Thermochimica Acta, 141 (1989) 125–130
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

NEW ESTIMATES FOR THE THERMODYNAMIC FUNCTIONS OF MOLECULAR BORIC ACID

B.R. BOWSHER and S. DICKINSON

United Kingdom Atomic Energy Authority, Winfrith, Dorchester, Dorset (Gt. Britain)

J.S. OGDEN * and N.A. YOUNG

Dept. of Chemistry, University of Southampton, Southampton (Gt. Britain)

(Received 26 April 1988)

ABSTRACT

Thermodynamic functions for molecular boric acid (H_3BO_3) have been calculated, based on vibration frequencies recently obtained from matrix isolation IR studies. Comparison with existing JANAF data shows a number of significant differences, and the effect of these on selected high temperature equilibria involving H_3BO_3 is explored.

INTRODUCTION

The behaviour of boric acid at high temperatures has been the subject of numerous publications [1], and is of particular interest in view of the possible equilibria which may exist between certain fission product species, for example CsI, and H_3BO_3 [2]. Compilations of thermodynamic data such as JANAF [3] include data for molecular H_3BO_3, but, unlike many similar tabulations, the thermodynamic data available for this species are not firmly based on experimental data. The principal reason for this is that, apart from the mass spectrometric detection of the ion $H_3BO_3^+$ in the high temperature reaction between B_2O_3 and H_2O [4], there are very few reports describing the definitive characterization of this molecule.

As a result, the vibration frequencies and structural parameters of molecular boric acid have generally been assumed to be the same as those found in the solid, or, if these data are not available, have been estimated. Thermodynamic data obtained in this way might still be expected to be reasonably valid at low temperatures, but at higher temperatures any errors associated with, for example, absolute entropies, will become more significant. In this event, predictions of thermodynamic equilibria will be correspondingly less reliable.

---

* Author to whom correspondence should be addressed.

0040-6031/89/$03.50

However, very recent mass spectrometric and matrix isolation studies on boric acid [5] have not only provided firm evidence for the existence of molecular H_3BO_3 at relatively low temperatures (300–400 K), but have also established both the frequencies and assignments for several of the fundamentals, notably the low frequency torsion modes.

The purpose of this note is to provide new estimates for the thermodynamic functions of molecular H_3BO_3 based on these most recent spectroscopic data, and to re-investigate predictions of selected thermodynamic equilibria to assess the significance of these results.

SPECTROSCOPIC STUDIES ON MOLECULAR H_3BO_3 [5]

When crystalline orthoboric acid is heated in vacuo to about 310 K, it vaporizes to yield molecular H_3BO_3. Under these conditions, both the parent ion and the fragment $H_2BO_2^+$ may readily be observed by mass spectrometry. Corresponding matrix isolation IR studies have revealed six of the ten vibrational fundamentals directly, and a further three may be estimated to within approximately 10 cm^{-1} on the basis of a restricted force constant analysis. Table 1 compares these nine fundamentals with previously accepted values, and also includes the frequency of the remaining fundamental (A′ BO stretch) which has been estimated from Raman studies on the solid [1,6,7].

The principal difference between the matrix IR data and the vibration frequencies of the solid lies in the positions of the modes involving significant hydrogen atom motion. This difference arises primarily from the

TABLE 1

Fundamental frequencies (cm^{-1}) of molecular boric acid

Most recent work [5,11]	Previous			Assignment
A	a	b	c	
3672.6 d	3250	3250	3600	A′ OH stretch
1020.0 d	1060	1060	1080	A′ HOB bend
(880.0)	881	881	880	A′ BO stretch
675.0	648	652	625	A″ BO_3 bend
3668.5	3150	3150	3600	E′ OH stretch
1426.2	1428	1440	1490	E′ BO stretch
1009.9	1183	1185	1200	E′ HOB bend
448.9	544	544	540	E′ OBO bend
513.8	824/303	(rotation)	600	A″ torsion
577.7 d	209	(rotation)	600	E″ torsion

Key: A, values used to determine thermodynamic functions; a, data from refs. 1, 6 and 7; b, data used in JANAF [3]; c, data used by Glushko et al. [8]; d, calculated values.

extensive hydrogen bonding network which is present in the solid, but absent in the isolated molecule, and is particularly significant in connection with the out-of-plane torsion modes. These modes have variously been assigned at 824 or 303 cm^{-1} (A″), and at 209 cm^{-1} (E″), and these three degrees of freedom were treated as internal rotations in the JANAF compilation of thermodynamic data [3].

The matrix IR experiments place these torsion modes at 513.8 and approximately 577 cm^{-1} on the basis of isotope studies, and also establish the overall planarity of the molecule (symmetry C_{3h}). This shape is consistent with a π-system extending over the central BO_3 unit, and such a bonding scheme would be expected to provide a substantial barrier to free internal rotation. A further consequence of these isotope studies is that they permit reasonably precise estimates for two of the three inactive A′ modes:

TABLE 2

Thermodynamic functions for molecular boric acid

T (K)	$H_T - H_{298}$ ($J\ mol^{-1}$)	C_{p_T} ($J\ mol^{-1}\ K^{-1}$)	S_T ($J\ mol^{-1}\ K^{-1}$)	$-(G_T - H_{298})/T$ ($J\ mol^{-1}\ K^{-1}$)
(a) Present work				
100	−10200	34.96	215.37	317.37
200	−5972	51.42	244.01	273.87
298	0	70.02	268.07	268.07
300	140	70.37	268.54	268.07
400	7971	85.54	290.96	271.03
500	17116	96.80	311.32	277.09
600	27233	105.12	329.74	284.35
700	38075	111.46	346.44	292.05
800	49482	116.52	361.67	299.81
900	61350	120.72	375.64	307.47
1000	73607	124.32	388.55	314.94
1100	86200	127.47	400.55	322.19
1200	99090	130.26	411.76	329.19
1300	112241	132.73	422.29	335.95
1400	125627	134.93	432.21	342.47
1500	139220	136.90	441.59	348.77
(b) Selected JANAF data [3]				
298	0	65.27	294.85	294.85
500	15416	86.28	333.87	303.03
1000	66391	113.69	403.45	337.06
1500	126838	126.64	452.29	367.73
(c) Selected data (Glushko [8])				
298	0	65.82	264.52	264.52
500	16268	92.90	305.60	273.06
1000	71444	122.76	380.91	309.46
1500	136562	136.31	433.53	342.49

the symmetric OH stretch, and the symmetric HOB bend. These vibration frequencies may be estimated to a precision of better than about 10 cm^{-1} from a detailed analysis of the spectrum of partially enriched molecules such as H_2DBO_3 or $H_3B^{16}O_2^{18}O$.

As a result of these IR studies, the only fundamental of molecular H_3BO_3 for which no experimental estimate is available is the symmetric BO stretch. However, this mode is not expected to involve significant hydrogen atom motion, and its value in the vapour phase molecule is therefore likely to be very similar to the value of 880 cm^{-1} found in the solid (Table 1).

THERMODYNAMIC FUNCTIONS FOR MOLECULAR H_3BO_3

The new thermodynamic functions for molecular H_3BO_3 have been calculated using standard procedures, and these data are listed in Table 2(a). The vibration frequencies used are those listed in column A of Table 1, and the geometrical parameters for the monomer are taken to be: r(B–O) = 136 pm; r(O–H) = 96 pm; O–B–O = 120°; and H–O–B = 130°. This table also includes corresponding thermodynamic data from JANAF [3], and it is evident that there are significant differences, notably in respect of entropies and specific heats. Over the temperature range 500–1500 K, these differences are typically ~ 5%, and the resulting effect on chemical equilibria involving molecular H_3BO_3 could therefore be substantial. This may be illustrated by considering the high temperature reactions between H_3BO_3 and the alkali metal iodides, which have attracted considerable attention in recent years [2]. Also included in this table is a more recent compilation by Glushko et al. [8] based on an alternative set of estimated parameters.

THE REACTIONS OF BORIC ACID WITH ALKALI METAL IODIDES AT ELEVATED TEMPERATURES

Contrary to earlier assumptions, it is now generally accepted that boric acid will react with alkali metal iodides at elevated temperatures to form hydrogen iodide [9]

$$MI + H_3BO_3 \rightarrow MBO_2 + HI + H_2O$$

where M is Li–Cs. This reaction is of particular interest in the nuclear industry, where there is the possibility of reaction between boric acid and the fission products caesium and iodine.

Walton [10] has attempted to assess the extent of this reaction for all the alkali metal iodides, and he has obtained values for the appropriate equilibrium constants over a wide range of experimental conditions. These values are based on the JANAF tabulations of thermodynamic data, and as a result, all equilibria involving molecular H_3BO_3 use data based on estimated vibration frequencies. As indicated above, this may lead to significant errors at high temperatures.

We have carried out similar calculations for two of the above reactions using firstly the new data for molecular H_3BO_3, and secondly the JANAF data presented in Table 1. The two systems chosen were

(a) $LiI(s) + H_3BO_3(g) \rightarrow LiBO_2(s) + HI(g) + H_2O(g)$ and

(b) $CsI(s) + H_3BO_3(g) \rightarrow CsBO_2(s) + HI(g) + H_2O(g)$

The values obtained are summarized in Table 3 and, for the $CsI–H_3BO_3$ system in particular, it is found that the new data lead to equilibrium constants which are typically approximately 20 times greater over the temperature range 500–1500 K.

These new calculations predict that hydrogen iodide evolution from this system will in practice take place at a significantly lower temperature than might previously have been anticipated. This conclusion is supported by recent experimental studies which have established that such evolution can occur at temperatures as low as around 700 K [11].

TABLE 3

Free energy changes for the reactions [a] $MI(s) + H_3BO_3$

	T (K)	ΔG_T (kJ mol^{-1})		Equilibrium constant (atm)	
		(a)	(b)	(a)	(b)
(i) $LiI–H_3BO_3$	298	1.06	9.08	6.5×10^{-1}	2.5×10^{-2}
	500	−17.82	−4.64	$7.3\times10^{+1}$	3.0
	700	−36.72	−18.08	$5.5\times10^{+2}$	$2.5\times10^{+1}$
	900	−55.75	−33.09	$1.7\times10^{+3}$	$8.7\times10^{+1}$
	1100	−74.88	−48.28	$3.6\times10^{+3}$	$2.0\times10^{+2}$
	1300	−94.11	−63.45	$6.1\times10^{+3}$	$3.5\times10^{+2}$
	1500	−113.04	−78.83	$9.0\times10^{+3}$	$5.6\times10^{+2}$
(ii) $CsI–H_3BO_3$	298	114.23	112.25	9.0×10^{-21}	3.5×10^{-22}
	500	91.21	104.04	2.9×10^{-10}	1.2×10^{-11}
	700	66.73	84.65	1.0×10^{-5}	4.7×10^{-7}
	900	41.07	63.43	4.0×10^{-3}	2.1×10^{-4}
	1100	14.49	41.09	2.0×10^{-1}	1.1×10^{-2}
	1300	−12.83	17.83	3.3	1.9×10^{-1}
	1500	−40.79	−6.21	$2.6\times10^{+1}$	1.6

[a] Calculated for $MI(s) + H_3BO_3(g) \rightarrow MBO_2(s) + HI(g) + H_2O(g)$, assuming the relationship [10] $\Delta G_T = \Delta H_{298} + \Delta C_{p_{298}}(T - 298) - T(\Delta S_{298} + \Delta C_{p298} \ln(T/298))$, with data for H_3BO_3 based on (a) matrix IR vibrational data and (b) the JANAF tabulations.

CONCLUSIONS

New thermodynamic data are presented for molecular boric acid, based almost entirely on experimental observations. In general, it is found that over the temperature range 500–1500 K the specific heat and absolute entropy show differences of ~ 5% compared with the JANAF tabulations. As a result the equilibrium constants of high temperature reactions between molecular H_3BO_3 and alkali metal iodides are predicted to be significantly larger than the available estimates. Other high temperature reactions involving molecular H_3BO_3 may similarly need to be re-examined.

ACKNOWLEDGEMENTS

We gratefully acknowledge the support of the SERC for this work through the provision of a CASE studentship (to N.A.Y.), and wish to thank Dr A.L. Nichols (Winfrith) and Dr P.E. Potter (Harwell) for their interest in this project.

REFERENCES

1 J.W. Mellor, (Ed), A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, London, 1980, Vol 5, Suppl. 1, Part A.

2 B.R. Bowsher, Prog. Nucl. Energy, 20 (1987) 199.

3 JANAF, Thermochemical Tables, 2nd edn., NSRDS-NBS 37, Nat. Bur. Stand. (US), 1971.

4 D.J. Meschi, W.A. Chupka and J. Berkowitz, J. Chem. Phys., 33 (1960) 530.

5 J.S. Ogden and N.A. Young, J. Chem. Soc. Dalton Trans., (1988) 1645.

6 F.T. Green, G.E. Leroi, S.P. Randall, J.R. Soulen, L.H. Spinar and J.L. Margrave, Proc. Propellant Thermodynamics and Handling Conf., 20–21 July 1959, Ohio State University Special Report, 1960, p. 12 and p. 23.

7 L.A. Kristiansen, R.W. Mooney, S.J. Cyvin and J. Brunvoll, Acta Chem. Scand., 19 (1965) 1749.

8 V.P. Glushko, L.V. Gurvich, G.A. Bergman, I.V. Veits, V.A. Medvedev, G.A. Khachkuruzov and V.S. Yungman, Thermodynamic Properties of Individual Substances, Pergamon, 1988, 3rd edn. part 1.

9 A.M. Deane and P.E. Potter, (Eds), Proc. Specialists Workshop on Iodine Chemistry in Reactor Safety, AERE Harwell, 11–12 September 1985, UKAEA Report AERE-R 11974, 1986.

10 G.N. Walton, AERE Harwell, unpublished data, 1987.

11 N.A. Young, PhD Thesis, University of Southampton, 1988.