Enthalpy and Entropy Increments above 298° K. for $BiBr_3$, Bi_2O_3, Tl_2O_3, and Tl_2O

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Enthalpy increments above 298° K. were measured in a drop calorimeter for solid and liquid $BiBr_3$, Bi_2O_3, and Tl_2O, and for solid Tl_2O_3. The values were fitted to polynomial equations, from which enthalpy and entropy increments above 298° K. were calculated at even temperatures.

THE RESULTS in this paper are from studies of the thermodynamics of vaporization of inorganic substances. Enthalpy increment data of this type are needed to evaluate the enthalpy of vaporization from vapor pressure data and to convert the data from high temperatures to room temperature.

EXPERIMENTAL

Method. The enthalpy measurements were made by essentially the same method as that reported previously (*1*, *3*).

Materials. Bismuth tribromide was prepared by dissolution of reagent grade Bi_2O_3 in reagent grade HBr solution,

Table I. Measured Enthalpy Increments,

(*A*) $BiBr_3$, Solid I

$$(H_T - H_{298}) = (-10.68 + 4.355 \times 10^{-2}T - 2.587 \times 10^{-5}T^2)\ (\pm 0.048),\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
298	0	-0.001
373	1.95	0.00
397	2.50	-0.037
397	2.60	0.072
404	2.70	0.003
409	2.77	-0.038
426	3.14	-0.04
427	3.25	0.05
429	3.19	-0.06
431	3.29	0.009

(*B*) $BiBr_3$, Solid II

$$(H_T - H_{298}) = (-33.46 + 0.14411T - 1.3259 \times 10^{-4}T^2)\ (\pm 0.058),\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
437	4.27	0.081
442	4.31	-0.019
443	4.27	-0.008
444	4.37	0.010
447	4.42	-0.049
450	4.55	0.019
460	4.73	-0.038
461	4.88	0.075
481	5.20	0.007
482	5.25	0.054
483	5.13	-0.083
483	5.26	0.048
487	5.29	0.008
489	5.27	-0.033

(*C*) $BiBr_3$, Liquid

$$(H_T - H_{298}) = (-7.95 + 3.974 \times 10^{-2}T - 5.27 \times 10^{-6}T^2)\ (\pm 0.20)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
497	10.24	-0.26
513	10.93	-0.11
502	10.59	-0.10
512	11.00	-0.01
541	11.93	-0.07
577	13.33	0.10
535	12.24	0.42
541	12.16	0.15
650	15.62	-0.04
748	18.70	-0.11
813	21.11	0.23
848	21.73	-0.23
942	24.70	-0.12
999	26.69	0.19
1022	27.10	-0.07
1129	30.41	0.20
1131	30.07	-0.18

(*D*) Bi_2O_3, Solid I

$$(H_T - H_{298}) = (-6.91 + 1.957 \times 10^{-2}T + 1.398 \times 10^{-5}T^2 - 5.39 \times 10^{-9}T^3)\ (\pm 0.089)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
298	0	-0.02
329	0.828	-0.01
371	2.047	0.05
372	2.111	0.08
430	3.52	-0.13
464	4.58	-0.06
495	5.60	0.07
509	5.92	-0.04
582	8.13	-0.03
639	10.00	0.12
645	10.12	0.04
788	14.44	-0.11
818	15.43	-0.06
879	17.48	0.04
882	17.46	0.05
926	19.08	0.16
972	20.28	-0.07

evaporation to dryness, and distillation, under dry N_2, to separate it from the oxybromide formed. This material was redistilled, under dry N_2, into quartz glass sample tubes; the tubes were then sealed off. Analysis for bromide indicated 53.39 ± 0.01% as compared with 53.43% (theoretical).

The Bi_2O_3 used was Baker and Adamson reagent grade material. The Tl_2O_3 was part of the sample used previously for vaporization studies (2). The Tl_2O was prepared as follows: Tl was dissolved in ethyl alcohol while a slow stream of O_2 bubbled through the alcohol to form thallous ethylate. Air was excluded from the solution to avoid CO_2 contamination. The ethylate was hydrolyzed with CO_2-free water. The alcohol and excess water were removed by warming to about 150° C. in a stream of dry N_2 to form Tl_2O. The product, handled in a gloved box under dry N_2 to avoid contamination by CO_2 or O_2, was then analyzed for Tl by the chromate method and was found to contain 96.54 ± 0.04% Tl as compared with 96.23% (theoretical). For each of the three oxides, a sample was placed in a platinum test tube and the end sealed by crimping and soldering with platinum solder.

The melting and transition temperatures of the Bi_2O_3, Tl_2O_3, and Tl_2O were determined by thermal analysis. A Pt-Rh thermocouple, calibrated against the melting point of NaCl, was wired tightly to the outside middle of each platinum capsule. Replicate cooling and heating curves were obtained on each sample.

For Bi_2O_3, a sharp melting point of 828 ± 1° C. was observed. This value compared with the literature (*7, 9*) values, which range from 817° to 825° C. The transition temperature, near 730° C., showed supercooling and superheating effects. The transition temperatures observed during heating and cooling were most nearly alike when observed on a powdered sample that had not been melted and when the heating and cooling rates were smallest (0.8° C. per minute for heating and 0.3° per minute for cooling). The transition temperatures observed were 725° C. on cooling and 734° C. on heating. The equilibrium value is presumed to lie between these, and 730 ± 5° C. was selected to represent it. This value compared well with the literature value (*7*) of 730° C.

The freezing point of Tl_2O was 579° C. The break in the cooling curve was not so sharp as that of the other

Analytical Equations, and Deviations

(*E*) Bi_2O_3, Solid II

$$(H_T - H_{298}) = (-7.35 + 3.588 \times 10^{-2}T)\ (\pm 0.18)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
1006	28.95	0.19
1019	28.97	−0.23
1019	29.06	−0.15
1022	29.39	0.08
1051	30.50	0.14
1072	31.17	0.08
1077	31.19	−0.12

(*F*) Bi_2O_3, Liquid

$$(H_T - H_{298}) = (861.03 - 1.12052T + 3.0636 \times 10^{-7}T^3)\ (\pm 0.18)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
1109	36.32	0.11
1111	36.08	−0.16
1117	36.36	0.01
1129	36.85	0.02
1140	37.68	0.20
1150	38.10	−0.23
1168	43.00	0.06

(*G*) Tl_2O, Solid

$$(H_T - H_{298}) = (-5.44 + 1.736 \times 10^{-2}T + 2.85 \times 10^{-6}T^2)\ (\pm 0.035)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
298	0	0.007
372	1.40	−0.02
373	1.43	−0.01
427	2.54	0.04
465	3.25	0.005
493	3.76	−0.05
491	3.81	0.04
506	4.07	−0.004
579	5.52	−0.05
642	6.94	0.06
745	9.07	−0.002
785	9.93	−0.008
811	10.51	−0.001

(*H*) Tl_2O, Liquid

$$(H_T - H_{298}) = (35.09 - 3.950 \times 10^{-2}T + 2.787 \times 10^{-8}T^3)\ (\pm 0.032)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
857	18.73	−0.03
859	18.81	0.001
864	18.98	0.05
872	19.11	−0.005
926	20.65	0.02
913	20.21	−0.02
914	20.26	−0.004

(*I*) Tl_2O_3, Solid

$$(H_T - H_{298}) = (-4.43 + 5.05 \times 10^{-3}T + 3.970 \times 10^{-5}T^2 - 1.897 \times 10^{-8}T^3)\ (\pm 0.16)\ \text{kcal./mole}$$

Temperature, °K.	$H_T - H_{298}$ Measured, Kcal./Mole	Deviation, Obsd. Minus Calcd., Kcal./Mole
298	0	−0.10
372	2.02	0.05
427	3.66	0.16
466	4.72	0.11
493	5.30	−0.13
507	5.91	0.04
580	8.08	−0.07
643	10.10	−0.08
742	13.27	−0.14
850	16.89	0.006
860	17.30	0.11
868	17.60	0.14
922	19.19	0.09
925	18.95	−0.02
968	20.71	0.27
978	20.70	−0.02
979	20.85	0.09
1000	21.07	−0.03

compounds. Since the analysis for Tl was higher than theoretical, there may have been some Tl dissolved in the sample. After the enthalpy measurements were made, the platinum container was opened and examined. The container had not changed weight and did not appear corroded.

An attempt was made to determine the melting point of the Tl_2O_3. On heating, there was a break in the curve at 834° C. A few minutes later, a leak appeared in the platinum container, which was later found to be badly corroded—possibly by the formation of $Tl_2Pt_2O_7$ (*5*). Therefore, enthalpy measurements were made on a fresh sample but only up to 700° C. After the measurements had been taken, the container was opened and examined for corrosion. Its weight had increased and a thin black deposit had formed inside—presumably a mixed thallium-platinum oxide. Because the corrosion was not severe, the enthalpy measurements were considered to be valid for Tl_2O_3, especially for temperatures below 700° C.

Because the $BiBr_3$ was sealed in relatively thick-walled quartz glass ampoules, the melting and transition points could not be determined. Literature values were used instead. Yosim *et al.* (*12*) give the melting point as 491.7° K. and from this value, the transition temperature was calculated as 431° K. Topol and Ransom (*10*) report the same transition temperature.

Table II. Enthalpy and Entropy Increments above 298° K., Calculated from Equations

Temperature, ° K.	$H_T - H_{298}$, Kcal./Mole	$S_T - S_{298}$, E.U.
	(*A*) $BiBr_3$	
350	1.39	4.30
400	2.60	7.53
431(I)	3.28	9.18
ΔH (trans) = 0.74 kcal./mole		
ΔS (trans) = 1.71 e.u.		
431(II)	4.02	10.89
450	4.54	12.07
491.7(II)	5.34	13.45
ΔH (fusion) = 4.98 kcal./mole		
ΔS (fusion) = 10.11 e.u.		
491.7(l)	10.32	23.56
500	10.60	24.14
600	14.00	30.34
700	17.29	35.41
800	20.47	39.66
900	23.55	43.29
1000	26.52	46.43
	(*B*) Bi_2O_3	
400	2.80	8.02
500	5.69	14.46
600	8.69	19.93
700	11.78	24.68
800	14.92	28.88
900	18.09	32.60
1000	21.23	35.92
1003(I)	21.32	36.01
ΔH (trans) = 7.31 kcal./mole		
ΔS (trans) = 7.29 e.u.		
1003(II)	28.63	43.31
1101(II)	32.15	46.65
ΔH (fusion) = 3.99 kcal./mole		
ΔS (fusion) = 3.62 e.u.		
1101(l)	36.14	50.27
1200	45.69	58.47
	(*C*) Tl_2O	
400	1.96	5.69
500	3.96	10.11
600	6.01	13.86
700	8.12	17.10
800	10.28	19.99
852(s)	11.42	21.39
ΔH (fusion) = 7.24 kcal./mole		
ΔS (fusion) = 8.50 e.u.		
852(l)	18.66	29.89
900	19.85	31.14
1000	23.45	35.02
	(*D*) Tl_2O_3	
400	2.73	7.55
500	5.65	14.05
600	8.79	19.79
700	12.05	24.80
800	15.30	29.15
900	18.44	32.85
1000	21.34	35.91

RESULTS AND DISCUSSION

Enthalpy and Entropy Increments. The enthalpy increments above 298° K. measured for each phase were fitted to polynomial equations in T, T^2, and T^3 by a least squares method. The equation giving the smallest standard deviation from the experimental points was selected to represent the data. The fitting was done by computer using the Institute's Regression Program. The measured enthalpy increments, the equations selected to represent them, and the deviations of the observed points from the equations are given in Table I. The uncertainties quoted for the equations are the standard deviations of the points from the equations. The enthalpy and entropy increments calculated from the equations at uniform temperatures above 298° K. are given in Table II.

The measurements on all the samples, except $BiBr_3$, were straightforward. The results obtained on solid $BiBr_3$ in the range 431° to 491.7° K. were erratic (Figure 1). They fell into two groups—an upper set that defined a curve well and a lower set that was scattered. The authors assumed that this indicated that the transformation to the low temperature form in the calorimeter, after the drop, was incomplete. Thus, the upper set of points represents the enthalpy increments of the high temperature form, and the lower set of data represents results on material that was only partially transformed.

Comparison of Results with Literature. There are no literature values for enthalpy increments for Tl_2O and Tl_2O_3. For $BiBr_3$, Topol and Ransom (*10, 11*) have reported enthalpy increments for the solid and liquid at the melting point and the enthalpy of fusion. Their values for these quantities are 5.11, 10.30, and 5.19 kcal. per mole, respectively, while the present authors' values for the same quantities are 5.34, 10.32, and 4.98. Their data point for the solid is shown in Figure 1. However, their value may be low for the same reason that several of our points were low—because of incomplete transformation. Their value for the liquid at the melting point is in good agreement with ours.

For Bi_2O_3, the only heat capacity data available for comparison are those of Hauser and Steger (*4*). They reported enthalpy increments (above 20° C.) for six temperatures. In Table III, their data have been converted to kilocalories per mole of Bi_2O_3, and the enthalpy increment has been

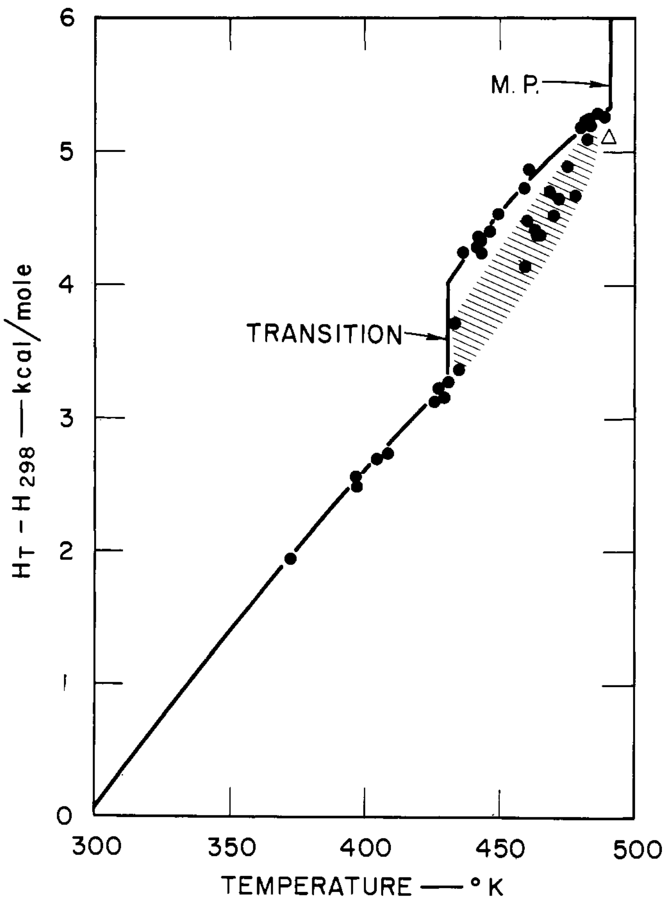

Figure 1. Enthalpy increment data for solid $BiBr_3$

Data points are indicated by dots. Curves represent the analytical expressions given in Table I. Shaded region indicates data observed for only partially transformed material. Triangle is value given for the solid by Topol and Ransom (*10*)

Table III. Comparison of Data for Bi_2O_3

Temperature, °K.	$H_T - H_{298}$ Data of Hauser and Steger (*4*), Kcal./Mole	$H_T - H_{298}$ Calcd. from Data in Table II, Kcal./Mole
373	2.12	2.19
477	5.13	5.16
585	8.23	8.38
686	11.31	11.49
766	14.03	14.31

calculated from our equation (adding 0.14 kcal. per mole to each value to give the increment above 20° C.). The comparison shows that our enthalpy increments are slightly larger than those of Hauser and Steger (*4*). The enthalpy increment values given by Kelley (*6*) are based on those of Hauser and Steger and are also slightly smaller than our values. Levin and McDaniel (*8*) have determined the heats of transformation and fusion for Bi_2O_3 by a DTA method. They found 9.9 and 3.9 kcal. per mole compared with the present values of 7.31 and 3.99 for transformation and fusion, respectively. No explanation for the large difference between these values of the heat of transformation is apparent.

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Received for review May 8, 1967. Accepted June 23, 1967. Work supported by the Research Division of the U. S. Atomic Energy Commission under Contract No. AT(04-3)-106.