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 carried out by using the Tobey modification (7) of the classical Ramsay-Young apparatus and following the prescribed procedure (2); reagent grade toluene was used to check the reliability of subsequent observations. Vapor pressures were recorded to within ±0.5 mm. of Hg and temperatures to ±0.1° C.

RESULTS AND DISCUSSION

On the assumption that the latent heat of vaporization, ΔH_v, is related to the absolute temperature, T, by the equation

$$\Delta H_v = A' + B'T \tag{1}$$

the vapor pressure data were fitted into the conventional form of the Clausius-Clapeyron relationship:

$$\log_{10} P_{\text{mm.}} = A/T + B \log_{10} T + C \tag{2}$$

and constants A, B, and C were evaluated from a least-squares calculation on the IBM 1620 computer (constants A' and B' being related to A and B in the usual manner). The observed data, along with pressures calculated from Equation 2 are given in Table I; the per cent deviation is equal to $(P_{\text{obsd.}} - P_{\text{calcd.}}) \times 100/P_{\text{obsd.}}$.

Table II presents the results of the earlier investigation (8) for methyl and ethyl borate.

Table III lists constants A, B, and C for Equation 2, and A' and B' for Equation 1; the standard error of estimate, S, is also given, where

$$S = \sum\left(\frac{|P_{\text{obsd.}} - P_{\text{calcd.}}|^2}{n}\right)^{1/2}$$

The Table III values of A, B, and C were used in Equation 2 for the calculation of the normal boiling point, T_b, and T_b was then introduced into Equation 1, along with A'

Table I. Observed Vapor Pressure–Temperature Data, and Pressures Calculated from the Equation, $\log_{10} P_{\text{mm.}} = A/T + B \log_{10} T + C$

Borate	T, ° C.	$P_{\text{mm.}}$ Obsd.	$P_{\text{mm.}}$ Calcd.	Deviation, %
Methyl	31.2	180.4	181.27	−0.48
	38.0	244.9	242.83	0.84
	45.0	325.7	324.24	0.44
	50.2	397.1	398.98	−0.47
	54.1	465.0	464.65	0.14
	56.7	513.2	512.79	0.07
	60.4	591.1	589.19	0.32
	63.4	662.7	658.09	0.69
	67.4	757.1	760.57	−0.45
Ethyl	29.1	20.3	21.01	−3.54
	39.0	36.0	35.07	2.57
	44.9	47.3	46.79	1.07
	55.9	79.0	77.69	1.65
	60.3	93.3	94.17	−0.93
	71.2	149.3	148.13	0.77
	80.0	212.0	208.73	1.54
	84.6	247.0	247.83	−0.33
	88.9	288.0	289.70	−0.59
	96.0	369.0	371.50	−0.67
	104.2	488.0	488.66	−0.13
	108.7	570.8	564.76	1.05
Propyl	85.1	28.5	28.50	0.00
	111.2	82.2	83.33	−1.37
	131.3	174.6	173.63	0.55
	136.5	212.0	207.56	2.09
	146.5	296.0	289.07	2.34
	154.8	369.4	376.21	−1.84
	167.1	548.0	546.16	0.34
	171.2	622.6	615.67	1.11
	175.8	692.6	702.47	−1.42
	178.8	764.0	764.50	−0.07
Isopropyl	65.1	56.4	55.31	1.92
	85.7	120.8	125.15	−3.60
	98.1	198.1	197.22	0.44
	107.1	272.3	270.13	0.79
	114.5	348.4	346.71	0.48
	119.1	411.2	403.31	1.91
	124.9	485.2	486.02	−0.16
	129.9	563.9	568.79	−0.86
	133.5	631.0	635.73	−0.75
	136.9	707.8	705.13	0.37
	138.9	757.2	748.95	1.08
Butyl	116.8	14.6	14.66	−0.44
	158.8	76.7	76.90	−0.26
	172.0	121.7	121.61	0.07
	178.2	150.7	149.48	0.80
	184.1	185.2	181.00	2.26
	191.2	226.7	226.46	0.10
	198.6	282.2	284.07	−0.66
	203.2	329.2	325.92	0.99
	210.3	392.2	400.97	−2.23
	217.7	496.4	494.60	0.36
Isobutyl	99.3	18.5	18.02	2.58
	106.6	24.5	24.49	0.01
	114.6	33.5	33.87	−1.11
	126.0	50.5	52.65	−4.26
	142.3	95.5	95.17	0.33
	155.9	153.5	151.12	1.54
	166.0	210.5	209.44	0.49
	173.1	266.5	261.34	1.93
	179.5	324.5	317.33	2.20
	185.5	380.5	378.96	0.40
	190.2	436.5	434.23	0.51
	195.0	492.5	497.71	−1.05
	199.2	548.5	559.67	−2.03

Table II. Observed Vapor Pressure–Temperature Data (8), and Pressures Calculated from the Equation, $\log_{10} P_{\text{mm.}} = A/T + 1.75 \log_{10} T + BT + C$

Borate	T, ° C.	$P_{\text{mm.}}$ Obsd.	$P_{\text{mm.}}$ Calcd.
Methyl	−41.0[a]	2	2
	−33.0	4	4
	−25.5	7	7
	−16.3	14	13
	−6.0	25	25
	0.0[a]	36	36
	11.7	70	69
	30.3	171	171
	40.1	261	261
	50.1	388	391
	60.0[a]	563	563
	68.0	746	742
Ethyl	0.0	3	3
	20.0[a]	12	12
	31.3	23	23
	40.0	37	37
	50.5	63	62
	60.5	98	98
	70.5[a]	149	149
	80.2	219	219
	90.0	315	314
	100.5	450	449
	110.5	613	618
	117.0[c]	751	751

[a] Constants A, B, and C for the equation were evaluated for each borate by introducing the experimental temperatures (and corresponding pressures) (8).

Table III. Constants A, B, C, A', and B'

R in $B(OR)_3$	$-A$	B	C	S	A'	B'
CH_3	1445.8	2.4187	1.0023	2.31	6616.0	4.8059
C_2H_5	2569.4	−3.3726	18.1860	2.09	11757	−6.7013
C_3H_7	2328.4	0.8054	5.8976	5.15	10665	1.6003
iso-C_3H_7	1410.1	4.4956	−5.4578	4.40	6452.4	8.9327
C_4H_9	2693.3	1.0865	5.2574	3.37	12324	2.1588
iso-C_4H_9	2182.6	2.4527	0.8101	4.38	9987.6	4.8735

Table IV. Values of T_b, ΔH_b, ΔS_b

	T_b, °C.		ΔH_b, Cal./Mole		ΔS_b, Cal./Deg.	
R in $B(OR)_3$	This work	Other	This work	Other	This work	Other
CH_3	67.4	68.7 (*8*)	8253	7712 (*8*)	24.23	22.6 (*8*)
C_2H_5	118.3	117.4 (*8*)	9134	8863 (*8*)	23.33	22.7 (*8*)
C_3H_7	178.6	177 (*4*)	11378	11720 (*1*)	25.18	26.04 (*1*)
iso-C_3H_7	139.4	140 (*4*)	10138		24.57	
C_4H_9	233.5	230.0–231.0 (*5*)	13418	13200 (*1*)	26.48	26.21 (*1*)
iso-C_4H_9	210.4	211.5–213.0 (*5*)	12345	11440 (*1*)	25.52	23.57 (*1*)

and B', in order to compute the latent heat of vaporization at the boiling point, ΔH_b; the entropy of vaporization at the boiling point, ΔS_b (Trouton's constant), was evaluated in the usual manner. The results of these calculations are presented in Table IV.

In view of the extreme reactivity of methyl and ethyl borate toward atmospheric moisture, and the difficulty of working with these compounds over extended periods of time, the results of this investigation are in fair accord with those previously reported (*8*).

Despite the fact that the other calculations of ΔH_b and ΔS_b for propyl, butyl, and isobutyl borate (*1*) were deduced from a very limited amount of experimental information, there is fair agreement (at least for the propyl and butyl borate) between the earlier results and those given by the present work (Table IV).

The rather high values of Trouton's constant in the sixth column of Table IV would seem to indicate a goodly amount of intermolecular association to be present in liquid trialkyl borates. Other observations of ΔS_b, deduced from experimental data for compounds of similar structure, are also high—viz., the Trouton's constants for $B(OCH_2CH_2Cl)_3$ and $B[OCH(CH_2Cl)_2]_3$ are 25.32 and 29.18, respectively (*1*, *3*), and ΔS_b for n-$B(C_4H_9)_3$ is 27.07 (*1*, *6*).

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