concentration of this certain component and relatively small weights are used for the other components. Furthermore, instead of the least squares criterion, any other criterion can also be used in the procedure discussed above.

An estimation problem with multipoint boundary value (3) in difference equations can also be solved by essentially the same approach. For example, it is frequently necessary to have a certain specified purity of a certain side stream. Since this side stream is located at a plate inside the column and not at the terminals, a multipoint boundary-value problem is formulated. Many other specifications of the conditions of a distillation column are possible (5). As we shall see in later papers, the present approach has certain distinct advantages over the conventional procedures for some of the specifications.

It should be emphasized that the problem formulated does not always have solution. For example, the specified purity of the end product must be within the capability of the specified column in order for a solution to exist. The estimation approach avoids this problem. This is because of the fact that the least squares criterion only demands a solution that is as near as possible to the desired one.

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The PVT Behavior of Isopropyl Alcohol at Elevated Temperatures and Pressures

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Experimental PVT data have been obtained for isopropyl alcohol by the use of a constant-volume apparatus. Smoothed values of the compressibility factor are presented for temperatures from 200° to 300°C. and pressures from 1,000 to 8,000 lb./sq. in. The experimental data are estimated to be accurate to within 0.1%. The compressibility factor of isopropyl alcohol is also analyzed by the fourth-parameter approach. It is shown that the normal fluid relationship for the compressibility factor can be extended to polar fluids by the inclusion of linear and quadratic terms in the fourth parameter.

Experimental volumetric data are not available for most polar fluids, particularly at elevated temperatures and pressures. In previous studies, PVT data have been obtained for methyl alcohol (3) and ethyl alcohol (*12*) for the dense gaseous and liquid regions. These data are useful for the development of a generalized relationship for the thermodynamic properties of polar fluids by an extended theorem of corresponding states.

No previous volumetric data are available for isopropyl alcohol at elevated temperatures in the dense gaseous and liquid regions. In addition, since this substance has a relatively low critical temperature, experimental PVT data can be obtained for higher reduced temperatures than for most other alcohols of large molecular size.

For isopropyl alcohol, Ambrose and Townsend (*1*) have reported critical constants, vapor pressure data, and densities of the saturated liquid and vapor to the critical point (235.25°C., 47.02 atm.). Moreland, McKetta, and Silberberg (*13*) have presented compressibility factors for gaseous isopropyl alcohol from 100° to 200°C. to pressures slightly below the vapor pressure at each temperature (maximum pressure 24.64 atm.). Smoothed compressibility factors were presented for this region, and second and third virial coefficients were determined. Second virial coefficients have also been reported by Cox (*2*), Foz, Morcillo, and Mendez (*4*), and Kretschmer and Wiebe (*8*). Moreland, McKetta, and Silberberg (*14*) also presented a table of derived thermodynamic properties for isopropyl alcohol for the range of their experimental investigation. Experimental PVT data were presented by Ramsay and Young (*15*) for *n*-propyl alcohol temperatures to 280°C. and pressures to 63 atm.

EXPERIMENTAL INVESTIGATION

The constant-volume apparatus described in detail elsewhere (*11, 12*) was utilized in the present study. A schematic diagram of the apparatus is presented in Figure 1. A liquid sample of a determined weight is injected into the evacuated constant-volume vessel, approximately 300 ml. in volume. The constant-temperature bath containing a high temperature heat transfer fluid is raised by a cable, pulley, and winch arrangement. The bath fluid is heated by external heaters which are controlled manually. The bath temperature is controlled to within 0.05°C. with a tubular heater inside the bath. The controller is initially set to the desired temperature, and when equilibrium is attained the temperature is measured with a special grade, protected chromel-alumel thermocouple in conjunction with a precision potentiometer. The thermocouple was calibrated with an accurate high temperature thermometer.

The pressure is measured with the use of a high temperature differential pressure indicator. The test fluid is confined on one side of a metallic diaphragm linked to an electrical transformer. The diaphragm is balanced with high pressure nitrogen, as indicated on a null-type control box. Fine adjustment of the nitrogen gas pressure is provided with a volumetric pressure controller. The nitrogen pressure is measured with a dead weight gauge. Additional measurements for the sample are conducted at approximately 10°C. intervals.

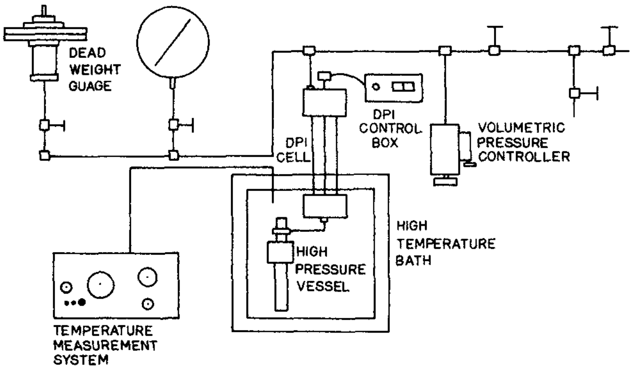

Fig. 1. Schematic diagram of apparatus.

The volume of the high pressure system, including the constant-volume vessel, lower chamber of the differential pressure indicator cell, and connecting tubing, was previously calibrated (*11*) from the known PVT behavior of nitrogen for temperatures from 200° to 350°C.

The isopropyl alcohol utilized in this investigation was Baker Instra-Analyzed grade, with a stated purity of better than 99.9%. The spectrophotometric analysis supplied by the manufacturer indicated that water, present at 0.02%, was the major impurity. No further purification was performed.

EXPERIMENTAL RESULTS

Thirty runs were made for isopropyl alcohol for temperatures from 200° to 300°C., pressures from 900 to 9,000 lb./sq. in., and densities from 0.15 to 0.70 g./cc. at increments of about 0.02 g./cc. No chemical reaction was detected for this range by an increase in pressure after thermal equilibrium had been attained.

In order to smooth the experimental data, for each constant mass run, a polynomial relationship between the

TABLE 1. SMOOTHED COMPRESSIBILITY FACTORS FOR ISOPROPYL ALCOHOL

Pressure, lb./sq.in.abs.	Temperature, °C. 200°	220°	240°	260°	280°	300°
1,000	0.1860	0.1909				
1,200	0.2203	0.2265	0.2467	0.2864		
1,400	0.2542	0.2612	0.2778	0.3109		
1,600	0.2877	0.2951	0.3085	0.3365	0.3802	
1,800	0.3209	0.3283	0.3393	0.3630	0.3994	0.4469
2,000	0.3538	0.3609	0.3701	0.3903	0.4210	0.4648
2,200	0.3863	0.3929	0.4008	0.4182	0.4445	0.4840
2,400	0.4185	0.4244	0.4316	0.4465	0.4695	0.5044
2,600	0.4504	0.4555	0.4623	0.4752	0.4955	0.5259
2,800	0.4820	0.4862	0.4929	0.5040	0.5221	0.5484
3,000	0.5133	0.5166	0.5234	0.5329	0.5491	0.5718
3,200	0.5444	0.5467	0.5537	0.5618	0.5764	0.5959
3,400	0.5751	0.5766	0.5838	0.5906	0.6036	0.6208
3,600	0.6057	0.6063	0.6136	0.6192	0.6308	0.6461
3,800	0.6359	0.6358	0.6431	0.6477	0.6578	0.6719
4,000	0.6660	0.6651	0.6722	0.6760	0.6845	0.6979
4,200	0.6958	0.6943	0.7009	0.7041	0.7111	0.7241
4,400	0.7254	0.7240	0.7291	0.7319	0.7375	0.7502
4,600	0.7549	0.7524	0.7569	0.7594	0.7637	0.7763
4,800	0.7841	0.7813	0.7842	0.7868	0.7899	0.8022
5,000	0.8132	0.8101	0.8110	0.8138	0.8159	0.8277
5,200	0.8420	0.8388	0.8375	0.8407	0.8420	0.8529
5,600	0.8994	0.8958	0.8894	0.8937	0.8944	0.9022
6,000	0.9562	0.9523	0.9409	0.9462	0.9473	0.9500
6,400	1.013	1.008	0.9931	0.9982	1.001	0.9968
6,800	1.069	1.063	1.048	1.050	1.054	1.044
7,200	1.124	1.116	1.109	1.102	1.106	1.093
7,600	1.180	1.167	1.178	1.153	1.154	1.147
8,000	1.235	1.216	1.260	1.205	1.196	1.210

pressure and temperature was obtained by a least squares procedure. Pressures were calculated from the resulting equations at temperatures from 200° to 300°C. in 10° increments. Polynomial relationships were then obtained between the compressibility factor and pressure for each temperature. Smoothed values of the compressibility factors of isopropyl alcohol obtained in this manner are presented in Table 1.

In Figure 2 isotherms of the compressibility factor for isopropyl alcohol are presented for 200° to 300°C. and pressures to 4,500 lb./sq. in. In Figure 3 a plot of pressure against specific volume at constant temperature is presented for the range investigated in this study.

An analysis of the combined experimental errors for temperature measurement, pressure measurement, and volume calibration indicates that the experimental compressibility factors for isopropyl alcohol should be accurate to approximately 0.4%. For the initial smoothing of the experimental data in which the pressure was related to temperature at constant mass, the average percent deviation between experimental and calculated pressures was under 0.1% for most of the runs.

DISCUSSION OF RESULTS

Halm and Stiel (5) have expressed the vapor pressure of a polar fluid as

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

where ω is Pitzer's acentric factor (9)

$$\omega = -\log P_R|_{T_R=0.7} - 1.000 \quad (2)$$

and the fourth parameter x is defined as

$$x = \log P_R|_{T_R=0.6} - \log P_{Rn}|_{T_R=0.6} = \log P_R|_{T_R=0.6} + 1.70\omega + 1.552 \quad (3)$$

Polar fluids of relatively large molecular size such as isopropyl alcohol have negative values of x. This is because only linear terms are used in the defining relationships, Equations (2) and (3), and the effects of shape and polarity are not separated.

For polar fluids in the dense gaseous region, Lo and Stiel (*12*) found that the compressibility factor is essentially linear in ω and x for ethyl alcohol, sulfur dioxide, methyl chloride, ammonia, and water, all of which have small values of x. However, the experimental compressibility factors for methyl alcohol which has a large value of x deviate from a linear relationship (3), indicating that higher order terms in x are also required in the relationship for the compressibility factor. These conclusions are confirmed by an examination of the isopropyl alcohol data of this study. It is shown in Figure 4 that at $T_R = 1.10$ and $P_R = 4.0$ the compressibility factor of isopropyl alcohol deviates considerably from the value from the linear polar fluid relationship. Since isopropyl alcohol has a large value of the product ωx, higher order terms in x must be included to obtain good results for this substance.

For the development of functions for the compressibility factor of polar fluids in the dense gaseous and liquid regions, accurate PVT data are available only for sulfur dioxide, water, ammonia, methyl chloride, methyl alcohol, ethyl alcohol, and isopropyl alcohol. Therefore in this study, the compressibility factors for these seven substances at $T_R = 1.05$ and $P_R = 4.0$ were related to ω and x as follows:

$$z = 0.580 - 0.14\omega - 7.43x - 11.9x^2 + 9.92\omega x \quad (4)$$

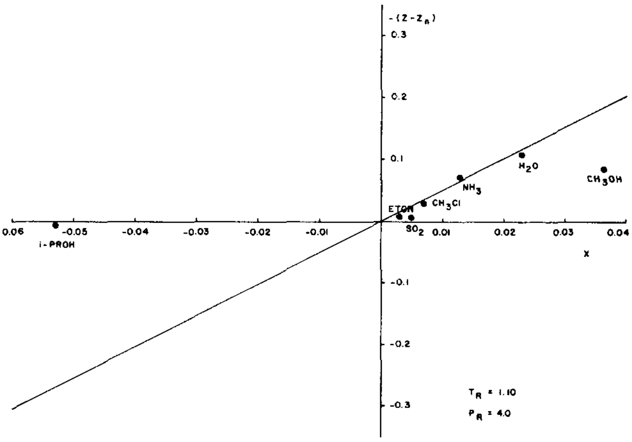

Fig. 4. Relationship between $-(Z\text{-}Z_n)$ and x for $T_R = 1.10$ and $P_R = 4.0$.

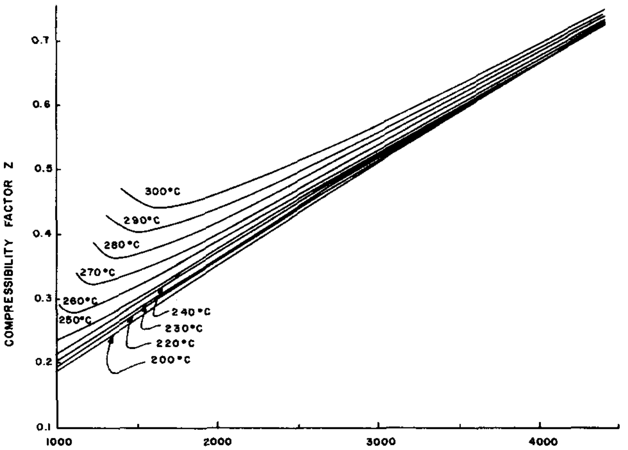

Fig. 2. Compressibility factor of isopropyl alcohol as a function of temperature and pressure.

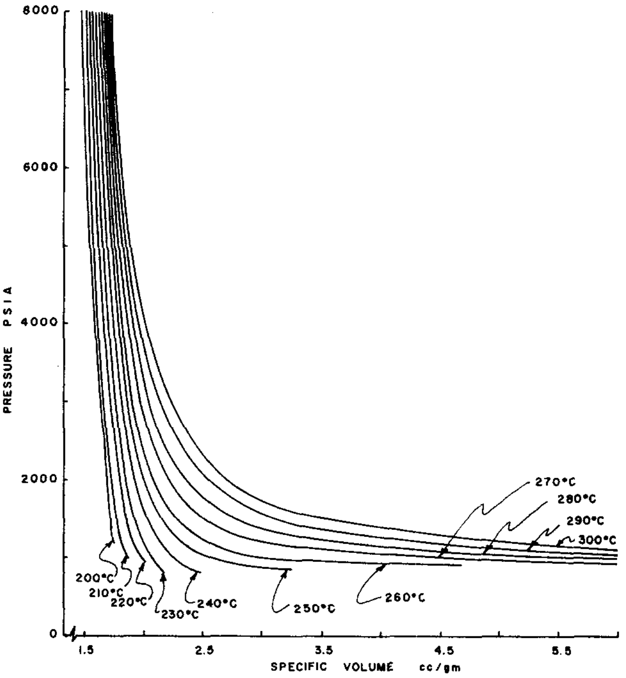

Fig. 3. Relationship between pressure and specific volume for isopropyl alcohol at constant temperature.

Table 2. Percent Errors for Polar Fluids at $T_R = 1.05$ and $P_R = 4.0$

Substance	z	*Source*	ω	x	% Error Equation (4)	% Error Equation (4), $x = 0$
Sulfur dioxide	0.537	*7*	0.262	0.005	−3.33	+1.11
Water	0.422	*6*	0.344	0.023	+2.55	+26.1
Ammonia	0.472	*10*	0.252	0.013	+1.31	+15.5
Methyl alcohol	0.419	*3*	0.556	0.037	−0.87	+19.8
Ethyl alcohol	0.485	*12*	0.639	0.003	+0.53	+1.23
Isopropyl alcohol	0.499	This study	0.663	−0.053	−0.04	−2.40
Methyl chloride	0.534	*16*	0.152	0.007	−3.25	+4.68

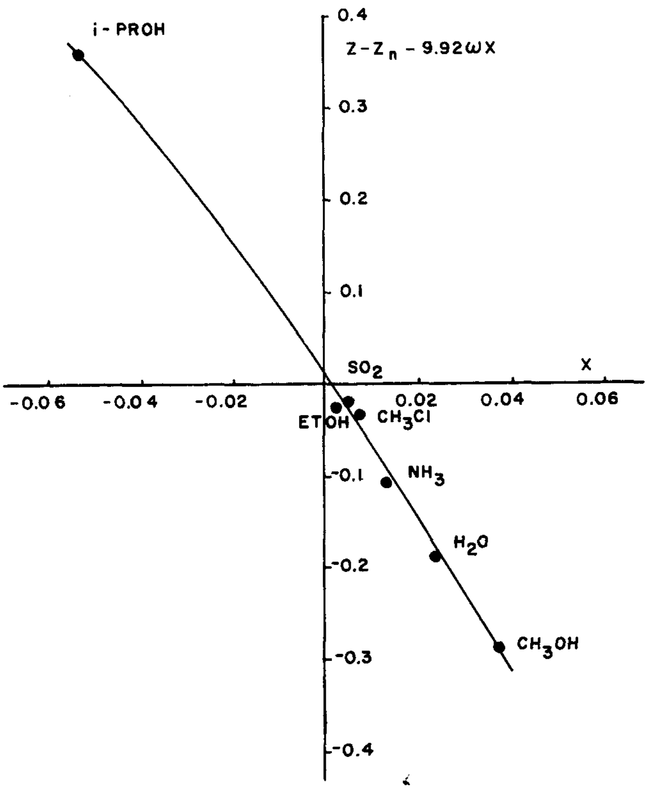

Fig. 5. Relationship for compressibility factor of polar fluids for $T_R = 1.05$ and $P_R = 4.0$.

In Equation (4) the values of $z^{(0)}$ and $z^{(1)}$ were obtained from the normal fluid functions (9), and the coefficient of ω^2 was taken as zero.

In Table 2 experimental values of z at $T_R = 1.05$ and $P_R = 4.0$ are compared with the values calculated with Equation (4) and the values from the normal fluid relationship [Equation (4) with $x = 0$]. The sources of the experimental compressibility factor data are included in Table 2. It can be seen that the use of a fourth parameter results in substantial improvement for the polar fluids considered. For the seven polar fluids the average deviation between the experimental values and those calculated from Equation (4) is 1.94%.

In Figure 5 values of $z - z_n - 9.92\ \omega x$ for the polar fluids at $T_R = 1.05$ and $P_R = 4.0$ are plotted against x. The inclusion of the ωx term enables all the polar fluids to be treated satisfactorily, and evidently helps to account for dipole-induced dipole interactions.

The results of this study indicate that Pitzer's normal fluid relationships can be extended by the inclusion of a fourth parameter to the compressibility factor of polar fluids in the dense gaseous region. However, since quadratic terms in x are required, the polar fluid functions can only be accurately determined for polar substances of substantial molecular size, such as isopropyl alcohol, for a region of reduced temperatures and reduced pressures for which sufficient experimental PVT data are available.

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NOTATION

P = pressure, lb./sq.in. abs.
P_R = reduced pressure
T = temperature, °C.
T_R = reduced temperature
V = volume, cc.
x = fourth parameter, defined in Equation (3)
z = compressibility factor
ω = acentric factor, defined in Equation (2)

Subscript

n = normal fluid

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