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Compressibility Factors and Virial Coefficients of 2-Propanol

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The compressibility factor isotherms of gaseous 2-propanol were determined by the Burnett method at 100°, 125°, 150°, 175°, and 200° C. At each temperature, vapor pressures were measured, and the second and third virial coefficients were determined by graphical methods.

THE BURNETT method (*3*) essentially consists of measuring a series of pressures obtained by making repetitive expansions of a gas from one chamber into a previously evacuated second chamber under isothermal conditions. The method and apparatus have been thoroughly discussed by Silberberg, Kobe, and McKetta (*8*). The basic equation relating the compressibility factor of the gas to the pressure and temperature of the gas after the *r*th expansion is

$$Z_r = \frac{P_r N^r / T_r}{P_0 / Z_0 T_0} = \frac{P_r N^r}{\rho_0 R T_r} \tag{1}$$

In Equation 1, the quantity N is the apparatus constant, defined as

$$N = \frac{V_{\mathrm{I}} + V_{\mathrm{II}}}{V_{\mathrm{I}}} \tag{2}$$

where V_{I} is the volume of the first chamber and V_{II} is the volume of the second chamber into which the expansions are made. The zero-subscripted quantities refer to the condition of the gas before the first expansion in a particular run. The details of determining the values of N and P_0/Z_0T_0 (or ρ_0) have been discussed by Silberberg and coworkers (*8, 9*).

The experimental apparatus employed in this work was that used by Heichelheim and coworkers (*6*), with the inclusion of a platinum resistance thermometer for more accurate temperature measurement and a fused quartz Bourdon tube pressure gage for low pressure determinations. The apparatus was a modified Burnett apparatus utilizing a third chamber of small volume into which expansions could be made in order to provide closer spacing of data points within a run. During any particular run, expansions could be made into either of the two expansion chambers in any order. Equation 1 then becomes

$$Z_r = \frac{P_r \Pi_r / T_r}{P_0 / Z_0 T_0} = \frac{P_r \Pi_r}{\rho_0 R T_r} \tag{3}$$

where

$$\Pi_r = \prod_{i=1}^{r} N_i$$

and N_i is the value of the apparatus constant applicable to the *i*th expansion.

The compressibility factor can be expressed in terms of molal density by the Leiden virial expansion

$$Z = 1 + B\rho + C\rho^2 + D\rho^3 + \ldots \tag{4}$$

The coefficients B, C, and D are the second, third, and fourth virial coefficients, respectively, and are functions

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of temperature only. The basic relationship of the Burnett method, Equation 3, may also be written as

$$\rho_r = \rho_0 \Pi_r^{-1} \tag{5}$$

Applying Equations 3 and 5 to Equation 4 yields the relation

$$P_r \Pi_r / RT_r = \rho_0 + B\rho_0^2 \Pi_r^{-1} + C\rho_0^3 \Pi_r^{-2} + D\rho_0^4 \Pi_r^{-3} + \dots \tag{6}$$

A residual type of function can be obtained by rearranging Equation 6 into

$$[P_r \Pi_r / RT_r - \rho_0]\Pi_r = B\rho_0^2 + C\rho_0^3 \Pi_r^{-1} + D\rho_0^4 \Pi_r^{-2} + \dots \tag{7}$$

When the left side of Equation 7 is plotted as ordinate *vs.* Π_r^{-1} as abscissa for the data of a particular run, the resulting graph approaches linearity quite rapidly as the value of Π_r^{-1} approaches zero, that is, as the density approaches zero. Silberberg, Lin, and McKetta (*9*) have shown how this criterion of approach to linearity at low densities affords a means of determining the value of ρ_0 very accurately. The use of the correct value of ρ_0 in Equation 7 will result in linearity of the graph at low densities, whereas a value of ρ_0 slightly too large or too small will result in a graph curving sharply upward or downward as Π_r^{-1} approaches zero. This is a very sensitive trial-and-error test, and the value of ρ_0 so obtained is used in Equation 3 to calculate the compressibility factors at each pressure of the run.

When the correct value of ρ_0 has been determined in this manner, the zero-abscissa intercept of the resulting graph will be $B\rho_0^2$, and the slope at the intercept will be $C\rho_0^3$. From these values of the intercept and slope at the intercept, the second and third virial coefficients may be calculated.

MATERIAL

The 2-propanol used in this work was reagent grade material obtained from the J. T. Baker Chemical Co. The alcohol, analyzed by gas chromatography, contained 0.12% water and 0.003% of some lower-boiling compound. After the sample of alcohol used in the measurements was dried by being slowly dripped through a bed of Type 4A Linde molecular sieve, no water peak could be seen in the chromatogram of the material. After completion of the experimental measurements, a sample of the material was once again analyzed and no change in purity or evidence of decompositon was observed.

EXPERIMENTAL

Compressibility factor isotherms and vapor pressures were determined at 25° intervals from 100° to 200° C. No compressibility data could be taken at temperatures lower than

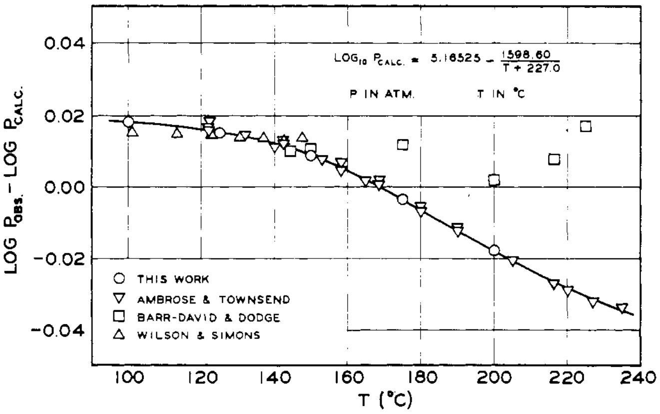

Figure 1. Vapor pressure residuals of 2-propanol

Table I. Smoothed Compressibility Factors of 2-Propanol

Temp., ° C.	Pressure, Atm.	$Z = PV/RT$
100	0.2	0.9943
	0.4	0.9887
	0.6	0.9827
	0.8	0.9763
	1.0	0.9696
	1.2	0.9623
	1.4	0.9546
	1.6	0.9450
	1.7	0.9382
	1.8	0.9286
	1.971[a]	...
125	0.5	0.9889
	1.0	0.9772
	1.5	0.9651
	2.0	0.9522
	2.5	0.9382
	3.0	0.9235
	3.5	0.9068
	3.8	0.8953
	4.0	0.8860
	4.1	0.8798
	4.2	0.8706
	4.3	0.8490
	4.357[a]	...
150	1.0	0.9836
	2.0	0.9663
	3.0	0.9481
	4.0	0.9292
	5.0	0.9090
	6.0	0.8870
	7.0	0.8626
	7.5	0.8491
	8.0	0.8339
	8.5	0.8150
	8.580[a]	0.8113
175	1.0	0.9873
	2.0	0.9742
	3.0	0.9609
	4.0	0.9473
	5.0	0.9331
	6.0	0.9184
	7.0	0.9031
	8.0	0.8870
	9.0	0.8703
	10.0	0.8528
	11.0	0.8344
	12.0	0.8149
	13.0	0.7938
	14.0	0.7704
	15.0	0.7413
	15.317[a]	0.7291
200	2.0	0.9794
	4.0	0.9584
	6.0	0.9368
	8.0	0.9140
	10.0	0.8897
	12.0	0.8644
	14.0	0.8373
	16.0	0.8182
	18.0	0.7768
	20.0	0.7429
	22.0	0.7051
	24.0	0.6617
	25.333[a]	0.6261

[a] Indicates saturated vapor.

100° C. because the vapor pressure of the alcohol was too low below this temperature to give a sufficient number of measurable points in a run. Above 200° C., the vapor pressure of the mercury used in the apparatus becomes great enough to introduce possible errors in the measured pressures.

Vapor Pressures. At each experimental temperature, at least three separate vapor pressure measurements were made with different ratios of vapor to liquid-phase volumes. No significant change in the vapor pressure with this ratio was observed, attesting to the purity of the alcohol. The averages of the experimental vapor pressures are compared on a residual basis with values reported by other investigators (*1, 2, 10*) in Figure 1. The smoothed values of vapor pressure are reported in Table I. These values are estimated to be in error by no more than 0.1%.

Compressibility Factors. At least two complete runs were made for each isotherm, and partial runs to define the high-pressure regions better were made for the 100°, 125°, 175°, and 200° C. isotherms. The maximum pressure of each run was slightly below the vapor pressure of the 2-propanol at that temperature. For each complete compressibility run, the value of ρ_0 was determined graphically as described earlier, and the compressibility factor Z_r was calculated at each pressure P_r according to Equation 3. Values of the apparatus constants at 100°, 150°, and 200° C. were determined with helium using the graphical pressure-ratio technique described by Silberberg, Kobe, and McKetta (*8*).

The experimental compressibility data for 2-propanol are presented in Table II and shown graphically in Figure 2. None of the data points deviates from a smooth curve drawn through the points by more than 0.15%, and the average deviation is less than 0.05%. The smoothed values of the compressibility factors at the saturation point are also listed in Table I for the 150°, 175°, and 200° C. isotherms. Because of the excessive curvature of the 100°

Table II. Experimental Compressibility Factors of 2-Propanol

Isotherm Temp., °C.	r	Expansion Chamber Used	P_r, Atm.	T_r, °K.	Z_r
100	0	...	1.7840	373.15	0.9330
	1	III	1.6134	373.15	0.9452
	2	III	1.4515	373.14	0.9527
	3	III	1.3037	373.15	0.9586
	4	III	1.1696	373.15	0.9635
	5	III	1.0482	373.15	0.9674
	0	...	1.8382	373.15	0.9250
	1	III	1.6700	373.14	0.9415
	2	III	1.5046	373.15	0.9503
	3	III	1.3519	373.15	0.9566
	4	III	1.2135	373.15	0.9620
	5	III	1.0878	373.15	0.9660
	6	III	0.9752	373.15	0.9702
	0	...	1.8504	373.16	0.9177
	1	III	1.6891	373.16	0.9386
	2	III	1.5247	373.16	0.9491
	0	...	1.8800	373.14	0.9060
	1	III	1.7328	373.15	0.9355
	2	III	1.5652	373.15	0.9466
	3	III	1.4085	373.15	0.9544
125	0	...	4.2171	398.17	0.8645
	1	II	3.1624	398.17	0.9176
	2	II	2.2976	398.16	0.9436
	3	II	1.6532	398.17	0.9610
	4	II	1.1821	398.18	0.9725
	0	...	4.1376	398.17	0.8773
	1	III	3.7731	398.17	0.8962
	2	II	2.7684	398.18	0.9307
	3	II	2.0012	398.18	0.9522
	4	II	1.4354	398.17	0.9668
	5	II	1.0250	398.17	0.9771
	0	...	4.2496	398.15	0.8614
	1	III	3.9220	398.15	0.8906
	2	III	3.5559	398.15	0.9047
	3	II	2.5986	398.15	0.9357
	4	II	1.8750	398.15	0.9556
	5	II	1.3434	398.15	0.9690
	0	...	4.1986	398.15	0.8722
	1	III	3.8441	398.16	0.8946
	2	III	3.4792	398.15	0.9072
	0	...	4.2341	398.16	0.8654
	1	III	3.8947	398.16	0.8918
	2	III	3.5289	398.16	0.9052
150	0	...	8.3770	423.16	0.8209
	1	III	7.6895	423.16	0.8440
	2	III	7.0102	423.16	0.8618
	3	II	5.1992	423.17	0.9047
	4	II	3.7899	423.15	0.9336
	5	II	2.7340	423.16	0.9534
150	6	II	1.9590	423.15	0.9670
	7	II	1.3983	423.16	0.9770
	0	...	8.0431	423.16	0.8327
	1	II	6.0420	423.16	0.8854
	2	II	4.4368	423.16	0.9204
	3	II	3.2158	423.16	0.9443
	4	II	2.3114	423.15	0.9608
	5	II	1.6530	423.15	0.9727
	6	II	1.1770	423.15	0.9804
175	0	...	14.8493	448.16	0.7465
	1	II	11.5558	448.15	0.8224
	2	II	8.6861	448.15	0.8750
	3	II	6.3948	448.15	0.9119
	4	II	4.6448	448.15	0.9376
	5	II	3.3460	448.14	0.9561
	6	II	2.3968	448.15	0.9695
	7	II	1.7088	448.15	0.9784
	8	II	1.2161	448.15	0.9857
	0	...	13.0527	448.15	0.7922
	1	II	9.9406	448.15	0.8541
	2	II	7.3800	448.16	0.8975
	3	II	5.3893	448.15	0.9278
	4	II	3.8946	448.15	0.9491
	5	II	2.7945	448.16	0.9640
	6	II	1.9962	448.15	0.9748
	7	II	1.4213	448.15	0.9825
	0	...	15.1248	448.19	0.7360
	1	III	14.1012	448.17	0.7686
	2	III	13.0013	448.17	0.7937
	3	III	11.9340	448.17	0.8160
	4	III	10.9155	448.17	0.8360
200	0	...	23.8631	473.14	0.6645
	1	II	19.2024	473.15	0.7569
	2	II	14.7969	473.15	0.8256
	3	II	11.0840	473.15	0.8754
	4	II	8.1520	473.15	0.9114
	5	II	5.9208	473.15	0.9370
	6	II	4.2648	473.15	0.9554
	0	...	17.0564	473.15	0.7932
	1	II	12.9494	473.15	0.8524
	2	II	9.6044	473.15	0.8950
	3	II	7.0154	473.14	0.9254
	4	II	5.0710	473.15	0.9468
	5	II	3.6417	473.15	0.9625
	0	...	24.6401	473.14	0.6456
	1	III	23.1879	473.15	0.6805
	2	III	21.6629	473.16	0.7120
	3	III	20.1237	473.15	0.7409
	4	II	15.6199	473.16	0.8140

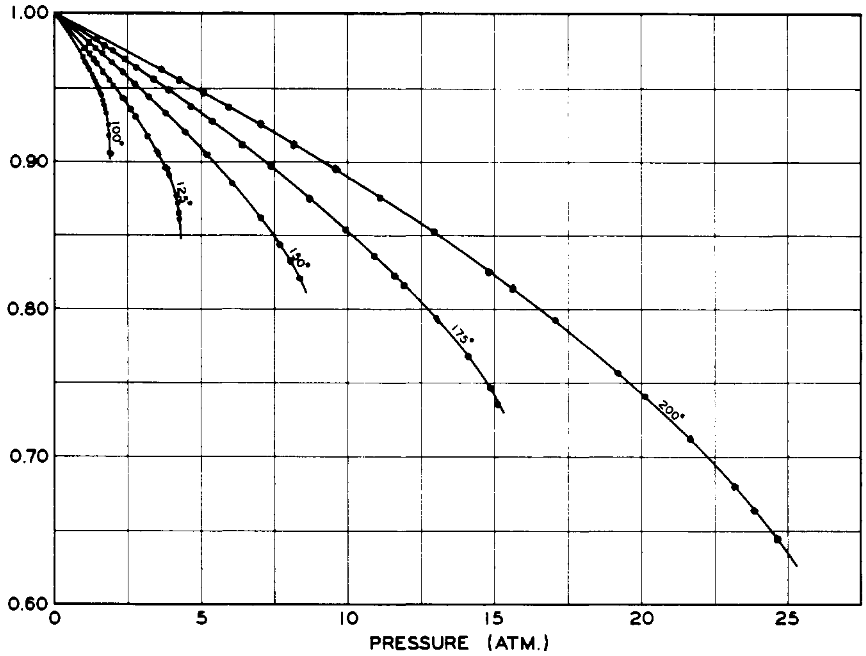

Figure 2. 2-Propanol compressibility factors

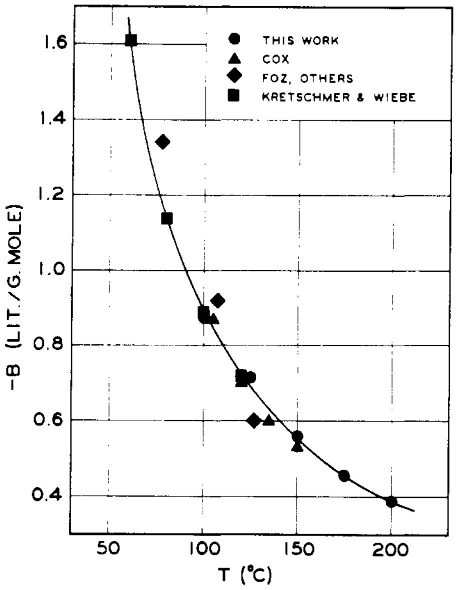

Figure 3. Second virial coefficients of 2-propanol

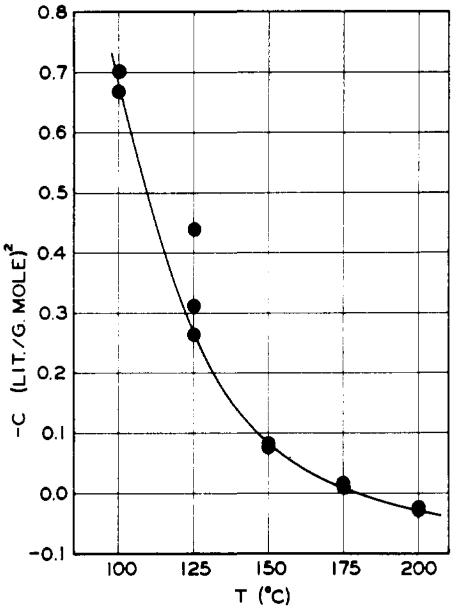

Figure 4. Third virial coefficients of 2-propanol

and 125° isotherms near the saturation point, it was not possible to extrapolate these curves to obtain values of the saturated vapor compressibility factors. This abnormal deviation of the compressibility factors, which becomes much more pronounced near the saturation point, is attributed to the formation of dimers and other higher alcohol polymers through hydrogen bonding.

Virial Coefficients. Second and third virial coefficients of 2-propanol were determined at each experimental temperature from the intercepts and limiting slopes of the residual function plots according to Equation 7. Table III lists these experimental values. The dependency of the virial coefficients upon temperature is shown in Figures 3 and 4. Figure 3 also shows values of the second virial coefficient reported by other investigators (*4*, *5*, *7*). Agreement among the sets of values is fairly good. A search of the literature revealed no values of the third virial coefficient with which the results reported here might be compared. Below about 180° C., the third virial coefficient has negative values, a further indication of the strong associative forces existing between the 2-propanol molecules. Smoothed values of the virial coefficients are given in Table IV.

Table III. Experimental Virial Coefficients of 2-Propanol

Temp., ° C.	$-B$, L./G. Mole	$-C$, (L./G. Mole)^2
100	0.8708	0.702
	0.8742	0.669
125	0.7160	0.439
	0.7145	0.312
	0.7145	0.264
150	0.5584	0.083
	0.5578	0.076
175	0.4599	0.009
	0.4541	0.017
200	0.3900	−0.024
	0.3875	−0.028

Table IV. Smoothed Virial Coefficients of 2-Propanol

Temp., ° C.	$-B$, L./G. Mole	$-C$, (L./G. Mole)^2
100	0.889	0.68
125	0.697	0.27
150	0.557	0.082
175	0.457	0.011
200	0.388	−0.026

ACCURACIES

Because of the large number of data points taken, the values of the smoothed compressibility factors are assumed to be free of random errors. The maximum systematic errors in the smoothed compressibility factor isotherms are estimated to be as follows: 0.19% at 100°, 0.14% at 125°, 0.12% at 150°, 0.10% at 175°, and 0.09% at 200° C.

Accuracy of virial coefficients obtained from Burnett data in the manner described here is difficult to evaluate. The effect of systematic errors in the temperature scale is entirely negligible. The effect of systematic errors in pressure would also be negligible, provided that they were uniform over the entire pressure scale used in this investigation. Errors in the values of the apparatus constants can introduce systematic errors into the calculations, but the nature of the graphical methods is such that these errors are self-cancelling to some extent. In view of these facts, the error analysis made by Silberberg, Lin, and McKetta (*9*) is equally applicable to the results of this study. Therefore, the error in the second virial coefficients is estimated to be less than 2% and in the third virial coefficients is estimated to be less than 5% or 0.002 liter^2/gram mole^2, whichever is the greater.

NOMENCLATURE

B = second virial coefficient, l./gram-mole
C = third virial coefficient, (l./gram-mole)^2
D = fourth virial coefficient, (l./gram-mole)^3
N = apparatus constant; ratio of system volumes after and before expansion
P = absolute pressure, atm.
R = gas constant, 0.0820544 (l.)(atm.)/(gram-mole)(° K.)
T = absolute temperature, ° K.
V = molal volume, l./gram-mole
Z = compressibility factor, PV/RT
Π_r = $\prod_{i=1}^{r} N_i = N_1 \cdot N_2 \ldots N_r$
ρ = molal density, gram-moles/liter

Subscripts

$_r$ = state of system after rth expansion
$_0$ = initial state of system

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Vapor Pressures of Trialkyl Borates

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Vapor pressure–temperature measurements have been observed for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The data were fitted into the equation, $\log_{10}P_{mm.} = A/T + B \log_{10}T + C$, and the constants A, B, and C, evaluated from a least-squares calculation on the IBM 1620 computer, were employed for finding the normal boiling point, latent heat, and entropy of vaporization for each of the borates.

A LIMITED amount of physical data for trialkyl borates is scattered throughout the literature (*1, 4*), and apparently only a very few systematic experimental investigations offer such information for this class of compounds. A search of published data revealed one work that involved vapor pressure–temperature measurements for methyl and ethyl borate (*8*), and another (*1*) concerned with the calculation of the latent heats and entropies of vaporization for 17 organoboron compounds, the calculations having been made on the basis of almost fragmentary experimental data. In the present instance, vapor pressures have been observed for the following trialkyl borates: methyl, ethyl, propyl, isopropyl, butyl, and isobutyl. The resulting data were fitted into an appropriate equation, and the constants evaluated from that equation were employed in the calculation of the normal boiling point, latent heat, and entropy of vaporization for each of the borates.

EXPERIMENTAL

The borates were distilled, then assayed by the standard mannitol-phenolphthalein method, and stored under nitrogen until ready for use; all samples showed a purity of better than 99.8 %. The vapor pressure measurements were