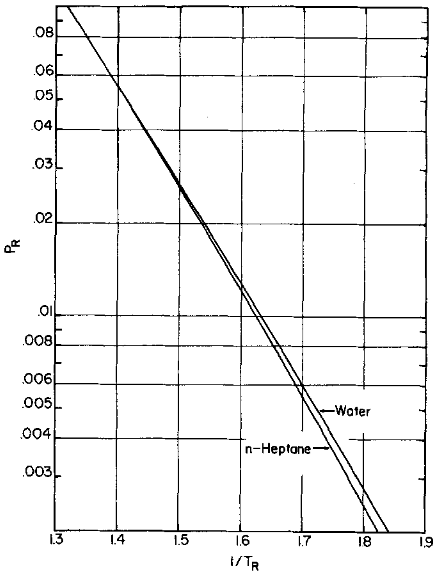

Fig. 1. Log P_R vs. $1/T_R$ for water and *n*-heptane.

Table 1. Acentric and Polarity Factors and Ranges and Sources of Vapor Pressure Data for Polar Substances Investigated

Substance	ω	x	Reduced temperature range of data	Sources of data
Methanol	0.556	0.038	0.54-0.70	*5, 24*
Ethanol	0.639	0.003	0.54-0.70	*14, 22*
n-Propanol	0.613	—0.064	0.54-0.70	*14, 15, 23*
n-Butanol	0.666	—0.035	0.54-0.70	*14*
Dimethyl ether	0.206	0.014	0.56-0.70	*14, 26*
Diethyl ether	0.275	—0.006	0.56-0.70	*14*
Methyl chloride	0.152	0.007	0.56-0.70	*14, 26*
Ethyl chloride	0.191	0.005	0.56-0.70	*14, 26*
Methyl amine	0.275	—0.017	0.44-0.70	*3, 16*
Ethyl amine	0.274	—0.027	0.46-0.70	*16*
Acetic acid	0.444	0.047	0.56-0.70	*14*
n-Propanoic acid	0.537	0.013	0.56-0.70	*14*
n-Butyric acid	0.672	0.026	0.56-0.70	*14*
Ammonia	0.251	0.009	0.50-0.70	*6*
Nitric oxide	0.577	—0.045	0.62-0.70	*14*
Nitrous oxide	0.160	—0.003	0.56-0.70	*11*
Water	0.344	0.023	0.44-0.70	*13*
Hydrogen chloride	0.128	0.016	0.50-0.70	*14*
Hydrogen bromide	0.083	0.011	0.56-0.70	*12*
Hydrogen cyanide	0.409	0.080	0.56-0.70	*26*
Acetone	0.304	0.013	0.56-0.70	*26*
Ethylene oxide	0.207	0.011	0.48-0.56	*8*
Methyl fluoride	0.191	0.012	0.44-0.56	*14*
Ethyl fluoride	0.221	0.019	0.46-0.56	*14*
Acetaldehyde	0.305	0.037	0.46-0.56	*14*
Acetonitrile	0.322	0.036	0.54-0.56	*26*
n-Propyl amine	0.207	—0.049	0.48-0.56	*14*

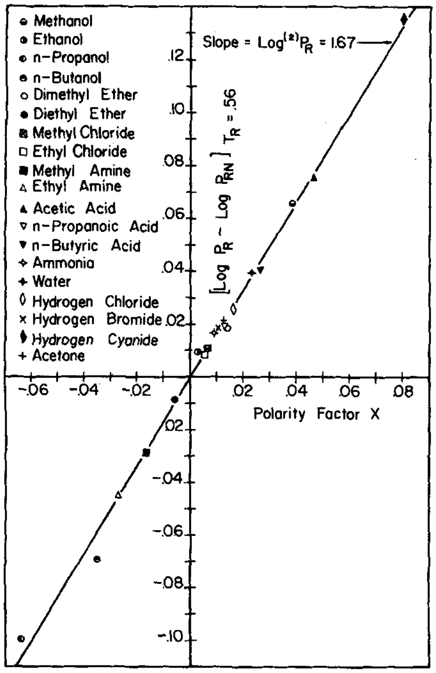

Fig. 2. Log P_R-log P_{RN} vs. x for T_R = 0.56.

The maximum error between calculated and experimental vapor pressures for the substances considered is 26.5% for hydrogen cyanide at T_R = 0.56 without a polar correction, while with the polar correction the maximum error is 2.5% for *n*-butanol at this reduced temperature. Errors with and without polar corrections were determined for three substances not in the correlation for this region by the use of two vapor pressure points (*26*) to establish ω and x as follows:

Substance	ω	x	T_R	Error without polar correction	Error with polar correction
Acetonitrile	0.322	0.037	0.5622	—12.7%	0.2%
Tert. butyl alcohol	0.625	—0.075	0.5761	26.2	—0.7
Methyl fluoride	0.191	0.012	0.5657	4.7	—0.2

It can be seen that the use of the polar correction leads to significant improvement in the calculation of vapor pressures for this region.

Since the deviations of polar fluids from normal fluid behavior increase with decreasing reduced temperature, the normal fluid functions $(\log P_R)^{(0)}$ and $(\log P_R)^{(1)}$ and the polar fluid function $(\log P_R)^{(2)}$ were determined for reduced temperatures below T_R = 0.56 to T_R = 0.44. The data for the normal fluids were obtained from API Project 44 (*1*) and Timmermans (*26*) for hydrocarbons, and for nitrogen from Armstrong (*2*). For each reduced temperature values of log P_R for the normal fluids were plotted against ω, as shown in Figure 3. The slope of the resulting line is $(\log P_R)^{(1)}$ and the intercept $(\log P_R)^{(0)}$. Experimental data for the polar fluids indicated in Table 1 were then used to establish values of $(\log P_R)^{(2)}$ for this region. The resulting values of the normal and polar fluid functions are included in Table 2. For this region the maximum deviation without a polar correction was 52.8% for water at T_R = 0.48, while with the polar correction the maximum deviation was 4.5% for water at this reduced temperature.

THE ENTROPY OF VAPORIZATION OF POLAR FLUIDS

The use of Equation (5) for the vapor pressure of polar fluids requires the availability of two vapor pressure points, one below T_R = 0.7, for the calculation of ω and

Table 2. Values of Normal and Polar Fluid Vapor Pressure Functions

T_R	$(\log P_R)^{(0)}$	$(\log P_R)^{(1)}$	$(\log P_R)^{(2)}$
0.70	—1.000	—1.00	0.000
0.68	—1.096	—1.12	0.156
0.66	—1.198	—1.25	0.324
0.64	—1.308	—1.39	0.520
0.62	—1.426	—1.54	0.745
0.60	—1.552	—1.70	1.00
0.58	—1.688	—1.88	1.31
0.56	—1.834	—2.08	1.67
0.54	—1.974	—2.34	2.11
0.52	—2.141	—2.61	2.41
0.50	—2.321	—2.90	2.87
0.48	—2.516	—3.25	3.44
0.46	—2.745	—3.54	3.78
0.44	—3.011	—3.81	4.60

Values of normal fluid functions for 0.56 ≤ T_R ≤ 0.70 from reference *19*.

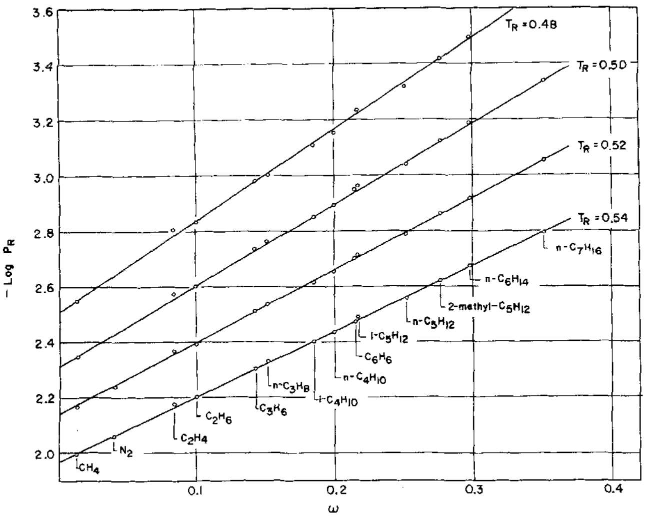

Fig. 3. Log P_R vs. ω for normal fluids.

x. Therefore, in order to establish an alternate procedure for the calculation of the polarity factor x and to confirm its validity as a fourth parameter, this approach has been extended to the entropy of vaporization. The entropy of vaporization of a polar fluid has been defined as

$$\Delta S = \Delta S^{(0)} + \omega \Delta S^{(1)} + x \Delta S^{(2)} \tag{7}$$

Pitzer et al. (*19*) presented values of $\Delta S^{(0)}$ and $\Delta S^{(1)}$ obtained from the vapor pressure and saturated vapor and liquid compressibility functions for normal fluids in conjunction with the Clapeyron equation. There is a slight second-order term for normal fluids, but experimental latent heat vaporization data were found to be reproduced within the experimental accuracy by the use of only the linear terms. The latent heat of vaporization is related to the entropy of vaporization by $\Delta H = T\Delta S$.

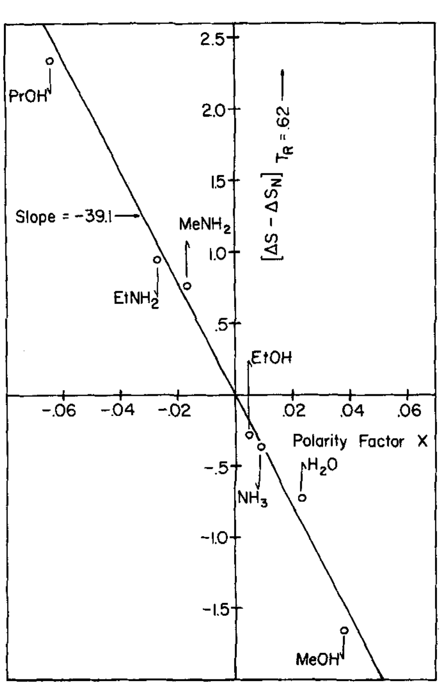

Fig. 4. ΔS-ΔS_N vs. x for $T_R = 0.62$.

TABLE 3. VALUES OF NORMAL AND POLAR FLUID ENTROPY OF VAPORIZATION FUNCTIONS

T_R	$\Delta S^{(0)}$	$\Delta S^{(1)}$	$\Delta S^{(2)}$
0.72	12.49	17.0	−24.8
0.70	13.19	18.1	−28.6
0.68	13.89	19.3	−31.8
0.66	14.62	20.5	−34.5
0.64	15.36	21.8	−36.9
0.62	16.12	23.2	−39.1
0.60	16.92	24.6	−41.1
0.58	17.74	26.2	−42.9
0.56	18.64	27.8	−44.7

Values of normal fluid functions from reference *19*.

Values of $\Delta S - \Delta S_n$ at a constant reduced temperature resulting from experimental data for methyl alcohol (*24*), ethyl alcohol (*22*), n-propyl alcohol (*15*), ammonia (*6*), water (*13*), methyl amine (*16*), ethyl amine (*16*), and ethylene oxide (*27*) were plotted against x, as shown in Figure 4 for $T_R = 0.62$. Straight lines were obtained for $0.56 \leqq T_R \leqq 0.72$, confirming the validity of x as a fourth parameter and the use of only linear terms in Equation (7) for this region. Values of $\Delta S^{(2)}$ obtained in this manner are presented in Table 3. There was considerable scatter in the similar plots for $T_R > 0.72$, indicating either that the data are poor in this region or that cross terms and/or higher-order terms in Equation (7) become significant for this region. However, the polar correction is very small for this region; the maximum error resulting from the use of the normal fluid relationship for the entropy of vaporization for the substances considered was only 8.1% for methanol at $T_R = 0.56$. The restriction of the tables to this region is not serious, since the primary motivation for the investigation of the entropy of vaporization was the establishment of an alternate procedure for the calculation of the polarity factor from the normal latent heat of vaporization, and the reduced normal boiling points of most substances fall between $T_R = 0.56$ and $T_R = 0.72$.

Tables 2 and 3 can be used with the normal boiling point and normal latent heat of vaporization (which are both usually readily available) to calculate the values of ω and x for a polar fluid. Values of ω and x were calculated in this manner for seventeen polar fluids (*10*). The average deviation in the vapor pressure without the polar correction at $T_R = 0.6$ for the substances considered was 6.1%, while with the polar correction the average deviation was only 0.6%.

Equation (7) can also be used with the tabulated values of $\Delta S^{(0)}$, $\Delta S^{(1)}$, and $\Delta S^{(2)}$ to calculate the latent heat of vaporization of polar fluids in the region $0.56 \leqq T_R \leqq 0.72$. Values of the heat of vaporization at the normal boiling point were calculated for thirteen polar fluids (*10*) with parameters ω and x established from two vapor pressure points for each substance. The average deviation between the experimental heat of vaporization and the calculated value without the polar correction was 4.0%, while with the polar correction the average deviation was 0.8%.

DISCUSSION OF RESULTS

As predicted by Pitzer's theoretical development, the deviations from normal fluid behavior are small for slightly polar substances such as halogenated hydrocarbons. The results of the present investigation indicate that a substance can be considered to be a normal fluid if $|x| <$

0.005. The present criterion for a normal fluid is preferable to that using Equation (4), since the procedure for calculating the constants σ_o and v_o is not clearly established for polar fluids.

It can be seen from Table 1 that several of the polar fluids have negative values of the polarity factor x. These negative values do not have physical significance but arise directly from the definition of ω in Equation (1). The restriction of $(\log P_R)^{(2)}$ to be zero for $0.7 \leq T_R \leq 1.0$ means that the value of ω obtained from Equation (1) for a polar fluid includes polarity effects. An alternate definition of the polarity parameter could be employed in which $\log P_R{}^{(2)}$ is not zero for this region, and two vapor pressure points could be used for a polar fluid to establish the corresponding values of the acentric and polarity factors. However, from Equations (5) and (6), the new value of the polarity factor x' is related to x by

$$x' = x \bigg/ \left[(\log P_R)^{(2)'}\Big|_{T_R=0.6} - \frac{(\log P_R)^{(2)'}\Big|_{T_R=0.7}}{(\log P_R)^{(1)}\Big|_{T_R=0.6}} \right] \quad (8)$$

where $(\log P_R)^{(2)'}$ is the new value of the polar correction term. Since x can be positive or negative, x' can also change sign independent of the definition of the $(\log P_R)^{(2)'}$ terms. Therefore, negative values of the polarity factor cannot be avoided unless an alternate definition of ω for normal fluids is used and different values of the functions $(\log P_R)^{(0)}$ and $(\log P_R)^{(1)}$ are established. The procedure used in the present investigation for the calculation of ω and x does not inhibit the extension of this approach to other thermodynamic properties, and it has the advantages that the normal fluid functions obtained by Pitzer and co-workers can be employed directly and that no polar correction is required for the vapor pressure for $T_R > 0.7$.

Although ω and x are basically empirical parameters, the theoretical considerations (*7*, *17*) indicate that the polarity factor x should be related to the reduced dipole group. However, no correlation was found when values of x were plotted against this parameter, because the dipole moments of a number of the substances are imbedded in the molecules (*7*). Also, the force constants for the analogous intermolecular potential function are not available, and approximate values of the dipole group reduced with critical constants had to be used.

The use of four parameters for polar fluids corresponds to an intermolecular potential function in which dispersion and dipole-dipole interaction effects are accounted for. For polar molecules other effects such as dipole-induced dipole, dipole-quadrupole, and quadrupole-quadrupole interactions may be present. The inclusion of these effects would require additional parameters for the thermodynamic properties of polar fluids. However, the use of only a fourth parameter provides considerable improvement for polar fluids over the three-parameter correlations of Pitzer and co-workers and of Hall and Ibele (*9*).

The fourth parameter approach developed in this investigation will be extended to other thermodynamic properties of polar fluids and mixtures.

ACKNOWLEDGMENT

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NOTATION

a = shape parameter for Kihara potential
b = reduced dipole group for Stockmayer potential
B = second virial coefficient, cc./g.-mole
ΔH = latent heat of vaporization, cal./(g.-mole) (°K.)
P_R = reduced vapor pressure
ΔS = entropy of vaporization, cal./g.-mole
T = temperature, °K.
T_B = Boyle temperature, °K.
T_c = critical temperature, °K.
T_R = reduced temperature, T/T_c
v_B = Boyle volume, cc./g.-mole
v_o = hypothetical volume of a liquid at absolute zero, cc./g.-mole
x = polarity factor as defined in Equation (6)
z = compressibility factor
σ_o = hypothetical surface tension at absolute zero, dynes/cm.
ω = acentric factor defined in Equation (1)

Subscripts and Superscripts

n = normal fluid
(0) = simple fluid function
(1) = normal fluid correction term
(2) = polar fluid correction term

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