Compressibility Factor of Polar Fluids in the Gaseous and Liquid Regions

The tables of Pitzer et al. for the compressibility factor of nonpolar substances have been extended to polar fluids for the gaseous and liquid regions for reduced temperatures from 0.8 to 1.15 and reduced pressures from 0.2 to 6.0. Available experimental PVT data for polar fluids were related to the acentric factor and fourth parameter at constant reduced temperature and pressure by a quadratic least squares procedure. The resulting relationships reproduced the data utilized with good accuracy for the entire region considered.

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SCOPE

Accurate values of the compressibility factor and derived thermodynamic properties of pure fluids and mixtures are required in many important applications, such as for the calculation of efficiencies of Rankine cycles. Procedures are available for the accurate calculation of these properties for nonpolar substances. Experimental PVT data have recently been obtained for several alcohols in the dense gaseous and liquid regions. In the present study, the available data for the compressibility factor of polar fluids have been utilized to develop generalized relationships for this property for the gaseous and liquid regions.

CONCLUSIONS AND SIGNIFICANCE

The compressibility factor of polar fluids has been expressed as

$$z = z^{(0)} + \omega z^{(1)} + x z^{(2)} + \omega x z^{(3)} + x^2 z^{(4)} \qquad \text{(I)}$$

where the parameters ω and x are defined through the vapor pressure, and $z^{(0)}$ and $z^{(1)}$ have been previously determined for nonpolar fluids. In this study, values of the polar fluid correction terms $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ were established for the gaseous and liquid regions for reduced temperatures from 0.8 to 1.15 and reduced pressures from 0.2 to 6.0. Available experimental PVT data for polar fluids were related to ω and x at constant T_R and P_R by a quadratic least squares procedure. Fine grid values of the functions were determined for P_R from 1.0 to 2.0 and T_R from 0.98 to 1.10.

In general, the tabulated functions reproduce the experimental compressibility factors utilized with an accuracy comparable to that obtained by this procedure for nonpolar fluids. Additional PVT data for acetone at elevated pressures in the gaseous and liquid regions were also compared with the values calculated by the method of this study, and an average deviation of under 1.0% resulted. The method of this study enables the accurate calculation of compressibility factors for polar fluids with ranges of parameters $0 < \omega < 0.65$ and $-0.06 < x < 0.04$.

For dilute polar gases, Hall and Ibele (1954) presented a correlation for the compressibility factor in which the reduced dipole group $\mu^2/T_c v_c$ is the third parameter. Eubank and Smith (1962) extended the correlations of Pitzer et al. (1955) for nonpolar fluids to the thermodynamic properties of dilute polar gases by the use of a fourth parameter involving the reduced dipole group. This approach requires a value of the shape parameter for an appropriate nonpolar substance having the same size as the polar fluid and is primarily restricted to organic substances.

For an intermolecular potential model for polar fluids consisting of the Kihara spherical core potential extended with a term for dipole-dipole interactions, the compressibility factor can be expressed in dimensionless form as

$$z = f\left(\frac{T}{\epsilon/\kappa}, \frac{P{\rho_0}^3}{T}, a^*, y\right) \qquad (1)$$

where a^* and y are the shape and polarity groups of the potential function. The molecular parameters of Equation (1) can be related to the macroscopic parameters T_c, P_c, ω, and x (Stiel, 1968, 1972). When these substitutions are made, the following generalized relationship results for the compressibility factor

$$z = g(T_R, P_R, \omega, x) \qquad (2)$$

The parameters ω and x are defined as (Pitzer, 1955; Halm and Stiel, 1967),

$$\omega = -\log \frac{P_s}{P_c}\Bigg|_{T_R=0.7} - 1.00 \qquad (3)$$

$$x = \log \frac{P_s}{P_c}\Bigg|_{T_R=0.6} + 1.70\omega + 1.552 \qquad (4)$$

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Although the effects of shape and polarity are not segregated by these definitions, ω and x are related by more complicated definitions to macroscopic parameters which follow realistic trends with the complexity of the molecules (Peng and Stiel, 1971). The definitions of Equations (7) and (8) have the advantage that most properties for slightly polar substances (approximately with $|x| < 0.005$), can be considered to follow the normal fluid behavior exhibited by nonpolar substances.

Equation (2) can be expanded in a quadratic Taylor series as

$$z = z^{(0)} + \omega z^{(1)} + x z^{(2)} + \omega x z^{(3)} + x^2 z^{(4)} + \omega^2 z^{(5)} \quad (5)$$

where $z^{(0)}, z^{(1)}, \ldots z^{(5)}$ are functions of reduced temperature and pressure. For nonpolar fluids, Pitzer et al. (1955) determined values of $z^{(0)}$ and $z^{(1)}$ from experimental PVT data for reduced temperatures from 0.8 to 4.0 and reduced pressures from 0.2 to 9.0. The use of a linear relationship in ω is strictly correct for substances with small values of this parameter. However, experimental compressibility factors for ethyl alcohol, for which ω is large and x is approximately zero, were found to essentially follow the linear normal fluid relationship in the dense gaseous region (Lo and Stiel, 1969). The use of a linear relationship in ω and x was also found to be valid for polar substances with moderate values of these parameters, but the PVT data for methyl alcohol (Finkelstein and Stiel, 1970) and isopropyl alcohol (Tseng and Stiel, 1971) indicated that the $z^{(3)}$ and $z^{(4)}$ functions are required for substances with large values of ω and x.

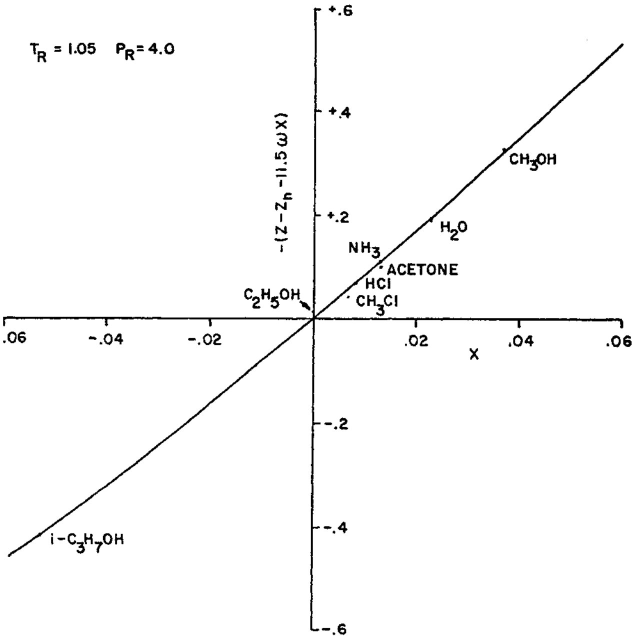

Fig. 1. Correlation for z of polar fluids at $T_R = 1.05$, $P_R = 4.0$.

In this study, experimental PVT data for a number of polar fluids have been utilized to determine the values of the polar correction terms of Equation (5) for the dilute gaseous, dense gaseous, and liquid regions for reduced pressures from 0.2 to 6.0 and reduced temperatures from 0.8 to 1.15. The substances are listed in Table 1 along with the critical constants and values of ω and x employed. The sources of the PVT data for each region are included in Table 2. For some of the references, the data were analyzed by graphical and least squares methods. At conditions for which more than one reference was available for a particular substance, the value of z was selected which gave best consistency with the data for the other substances.

TABLE 1. VALUES OF T_c, P_c, ω, x FOR POLAR FLUIDS

Substance	T_c	P_c	ω	x
Water	647.3	218.2	0.344	0.023
Ammonia	406.0	112.3	0.252	0.013
Methyl chloride	416.3	65.9	0.152	0.007
Methyl alcohol	513.2	78.5	0.556	0.037
Ethyl alcohol	514.0	60.5	0.641	0.0
n-propyl alcohol	536.7	51.0	0.626	−0.057
i-propyl alcohol	508.4	47.0	0.663	−0.053
Methyl fluoride	317.8	58.0	0.191	0.012
Ethylene oxide	468.9	71.0	0.207	0.012
Hydrogen chloride	324.6	81.5	0.126	0.008
Acetone	508.7	46.6	0.304	0.013

TABLE 2. SOURCES OF PVT DATA AND AVERAGE % ERRORS FOR POLAR FLUIDS

	Gaseous			Liquid		
Substance	Sources	No. of points	Avg. % error	Sources	No. of points	Avg. % error
Water	Holser and Kennedy (1962), Meyer et al. (1967)	93	1.00	Meyer et al. (1967)	81	1.07
Ammonia	Din (1962)	93	0.85	Din (1962)	81	1.29
Methyl chloride	Hsu and McKetta (1964)	85	1.60	Hsu and McKetta (1964)	81	2.27
Methyl alcohol	Bhattacharyya and Thodos (1964), Finkelstein and Stiel (1970), Smith (1948), Zubarev and Bagdonas (1967)	89	0.98	Finkelstein and Stiel (1970), *Intern. Critical Tables* (1928)	81	1.15
Ethyl alcohol	Bhattacharyya and Thodos (1965), Lo and Stiel (1969), Reid and Smith (1951)	47	2.32	*Intern. Critical Tables* (1928), Lo and Stiel (1969)	81	2.16
n-Propyl alcohol	Martin et al. (1963)	29	1.51	*Intern. Critical Tables* (1928)		*
i-Propyl alcohol	Tseng and Stiel (1971)	64	1.06	Tseng and Stiel (1971)	81	1.27
Methyl fluoride	Michels et al. (1952)	20	1.36			
Ethylene oxide	Walters and Smith (1952)	9	1.01			
Hydrogen chloride	Franck et al. (1962)	47	0.95			

* Low temperature data for *n*-propyl alcohol used to obtain interpolated values for iso-propyl alcohol.

GASEOUS REGION

Some deviations of the compressibility factor of ethyl alcohol from the linear normal fluid relationship were detected for the dilute gaseous region, including the critical point, when the critical constants utilized previously for this substance (Kobe and Lynn, 1953) were employed. However, by the use of the more recent critical constants determined by Skaates and Kay (1964), compressibility factors of ethyl alcohol could be calculated with good accuracy from the normal fluid relationship for the dilute gaseous region, while somewhat larger deviations resulted at higher pressures (with a maximum error of approximately 5%). Since the effect of $z^{(5)}$ in Equation (5) should be more pronounced at high pressures, the new critical constants and corresponding values of ω and x were utilized in this study. The inclusion of the $z^{(5)}$ term undoubtedly results in best accuracy for a wide group of polar substances, but because good results were generally obtained with the simpler relationship, this term was taken as zero. It was found that when the coefficient of ω^2 was included in Equation (5) the values of $z^{(4)}$ were smaller, while $z^{(2)}$ and $z^{(3)}$ remained essentially the same.

At constant reduced temperature and pressure, the experimental data were related to ω and x by a quadratic least squares procedure. The values of $z^{(0)}$ and $z^{(1)}$ were taken as those determined by Pitzer et al. (1955) for normal fluids. For most of the dilute gaseous region the polar substances essentially follow normal fluid behavior.

TABLE 3. VALUES OF $z^{(2)}$ FOR POLAR FLUIDS

				T_R				
P_R	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0.2		−0.02	−0.315	−0.53	−0.50	−0.32	−0.25	−0.15
0.4	−0.925	−0.97	−1.575	−1.25	−1.00	−0.69	−0.55	−0.40
0.6	−1.41	−1.43	−1.19	−1.75	−1.47	−1.05	−0.85	−0.60
0.8	−1.82	−1.875	−1.81	−1.69	−1.90	−1.42	−1.15	−0.87
1.0	−2.17	−2.37	−2.43	−2.35	−2.35	−1.775	−1.50	−1.18
1.2	−2.73	−2.71	−2.65	−2.59	−2.73	−2.32	−1.85	−1.50
1.4	−3.15	−3.13	−3.09	−3.02	−3.25	−2.75	−2.25	−1.82
1.6	−3.55	−3.54	−3.53	−3.51	−3.50	−3.375	−2.65	−2.30
1.8	−3.94	−3.95	−3.97	−3.98	−3.91	−3.925	−3.20	−2.82
2.0	−4.39	−4.32	−4.29	−4.29	−4.30	−4.35	−3.80	−3.43
2.2	−4.77	−4.72	−4.73	−4.75	−4.69	−4.76	−4.55	−4.18
2.4	−5.16	−5.12	−5.14	−5.18	−5.10	−5.19	−5.23	−5.10
2.6	−5.53	−5.53	−5.57	−5.60	−5.49	−5.54	−5.58	−5.80
2.8	−5.93	−5.92	−5.97	−6.02	−5.88	−5.96	−6.07	−6.20
3.0	−6.25	−6.40	−6.47	−6.42	−6.28	−6.31	−6.45	−6.60
3.2	−6.73	−6.72	−6.79	−6.85	−6.64	−6.75	−6.84	−7.00
3.4	−7.14	−7.14	−7.22	−7.275	−7.09	−7.14	−7.22	−7.40
3.6	−7.59	−7.54	−7.60	−7.66	−7.35	−7.51	−7.59	−7.80
3.8	−8.05	−7.95	−8.00	−8.07	−7.75	−7.95	−7.98	−8.20
4.0	−8.50	−8.39	−8.43	−8.49	−8.18	−8.34	−8.40	−8.60
5.0	−11.21	−10.72	−10.55	−10.52	−10.18	−10.33	−10.44	−10.64
6.0	−14.80	−13.47	−12.80	−12.80	−12.18	−12.33	−12.46	−12.66

TABLE 4. VALUES OF $z^{(3)}$ FOR POLAR FLUIDS

				T_R				
P_R	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0.2		0.11	0.35	0.60	0.80	0.90	1.00	1.10
0.4	1.24	1.35	0.85	1.08	1.42	1.65	1.80	1.90
0.6	1.925	2.00	1.81	1.66	2.10	2.30	2.50	2.59
0.8	2.66	2.48	2.45	2.53	2.70	2.97	3.15	3.22
1.0	3.14	3.22	3.28	3.34	3.30	3.50	3.67	3.85
1.2	3.91	3.70	3.60	3.63	3.83	4.08	4.20	4.40
1.4	4.48	4.29	4.21	4.24	4.45	4.60	4.75	4.90
1.6	4.96	4.93	4.92	4.96	4.95	5.15	5.30	5.46
1.8	5.46	5.53	5.58	5.62	5.50	5.68	5.80	5.95
2.0	6.09	6.04	6.03	6.05	6.07	6.20	6.30	6.42
2.2	6.62	6.58	6.62	6.68	6.58	6.70	6.85	7.05
2.4	7.18	7.11	7.16	7.26	7.10	7.35	7.40	7.55
2.6	7.62	7.77	7.85	7.82	7.65	7.78	7.90	8.10
2.8	8.27	8.22	8.305	8.395	8.10	8.30	8.45	8.66
3.0	8.72	8.89	8.99	8.95	8.67	8.72	9.00	9.16
3.2	9.38	9.36	9.46	9.55	9.24	9.38	9.51	9.71
3.4	9.98	9.93	10.02	10.115	9.73	9.87	10.05	10.25
3.6	10.58	10.52	10.615	10.70	10.36	10.44	10.55	10.78
3.8	11.24	11.11	11.17	11.25	10.80	10.95	11.10	11.30
4.0	11.93	11.71	11.74	11.82	11.31	11.50	11.60	11.83
5.0	15.93	15.07	14.75	14.64	13.94	14.15	14.30	14.50
6.0	21.31	19.19	18.06	17.49	16.67	16.80	17.00	17.20

For example, for water at $T_R = 1.00$, the deviation from the normal fluid relationship is 2.95% at $P_R = 0.8$, 21.2% at $P_R = 2.0$, and 28% at $P_R = 6.0$. The values of the polar correction terms at $P_R = 0.2$ were determined with the aid of second virial coefficient data.

The functions $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ were smoothed by graphical and analytical methods, and the resulting values are presented in Tables 3, 4, and 5 for even intervals of reduced temperature and pressure. For the gaseous region, the values of $z^{(2)}$ approach zero with increasing temperature at low reduced pressures and are essentially constant at higher reduced pressures. The values of $z^{(3)}$ are almost independent of temperature at constant reduced pressure, and above $P_R = 2.0$ the variation with P_R at constant T_R is virtually linear. At low reduced pressures the values of $z^{(4)}$ increase with increasing temperature. This effect is possibly due to the slight decomposition of some of the organic substances, such as the alcohols, in this region.

FINE GRID AND SATURATED VAPOR REGIONS

Pitzer, et al. (1955) determined fine grid values of $z^{(0)}$ and $z^{(1)}$ for the gaseous region for reduced pressures between 1.0 and 2.0, for which region the variation of z with T_R at constant P_R is s-shaped. Fine grid values of the polar correction terms are presented in Table 6. The func-

Table 5. Values of $z^{(4)}$ for Polar Fluids

	T_R							
P_R	0.80	0.85	0.90	0.95	1.00	1.05	1.10	1.15
0.2		−11.30	−9.45	−7.30	−2.90	2.30	2.40	4.05
0.4	0.89	1.96	−8.55	−6.50	−2.78	4.40	5.00	7.55
0.6	0.83	2.30	4.11	−6.10	−2.50	6.20	7.40	10.37
0.8	0.81	2.52	4.20	6.00	−2.20	7.50	9.58	12.78
1.0	0.82	2.63	4.16	5.86	−0.63	7.15	11.50	14.45
1.2	0.845	2.65	4.00	5.51	1.50	4.20	13.10	15.50
1.4	0.88	2.57	3.74	5.00	2.00	1.80	13.60	15.80
1.6	0.92	2.43	3.40	4.345	1.90	−0.30	12.85	15.40
1.8	0.96	2.22	2.98	3.59	1.50	−2.10	11.20	14.40
2.0	0.98	1.97	2.51	2.76	1.00	−3.40	7.50	12.50
2.2	0.99	1.67	1.98	1.87	0.20	−4.50	1.80	8.50
2.4	0.98	1.34	1.42	0.96	−0.60	−5.40	−2.50	−0.20
2.6	0.94	0.99	0.83	0.04	−1.50	−6.10	−5.60	−5.40
2.8	0.88	0.62	0.22	−0.855	−2.30	−6.80	−7.80	−8.80
3.0	0.79	0.25	−0.39	−1.73	−3.10	−7.40	−9.20	−11.30
3.2	0.67	−0.13	−1.00	−2.56	−3.80	−8.10	−10.40	−12.60
3.4	0.53	−0.50	−1.59	−3.35	−4.47	−8.70	−11.30	−13.20
3.6	0.36	−0.87	−2.17	−4.05	−5.18	−9.37	−12.10	−13.90
3.8	0.16	−1.22	−2.73	−4.69	−5.85	−10.00	−12.77	−14.60
4.0	−0.05	−1.56	−3.25	−5.265	−6.55	−10.60	−13.40	−15.26
5.0	−1.22	−2.60	−5.20	−7.08	−10.00	−13.85	−16.70	−18.60
6.0	−1.80	−3.89	−5.75	−7.945	−13.40	−17.00	−20.00	−22.00

Table 6. Values of Functions for Fine Grid Region

	T_R												
P_R	0.98	0.99	1.00	1.01	1.02	1.03	1.04	1.05	1.06	1.07	1.08	1.09	1.10
							$z^{(2)}$						
1.0	−2.25	−2.21	−2.35	−2.15	−2.02	−1.91	−1.85	−1.775	−1.725	−1.65	−1.60	−1.55	−1.50
1.2	−2.54	−2.53	−2.73	−2.65	−2.57	−2.47	−2.40	−2.32	−2.225	−2.15	−2.06	−1.975	−1.85
1.4	−2.97	−2.95	−3.25	−3.07	−2.98	−2.88	−2.825	−2.75	−2.65	−2.55	−2.45	−2.35	−2.25
1.6	−3.50	−3.50	−3.50	−3.58	−3.575	−3.55	−3.475	−3.375	−3.24	−3.10	−2.95	−2.78	−2.65
1.8	−3.99	−4.00	−3.91	−4.05	−4.10	−4.075	−4.02	−3.925	−3.80	−3.70	−3.50	−3.35	−3.20
2.0	−4.31	−4.32	−4.30	−4.40	−4.44	−4.44	−4.40	−4.35	−4.25	−4.15	−4.05	−3.925	−3.80
							$z^{(3)}$						
1.0	3.38	3.39	3.30	3.32	3.37	3.40	3.44	3.50	3.53	3.56	3.60	3.64	3.67
1.2	3.70	3.74	3.83	3.88	3.92	3.95	4.00	4.08	4.08	4.10	4.14	4.17	4.20
1.4	4.30	4.33	4.45	4.47	4.50	4.52	4.55	4.60	4.62	4.65	4.67	4.70	4.75
1.6	4.99	5.01	4.95	5.00	5.04	5.07	5.10	5.15	5.17	5.20	5.25	5.27	5.30
1.8	5.63	5.64	5.50	5.54	5.56	5.60	5.63	5.68	5.69	5.71	5.75	5.77	5.80
2.0	6.075	6.08	6.07	6.09	6.11	6.13	6.16	6.20	6.21	6.25	6.27	6.29	6.30
							$z^{(4)}$						
1.0	6.925	6.78	−0.63	1.80	3.60	4.925	6.10	7.15	8.10	9.00	9.80	10.70	11.50
1.2	6.99	6.59	1.50	1.20	1.60	2.20	3.10	4.20	5.70	7.30	9.10	11.00	13.10
1.4	6.79	6.425	2.00	1.10	0.50	0.45	0.90	1.80	3.20	5.10	7.50	10.35	13.60
1.6	6.32	6.18	1.90	−0.45	−1.40	−1.60	−1.20	−0.30	1.00	2.95	5.40	8.70	12.85
1.8	5.56	5.75	1.50	−1.90	−3.50	−3.80	−3.27	−2.10	−0.78	1.30	3.90	7.20	11.20
2.0	4.52	5.03	1.00	−3.30	−4.60	−4.80	−4.40	−3.40	−2.10	−0.50	1.80	4.40	7.50

Table 7. Values of Polar Correction Terms for the Saturated Vapor

T_R	$z^{(2)}$	$z^{(3)}$	$z^{(4)}$
0.80	−2.10	2.45	−16.70
0.82	−2.095	2.50	−16.55
0.84	−2.09	2.55	−16.30
0.86	−2.085	2.60	−16.00
0.88	−2.08	2.65	−15.60
0.90	−2.075	2.70	−15.20
0.92	−2.07	2.75	−14.68
0.94	−2.075	2.80	−14.10
0.96	−2.14	2.92	−13.10
0.98	−2.18	3.10	−10.00
0.99	−2.28	3.20	−7.20

tions were difficult to smooth at $P_R = 1.2$ and 1.4, for which conditions the data for alcohols are sparse. The errors for ethyl alcohol were also somewhat larger at some points in this region, which may be due to slight errors in the $z^{(1)}$ values. Experimental PVT data for *n*-heptane (Smith et al. 1937) indicate that a ω^2 term should be included in this region for nonpolar fluids with large values of ω. Because of the decomposition of the organic substances at high temperatures, the polar correction terms for the group of fluids considered could not be determined for reduced temperatures greater than 1.15. For most inorganic substances such as water and ammonia the variation of $z - z_n$ is linear with x for higher reduced temperatures.

For saturated polar vapors, Halm and Stiel (1970) presented values of $z^{(2)}$ for reduced temperatures from 0.70 to 0.98. In order to provide relationships for the same group of substances considered in this study, the data utilized by Halm and Stiel were related to ω and x by the quadratic least squares procedure. The resulting values of $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ are presented in Table 7 for reduced temperatures from 0.80 to 0.99. Values of $z^{(0)}$ and $z^{(1)}$ for the saturated vapor are presented by Pitzer et al. (1955).

LIQUID REGION

For ethyl alcohol (Lo and Stiel, 1969), methyl alcohol (Finkelstein and Stiel, 1970), and iso-propyl alcohol (Tseng and Stiel, 1971), experimental data were recently obtained for the liquid region only for temperatures above 200°C, corresponding to a minimum reduced temperature of approximately 0.92 for these substances. Additional PVT data are available for alcohols at elevated pressures and low temperatures to 80°C (*International Critical Tables*, 1928). In the liquid region, the variation of z with P_R at constant T_R is virtually linear. Therefore, the available PVT data for the alcohols were utilized to obtain quadratic relationships between z and P_R for 0.02 intervals of T_R. For iso-propyl alcohol, no low temperature data are available, but the data for *n*-propyl alcohol, which has approximately the same values of ω and x, were employed. Values of z for the saturated liquid were included in the development of the relationships. The three coefficients of the quadratic equations were then related to T_R by a least squares procedure. The resulting relationships were then utilized to obtain interpolated values of z from $T_R = 0.80$ to 1.00. It was found that the calculated values of z for the saturated liquid for this range agreed closely with the experimental data.

The calculated values of z for the alcohols were utilized in conjunction with data for water, ammonia, and methyl chloride to obtain the coefficients $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ included in Tables 3, 4, and 5 for the liquid region for T_R from 0.8 to 1.00 and P_R from 0.2 to 6.0. Fine grid values for $T_R = 0.98$ and 0.99 and P_R from 1.0 to 2.0 are presented in Table 6. For saturated polar liquids, Halm and Stiel (1970) determined quadratic relationships between $P_c v / R\, T_c$ and ω and x, for $T_R = 0.56$ to 1.00.

The values of $z^{(2)}$ and $z^{(3)}$ are quite constant with reduced temperature at constant reduced pressure for the liquid region. The values of $z^{(4)}$ are in general smaller for the liquid than for the gaseous region. The deviations were somewhat larger for ethyl alcohol in the vicinity of the critical point, which may again be due to the requirement of an ω^2 term for this region. At low pressures in the liquid region the values of z are small, and the quantity $P_c v / R\, T_c$ is more sensitive to the variation of the volume with temperature and pressure.

ERROR ANALYSIS

In Table 2, average percent errors between the interpolated experimental compressibility factors and those calculated with the smoothed correction terms for the T_R and P_R intervals of Tables 3 to 5 are presented for the dilute gaseous, dense gaseous, and liquid regions, along with the numbers of points included for each substance. It can be seen that good results were obtained for all the substances. For $P_R \geqq 1.8$, the tabulated functions reproduce the compressibility factors of each substance at every point considered for the gaseous and liquid regions with a maximum deviation of 4% (with the exception of the slightly higher deviations for ethyl alcohol in the dense gaseous region mentioned above). At these pressures the deviations from normal fluid behavior are large for most of the substances. For the saturated vapor region, the maximum average deviation for the substances considered was 1.21% at $T_R = 0.90$.

In order to check the accuracy of the method of this study for other polar fluids, experimental PVT data were obtained for acetone with a constant volume apparatus for the dense gaseous and liquid regions for temperatures from 180° to 265°C and pressures from 1000 to 6000 lb./sq.in. (Keller, 1971). For the gaseous region, interpolated values of z for acetone at $T_R = 1.0$ and $P_R = 2.0$, 3.0, 4.0, 5.0, and 6.0, and at $T_R = 1.05$ and $P_R = 3.0$, 4.0, 5.0, and 6.0, were compared with the values calculated from Equation (5). At $T_R = 1.00$, the maximum deviation was 0.83% at $P_R = 6.0$ with an average deviation of 0.38% for the five points. The use of the normal fluid relationship for acetone resulted in an average deviation of 13.4% for the same points. At $T_R = 1.05$, the maximum deviation was 0.70% at $P_R = 4.0$, with an average deviation of 0.40% for the four points and an average deviation of 13.7% for the normal fluid relationship. In Figure 1 the quantity $z - z_n - z^{(3)} \omega\, x$ at $T_R = 1.05$ and $P_R = 4.0$ is plotted against x for acetone and the polar fluids included in the least squares analysis.

For the liquid region at $T_R = 0.95$ and $P_R = 2.4$, 3.0, 4.0, 5.0, and 6.0, experimental compressibility factors for acetone were compared with values calculated from Equation (5) and Tables 3 to 5. The average deviation between calculated and experimental values was 1.05%, and 14.3% for values calculated from the normal fluid relationship. Compressibility factors determined from PVT data for hydrogen chloride (Thomas, 1962) were also compared with values calculated from Equation (5) for $T_R = 0.90$ and $P_R = 1.00$, 1.60, 1.80, 2.40, and 3.00. The average deviation was 0.33% for the five points compared to 10.35% for the normal fluid relationship.

DISCUSSION

The relationships of this study enable the accurate calculation of the compressibility factor of polar fluids for the gaseous and liquid regions. The class of fluids for which these relationships are applicable are those whose properties can be characterized by four molecular parameters, including shape and polarity groups. It has been found that a convenient method to estimate ω and x for these substances is through the normal boiling point with the tabulated vapor pressure functions (Halm and Stiel, 1967), and the relationship obtained in this study for z_c:

$$z_c = 0.291 - 0.08\omega - 2.35x + 3.30\omega x - 0.63x^2 \quad (6)$$

An attempt was made to determine the coefficients of the quadratic relationship for z by the use of alternate parameters ω' and x' (Peng and Stiel, 1971) which allow for some separation of shape and polarity effects. This approach has the advantage that ω' is smaller for polar fluids, and thus the ω'^2 term has much less effect. This approach worked well for $P_R < 2.0$, and the functions were easier to smooth, particularly for the dilute gaseous region. However, at higher reduced pressures, the deviations from the linear normal fluid equations were so large that relationships for z of higher order than quadratic were indicated, and the deviations between calculated and experimental compressibility factors for acetone were larger for this procedure.

In order to obtain accurate values of the polar correction terms for the class of fluids considered in this study, data must be included for substances with large positive or negative values of x, such as methyl alcohol and isopropyl alcohol. Therefore, the functions $z^{(2)}$, $z^{(3)}$, and $z^{(4)}$ could not be determined for $T_R > 1.15$. At high reduced temperatures in the gaseous region some decomposition of the organic substances may have affected the values of these functions, particularly the coefficients of x^2 which were difficult to smooth. Thus the functions may not completely represent the effects of molecular interactions for this region, but the calculated compressibility factors should be those that are required for real design conditions.

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NOTATION

a^* = shape group for spherical core potential for polar fluids
P = pressure, atm.
P_c = critical pressure, atm.
P_s = vapor pressure, atm.
P_R = reduced pressure, P/P_c
R = gas constant, 1.987 cal/g mole °K
T = temperature, °K
T_c = critical temperature, °K
T_R = reduced temperature, T/T_c
v = volume, cc/g mole
v_c = critical volume, cc/g mole
x = fourth parameter, defined in Equation (4)
y = polarity group for spherical core potential for polar fluids
z = compressibility factor, Pv/RT
$z^{(0)}, z^{(1)}, \ldots, z^{(5)}$ = normal and polar fluid correction terms of Equation (5)
z_c = critical compressibility factor, $P_c v_c/RT_c$

Greek Letters

ϵ/κ = energy group for spherical core potential, °K
μ = dipole moment, Debyes
ρ_0 = distance parameter of spherical core potential
ω = acentric factor, defined in Equation (3)

Subscripts

n = normal fluid

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Solubilities of Gases in Water and Other Associated Solvents

A method for estimating the effect of hydrogen-bonding on gas solubilities in polar solvents is presented. H-bonding factors, which are based on ideal gas solubilities and solubilities in water, appear to be closely related to H-bonding factors in the simple alcohols. Similarly, H-bonding factors in solvents containing a carbonyl group or dihydroxy groups were related to those in acetone. The relation between the various H-bonding factors can be used to estimate solubilities in these and other associated solvents.

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SCOPE

Equilibrium solubilities of gases in polar, associating solvents are frequently required in the design of absorption equipment. Methods which can be used to predict gas solubilities in nonpolar or regular solutions are not successful in polar, associating solvents such as water or alcohols. A systematic approach has been developed to relate the effect of association or H-bonding on gas solubilities.

Solubilities of 20 gases in water and in six other solvents (when available) were selected from the literature. H-bonding factors were defined for each gas based on the ratio of its actual solubility to its ideal solubility. A large reduction in solubility from the ideal solubility was attributed to strong H-bonds in the solvent. H-bonding factors in one solvent, such as water, were examined to determine if they were related to H-bonding factors in other associating solvents.

CONCLUSIONS AND SIGNIFICANCE

H-bonding factors for gases in water are related to those in the primary, normal alcohols but are essentially independent of H-bonding factors in chlorobenzene, a slightly polar solvent. Similarly, H-bonding factors in acetone are related to those in methyl acetate, acetic acid, and ethylene glycol. Except in those cases where the dissolved gas reacts chemically with the solvent, gas solubilities could be approximately predicted from the relation between H-bonding factors in the solvents, provided the solubility was known in at least one of them. It would appear that this simplistic approach may be used to estimate solubilities in other polar, associating solvents for nonreacting gases. It was also found that as for nonpolar solvents, solubilities of all gases in water tended toward a constant molar concentration at the solvent critical temperature.

Solubilities in water of many gases have been measured. They range in solute mole fraction from about 0.000007 for helium to about 0.3 for ammonia at 25°C. Whereas for nonpolar solvents a considerable degree of success has been achieved in explaining the order of gas solubilities and the variation with temperature, such success has largely eluded workers dealing with aqueous and similar solutions.