Thermodynamic Properties of Gaseous Boron Trifluoride, Boron Trichloride, and Boron Tribromide

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Thermodynamic Properties of Gaseous Boron Trifluoride, Boron Trichloride, and Boron Tribromide

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In this paper are presented tables of the thermodynamic functions heat content, free energy, entropy, and heat capacity of boron trifluoride, boron trichloride, and boron tribromide in the ideal gas state at 1 atmosphere from 298.16° to 1000°K. These functions were calculated from Raman and infra-red spectra in the case of the two first mentioned and from the Raman spectrum of liquid boron tribromide. A satisfactory calorimetric check of the entropy of boron trifluoride is presented.

I. INTRODUCTION

IN recent years much interest has been shown in the formation of addition compounds with the boron trihalides and the use of the trihalides, particularly of boron trifluoride, as catalysts, as is witnessed by the reviews of Kästner[1] and the series of papers by G. F. Hennion in the *Journal of the American Chemical Society*. These compounds have passed from academic to industrial interest.

The spectroscopic and molecular data (Part II) are sufficiently complete to permit the calculations of the thermodynamic functions of boron trifluoride, boron trichloride, and boron tribromide to the rigid rotator, harmonic oscillator approximation with some increase of uncertainty in that order (Part III). Low temperature calorimetric measurements and vapor pressure data permit a check of the entropy of boron trifluoride (Part IV).

The following physical constants and chemical atomic weights were used in the calculations:

$R = 1.98718$ cal. deg.$^{-1}$ mole^{-1},
$hc/k = 1.43847$ cm deg.,
$N = 6.02283 \times 10^{23}$ mole^{-1},
Atomic weight of $^{11}B = 11.00992$,
Atomic weight of $^{10}B = 10.01361$,
Atomic weight of equilibrium $B = 10.82$.

The constants are those selected by Wagman, Kilpatrick, Taylor, Pitzer, and Rossini.[2] The chemical atomic weights of boron of masses 10 and 11 are derived from the physical atomic

weights: $^{11}B = 11.01292$ and $^{10}B = 10.01631$ of Bainbridge and Jordan as reported by Livingston and Bethe[3] and the ratio of the physical to the chemical atomic scale, 1.000272.

Recently Ingraham[4] has satisfactorily determined the percentage abundance of the boron isotopes. His values of 81.17 percent for ^{11}B and 18.83 percent for ^{10}B and the chemical atomic weights of the isotopes yields 10.822 for equilibrium boron as compared to 10.82 of the international atomic weights.

II. SPECTROSCOPIC AND MOLECULAR DATA

The spectroscopic data for boron trifluoride include the infra-red spectra of Bailey, Hale, and Thompson[5] and of Gage and Barker[6] and the Raman spectrum of the vapor by Anderson, Lassettre, and Yost[7a] and by Yost, DeVault, Anderson, and Lassettre.[7b] Herzberg[8] has summarized these data and shown that they are in agreement with the plane symmetrical model (point group D_{3h}). This is also in agreement with the zero dipole moment and the electron diffraction measurements. The latter by Lévy and Brockway[9] fix the B−F distance as 1.30±0.02A. From the study of the fine structure of the

[1] B. Kästner, Zeits. f. angew. Chemie 54, 273, 296 (1941).
[2] D. D. Wagman, J. E. Kilpatrick, W. J. Taylor, K. S. Pitzer, and F. D. Rossini, J. Research Nat. Bur. Stand. 34, 143 (1945).
[3] M. S. Livingston and H. A. Bethe, Rev. Mod. Phys. 9, 245 (1937).
[4] M. G. Ingraham, Phys. Rev. 70, 119 (1946).
[5] C. R. Bailey, J. B. Hale, and J. W. Thompson, Proc. Roy. Soc. (London) A161, 107 (1937).
[6] D. M. Gage and E. F. Barker, J. Chem. Phys. 7, 455 (1939).
[7a] T. F. Anderson, E. N. Lassettre, and D. M. Yost, J. Chem. Phys. 4, 703 (1936); [b] D. M. Yost, D. DeVault, T. F. Anderson, and E. N. Lassettre, *ibid.*, 6, 424 (1938).
[8] G. Herzberg, *Infrared and Raman Spectra of Polyatomic Molecules* (D. Van Nostrand Company, Inc., New York, 1945), pp. 298–9.
[9] H. A. Lévy and L. O. Brockway, J. Am. Chem. Soc. 59, 2085 (1937).

TABLE I. Heat content, free energy, entropy, and heat capacity of boron trifluoride in the ideal gas state at 1 atmosphere. Molecular weight $= 67.82$. $\sigma = 6$. $I_2 = I_3 = 78.8_4 \times 10^{-40}$, $I_1 = 157.7 \times 10^{-40}$ g cm^2.

T°K	$\frac{H^0 - H_0{}^0}{T}$	$\frac{-(F^0 - H_0{}^0)}{T}$ cal deg.$^{-1}$ mole^{-1}	S^0	Cp^0
298.16	9.338	51.357	60.695	12.063
300	9.355	51.414	60.770	12.094
350	9.811	52.892	62.702	12.981
400	10.257	54.230	64.488	13.764
450	10.686	55.464	66.150	14.454
500	11.094	56.611	67.704	15.059
600	11.841	58.70	70.54	16.046
700	12.497	60.58	73.07	16.792
800	13.071	62.29	75.36	17.358
900	13.572	63.85	77.42	17.792
1000	14.012	65.31	79.32	18.128

parallel ν_2 band ($\Delta\nu = 0.71$ cm^{-1}), Gage and Barker determined this distance to be 1.29A. This value leads to $I_2 = I_3 = 78.8_4 \times 10^{-40}$ and $I_1 = 157.7 \times 10^{-40}$ g cm^2.

The Raman spectrum of liquid boron trichloride has been studied by Venkateswaran[10]; Anderson, Lassettre, and Yost[7a]; and Wagner.[11] The latter author confirmed the measurements of Anderson, Lassettre, and Yost and with greater dispersion found three of the four possible lines caused by the chlorine isotopic splitting of the symmetric valence vibration, ν_1, in approximately the separations and intensities to be expected. Anderson, Lassettre, and Yost's assignment of the fundamental frequencies is as follows: $\nu_1 = 471$; $2\nu_2 = 902(^{11}\text{BCl}_3)$; $\nu_3(2) = 946(^{11}\text{BCl}_3)$, $= 989(^{10}\text{BCl}_3)$; and $\nu_4(2) = 253$ cm^{-1}.[12] They also made a more plausible assignment of the fundamental frequencies for the infra-red absorption spectrum of boron trichloride vapor, based upon the data of Cassie,[13] as follows: $\nu_1 = 471$; $\nu_2 = 462(^{11}\text{BCl}_3)$; $\nu_3(2) = 958(^{11}\text{BCl}_3)$, $= 996(^{10}\text{BCl}_3)$; $\nu_4(2) = 243$ cm^{-1}. The dispersion of Cassie's measurements was insufficient to permit the determination of the fine structure. Lévy and Brockway's measurement[9] of the B$-$Cl distance, 1.73 ± 0.02A, yields $I_2 = I_3 = 264._3 \times 10^{-40}$ and $I_1 = 528._6 \times 10^{-40}$ g cm^2.

[10] S. Venkateswaran, Ind. J. Phys. 6, 275 (1931).
[11] J. Wagner, Zeits. f. physik. Chemie 193, 55 (1943).
[12] The totally symmetric vibration ν_1, involving motion of the halogen atoms, is independent of the mass of the boron isotope. For the doubly degenerate ν_4 the isotope effect, which should be small, has not been observed in the cases of boron trichloride and boron tribromide.
[13] A. B. D. Cassie, Proc. Roy. Soc. (London) A148, 87 (1935).

For boron tribromide there are no infra-red measurements and the Raman spectrum studies have been made with the liquid.[7a, 11, 14] Though the later measurements of Wagner give the frequencies $\nu_1 \cdots \nu_4$, less than those of Anderson, Lassettre, and Yost by 2, 2, 6, and 1 cm^{-1}, respectively, those of Anderson, Lassettre, and Yost have been accepted. They are $\nu_1 = 279$, $\nu_2 = 372(^{11}\text{BBr}_3)$, $\nu_3(2) = 806(^{11}\text{BBr}_3)$, $= 846(^{10}\text{BBr}_3)$ and $\nu_4(2) = 151$ cm^{-1}. Lévy and Brockway's measurement of the B$-$Br distance, 1.87 ± 0.02A, yields $I_2 = I_3 = 696 \times 10^{-40}$ and $I_1 = 1392 \times 10^{-40}$ g cm^2.

According to the Teller-Redlich product rule, for such isotopic molecules as $^{11}\text{BX}_3$ and $^{10}\text{BX}_3$, the product of the ratios of the frequencies for all vibrations of a given symmetry type is equal to the square root of the ratio of the reciprocal mean masses, i.e.,

$$\frac{\nu_2(^{10}\text{BX}_3)}{\nu_2(^{11}\text{BX}_3)} = \frac{\nu_3\nu_4(^{10}\text{BX}_3)}{\nu_3\nu_4(^{11}\text{BX}_3)} = \left[\frac{\mu(^{11}\text{BX}_3)}{\mu(^{10}\text{BX}_3)}\right]^{\frac{1}{2}}.$$

The ν_2's for boron trifluoride are in excellent agreement with this rule and $\nu_3\nu_4$ values agree satisfactorily.[8] For boron trichloride and boron tribromide for which $(\mu_{11}/\mu_{10})^{\frac{1}{2}}$ is 1.0441 and 1.0466, respectively, direct experimental test of this rule is not possible, since the ν_2's for $^{10}\text{BX}_3$ have not been measured and the ν_4's have not been resolved. The calculated values of the ν_2's given by Anderson, Lassettre, and Yost[7a] are not quite in accord with these ratios. For the present calculations the Teller-Redlich rule and the ν_i values for $^{11}\text{BX}_3$ have been accepted and values for $^{10}\text{BX}_3$ have been calculated. The former multiplied by the abundance fraction 0.8117 and the latter by 0.1883 yield for the equilibrium BX$_3$:

	ν_1	ν_2	$\nu_3(2)$	$\nu_4(2)$
BCl$_3$(g)	471	465.8	965.2	243.2 cm^{-1}
BBr$_3$(l)	279	375.3	812.0	151.2

III. THERMODYNAMIC FUNCTIONS

The frequencies given above for boron trichloride and boron tribromide, and ones calculated from Table 75 of reference 8 by combination in the relative proportions of 0.8117 and

[14] R. Ananthakrishnan, Proc. Indian Acad. Sci. A4, 74 (1936).

0.1883, have been used with the moments of inertia mentioned in Section II to calculate the thermodynamic functions of the three trihalides. The symmetry number, σ, is 6. Nuclear spins and the effect of isotopic mixing have been neglected. The values of the heat content, free energy, entropy, and heat capacity of boron trifluoride, boron trichloride, and boron tribromide in the ideal gas state at 1 atmosphere are summarized in Tables I–III. The precision of expression of the free energy and entropy does not reflect the uncertainty in the $B-X$ distances. Thus, e.g., if r_{B-X} were greater by 0.01A in each case, i.e., equal to the electron diffraction value for boron trifluoride, their values would be greater by 0.043, 0.034, and 0.033 cal. deg.$^{-1}$ mole^{-1}, respectively.

IV. CALORIMETRIC AND OTHER COMPARISONS

Eucken and Schröder[15] measured the heat capacities, heats of transition and fusion of boron trifluoride from 12° to 173°K, approximately the boiling point. The boiling point has been variously reported as -99.9 to $-101°C$.[16] Eucken and Schröder obtained the entropy of liquid boron trifluoride at 154.5°K from their calorimetric data. They combined this with a value of the entropy of vaporization at 154.5° and the saturation pressure, derived from the vapor pressure data and equation of Pohland and

TABLE II. Heat content, free energy, entropy, and heat capacity of boron trichloride in the ideal gaseous state at one atmosphere. Molecular weight $=117.911$. $\sigma = 6$. $I_2 = I_3 = 264._3 \times 10^{-40}$, $I_1 = 528._6 \times 10^{-40}$ g cm^2.

$T°K$	$\dfrac{H^0-H_0^0}{T}$	$\dfrac{-(F^0-H_0^0)}{T}$ cal. deg.$^{-1}$ mole^{-1}	S^0	Cp^0
298.16	11.262	58.03	69.29	14.97
300	11.284	58.10	69.38	15.00
350	11.873	59.88	71.75	15.79
400	12.415	61.51	73.93	16.43
450	12.879	62.99	75.87	16.94
500	13.306	64.37	77.68	17.36
600	14.04	66.86	80.90	17.99
700	14.63	69.08	83.71	18.42
800	15.13	71.06	86.19	18.72
900	15.54	72.87	88.41	18.94
1000	15.89	74.52	90.41	19.10

[15] A. Eucken and E. Schröder, Zeits. f. physik. Chemie **B41**, 307 (1938).
[16] Landolt-Börnstein, *Tabellen*, third edition, Vol. I, p. 338; Supplement III, p. 318.

TABLE III. Heat content, free energy, entropy, and heat capacity of boron tribromide in the ideal gaseous state at 1 atmosphere. Molecular weight $=250.568$. $\sigma = 6$. $I_2 = I_3 = 696 \times 10^{-40}$, $I_1 = 1392 \times 10^{-40}$ g cm^2.

$T°K$	$\dfrac{H^0-H_0^0}{T}$	$\dfrac{-(F^0-H_0^0)}{T}$ cal. deg.$^{-1}$ mole^{-1}	S^0	Cp^0
298.16	12.609	64.88	77.49	16.25
300	12.631	64.96	77.59	16.28
350	13.187	66.97	80.16	16.88
400	13.695	68.75	82.44	17.41
450	14.130	70.39	84.52	17.80
500	14.514	71.89	86.41	18.10
600	15.16	74.60	89.76	18.58
700	15.67	76.98	92.64	18.88
800	16.08	79.10	95.18	19.10
900	16.43	81.01	97.44	19.25
1000	16.72	82.76	99.47	19.37

Harlos,[17] and with the entropy of compression to 1 atmosphere to obtain the entropy in the ideal gas state at 1 atmosphere and 154.5°K. The entropy change, $S^0{}_{298.2} - S^0{}_{154.5}$, for the vapor was obtained from values of the characteristic temperatures of the fundamental vibrations supposedly based on the results of Yost, DeVault, Anderson, and Lassettre.[7b] Their result for the entropy in the ideal gas state at 1 atmosphere and 298.2°K was 61.17 cal. deg.$^{-1}$ mole^{-1}.

The calculations of Eucken and Schröder are subject to several minor and two major objections. Two of their graphically determined areas are in error by approximately 0.1 cal. deg.$^{-1}$ mole^{-1}. Inconsistent (and incorrect) values of hc/k appear to have been used in obtaining the characteristic temperatures. More important is the fact that no corrections for non-ideality appear to have been made in determining the heat of vaporization. The other major objection concerns their use of 1.13 cal. deg.$^{-1}$ mole^{-1} as the entropy change involved in going from 142.15° to 144.46°K, which purports to be that involved in the transition and

$$\int_{142.15}^{144.46} Cp \cdot d \ln T.$$

According to their Table 4 the energy input per mole in increasing the temperature 1.128° (including the transition) was 61.0 cal., the contribution of the normal molal heat was 42.6 cal., leaving 18.4 (given as *ca.* 18) as the true heat of

[17] E. Pohland and W. Harlos, Zeits. f. anorg. allgem. Chemie **207**, 242 (1932).

TABLE IV. Summary of the calculation of the entropy of boron trifluoride in the ideal gas state at 298.16°K and 1 atmosphere, based on calorimetric and vapor pressure data to 154.5°K and statistically calculated ΔS^0 from 154.5 to 298.16°K.

	cal. deg.$^{-1}$ mole^{-1}
Extrapolation, 0–12.6°K	0.55
Graphical, solid II, 12.6–142.15°K	18.42
Transition and $\int_{142.15}^{144.45} Cp(\text{solid I}) d \ln T$	0.74
Fusion, 1014/144.46	7.02
Graphical, liquid, 144.46–154.5°K	1.65
Vaporization at 154.5°K, $p=0.2185$ atmos.	28.55
Correction for gas imperfection	0.04
Entropy of ideal gas at 154.5°K and $p=0.2185$ atmos.	56.97
Compression to 1 atmos.	−3.02
Entropy of ideal gas at 154.5°K and $p=1$ atmos.	53.95
$S^0_{298.16} - S^0_{154.5}$	6.85
Entropy of ideal gas at 298.16°K and $p=1$ atmos.	60.80

transition. This indicates an average heat capacity in this narrow region of 37.8 cal. deg.$^{-1}$ mole^{-1}. This is in qualitative agreement with their statement: "In this region the heat capacity was abnormally high (the minimum value was ∼35 cal. deg.$^{-1}$ mole^{-1})." It would appear that the entropy change in going from 142.15° to 144.46°K should be 0.74 cal. deg.$^{-1}$ mole^{-1}.

Kelley[18] recalculated the entropy of boron trifluoride in essentially the same manner, but with satisfactory graphical areas. His result was $S^0_{298.1} = 61.4$ cal. deg.$^{-1}$ mole^{-1}.

Pohland and Harlos[17] determined the vapor pressure of liquid boron trifluoride at thirteen temperatures in the range 145.9° to 170.3°K. Their equation

$$\log p \text{ (in mm Hg)} = -1174.4/T + 1.75 \log T - 0.013350T + 8.0536$$

is a fair representation of their data, $\sum(p_{obs.} - p_{calcd.})$ for six positive and seven negative deviations totaling 5 and 7 mm, respectively. Four values in the range 187.5 to 653 mm by Fischer and Weidemann[19] are in good agreement with the equation of Pohland and Harlos. Other measurements extant in this pressure range[20] do

not merit equal consideration since the samples were not pure or the measurements were made with insufficient accuracy.

If one uses the equation of Pohland and Harlos, with the assumption that the vapor obeys the approximate Berthelot equation of state in the region concerned

$$\Delta H_{\text{vap}} = RT^2 \frac{d \ln p}{dT}\left[1 + \frac{9}{128}\frac{pT_c}{p_c T}\left(1 - \frac{pT_c^2}{T^2}\right)\right] - \frac{pV_{\text{liq}}}{RT},$$

where $p_c = 49.2$ atmos., $t_c = -12.25°C$,[21] and $\rho(\text{liquid}) = 2.25 - 0.003928T$, based on Fischer and Weidemann's data, the heat of vaporization at the temperature and pressure used by Eucken and Schröder and by Kelley is 4411 cal. mole^{-1}, and $\Delta S(\text{vap.}) = 29.55$ cal. deg.$^{-1}$ mole^{-1}. This replaces 28.68 and 28.74 given by Eucken and Schröder and Kelley, respectively.

The recalculation of the entropy of boron trifluoride in the ideal gas state at 298.16°K and 1 atmosphere is summarized in Table IV. For the present calculations the entropy change $S^0_{298.16} - S^0_{154.5}$ was obtained from the values of $S^0_{298.16}$ and $S^0_{154.5}$ derived from the spectroscopic data, rather than by an integration of calculated heat capacities in the region.

Similar calculations at each of the nine intermediate temperatures at which Pohland and Harlos measured the vapor pressure (i.e., excluding the three lowest and one highest temperatures) gave $S^0_{298.16} = 60.69$ (average) cal. deg.$^{-1}$ mole^{-1}, with six positive deviations totaling 0.37 and three negative deviations totaling 0.39. The agreement with the statistically calculated value of Table I, 60.70, is excellent. Eucken and Schröder and Kelley's statistically calculated values were 61.11 and 61.4 cal. deg.$^{-1}$ mole^{-1}, respectively.

The entropies of boron trichloride and boron tribromide calculated from the spectroscopic data by Kelley[18] 68.6 and 76.7 cal. deg.$^{-1}$ mole^{-1}, respectively, are in error as a result of the use of the harmonic $2\nu_2$ in place of the fundamental ν_2.

[18] K. K. Kelley, U. S. Bur. Mines, Bull. No. 434 (1941).

[19] W. Fischer and W. Weidemann, Zeits. f. anorg. allgem. Chemie 213, 106 (1933).

[20] O. Ruff et al., Zeits. f. anorg. allgem. Chemie 206, 59 (1932); L. LeBoucher and W. Fischer with W. Biltz, ibid., 207, 61 (1932).

[21] H. S. Booth and J. M. Carter, J. Phys. Chem. 36, 1359 (1932).