Thermodynamic Properties of Group 3 Oxides

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Contents

I. Introduction

The most recent review of the thermodynamic properties of the oxides was that made by Brewer[12] in 1953. At that time there were very few experimental data available and Brewer provided estimates for a great number of the species. However, during the last two decades numerous experimental papers have appeared involving thermodynamic properties of the oxides. The advent of the mass spectrometer as a research tool for obtaining thermal properties, bond energies, and other thermal data allowed publication of results for many of the previously uninvestigated gaseous oxides. The use of precision calorimetry for the condensed species and improved spectroscopic, mass spectroscopic, and other thermodynamic and thermochemical techniques also resulted in the reporting of considerable data in the literature. Since an undertaking to include thermodynamic properties of the oxides of the entire periodic table would result in too large a volume for a journal review article, this review is confined to periodic group 3.

The thermodynamic properties of boron and aluminum oxide species have been extensively researched in the last two decades, and for the most part definitive values can be presented for these species. However, fewer publications have appeared involving the other three elements and additional work will be required on some of these species before definitive values can be recommended.

II. Scope of the Review

This review paper discusses the literature through 1977 with 213 references presenting thermodynamic data for the group 3 oxides, B, Al, Ga, In and Tl, and includes recommendations for values to be employed by investigators in the field. It is more extensive than other compilations and contains results not previously presented.

Section III presents a critical review of the data on the heat of formation of the solid and liquid phases, as well as specific heats and entropies, and heat of fusion data. The heats of formation of the gaseous suboxides, including ionic species, are discussed in section IV.

Except for the species AlO, BO, BO_2, B_2O_2,[167] and GaO[187] very few experimentally determined spectroscopic constants have been reported for the gaseous oxides of the above-mentioned elements. In nearly all other cases the various table compilers have employed estimated constants for the calculation of $C_p{}^\circ{}_{298}$ and $S^\circ{}_{298}$ values by assuming that the molecules are rigid rotators and have harmonic vibrations. In the case of the gaseous boron and aluminum oxide species the JANAF Tables[167] have estimated electronic states, quantum weights, and vibrational and rotational constants as well as other structural parameters. From these they calculated the thermal functions to 5000 K at 100 K intervals. Therefore, unless otherwise specifically mentioned, the specific heats and entropies of the gaseous oxides of aluminum and boron at 298 K are taken from the JANAF Tables.[167] This excellent compilation is indispensable for any thermodynamic calculations. The $C_p{}^\circ{}_{298}$ and $S^\circ{}_{298}$ values for the oxides of Ga, In, and Tl, if reported, are referenced separately.

In order for the data in this review to be as widespread as possible, all values listed in the tables were calculated using a consistent set of auxiliary data. Thus, unless otherwise noted, the free energy functions and auxiliary data for boron and aluminum were taken from the JANAF Tables,[167] including all supplements through December 1976. The auxiliary data for the atoms Ga, In, and Tl were taken from Kubaschewski, Evans, and Alcock.[100] The values of $\Delta H_f{}^\circ$ and D° are in kilocalories per mole, and those of $C_p{}^\circ$ and S° are in gibbs per mole for the molecular formula written and at a temperature of 298 K, unless otherwise specified.

The values reported in the tables of this review may differ in some cases from those reported in the publications cited. This is the result of a recalculation of the original equilibrium data employing more recent auxiliary data, which were probably not available to the authors at the time of their publications. Caution should be exercised if these values must be combined with data taken from other compilations or sources, in order to avoid errors caused by a lack of consistency between the tables.

Where experimental data have been reported, the authors chose to recommend the value of the thermodynamic property which in their judgment was the most reliable and definitive. This may differ in some cases with other compilers who chose to recommend a value obtained by averaging several experimental results.

Recommended values for heats of formation, $\Delta H_f{}^\circ$, $C_p{}^\circ$, S°, melting temperatures, T_m, and heats of melting, $\Delta H_m{}^\circ$, for the

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TABLE I. Thermodynamic Data for B_2O_3(c)

heat of solution, kcal/mol		$\Delta H_r°$ [c]	$\Delta H_f°_{298}(B_2O_3(c))$,	
$H_{soln}(B_2O_3(c))$ [a]	$H_{soln}(H_3BO_3(c))$ [b]	kcal/mol	kcal/mol	ref
−3.56	5.30	−14.16	−303.8	180
−3.41	5.10	−13.61	−304.4	132
−3.49	5.30	−14.09	−303.9	89
−3.48	5.27	−14.02	−303.9	156
−3.49	5.17	−13.83	−304.2	177
−3.45	5.45	−14.35	−303.6	44
	$\Delta H_c°_{298}$ [d]	−238.8	−304.0	83

[a] $\Delta H_{soln}(B_2O_3(c))$ for $B_2O_3(c) + 3H_2O(l) \rightarrow 2H_3BO_3(aq)$. [b] $\Delta H_{soln}(H_3BO_3(c))$ for $H_3BO_3(c) \rightarrow H_3BO_3(aq)$. [c] ΔH_r for $B_2O_3(c) + 3H_2O(l) \rightarrow 2H_3BO_3(c)$. [d] ΔH_c for $B_2O_3(c) + 3F_2(g) \rightarrow 2BF_3(g) + 1.5O_2(g)$.

oxides (*c*,1) for which sufficient basic thermal data exist are given in Table VIII. Similarly, recommended $C_p°$, $S°$, and $\Delta H_f°$ values for the gaseous oxides, including ionic species, are summarized in Table IX. An effort has been made to give the probable limits of accuracy of the values in these tables. In some cases these limits of accuracy have been arbitrarily widened to take into account the reliability of the experimental results reviewed by the authors. In order to limit the length of the manuscript, discussions of results are kept to a minimum; however, all references are listed for the benefit of the readers.

III. Thermodynamic Properties of Solid and Liquid Phases

This section presents a critical review of the thermodynamic properties of the solid species B_2O_3, Al_2O_3, Ga_2O_3, In_2O_3, Tl_2O_3, and Tl_2O, and the liquid phase. Heats of formation of the various crystalline forms have been determined from calorimetric, solution, and DTA experiments. Calorimetric studies have established the heat of fusion and the heat capacity. A discussion of the individual oxides follows.

A. Boron Oxides

1. $B_2O_3(c, 1)$

Direct measurement of the heat of combustion of boron in oxygen is difficult since its combustion leads to ΔH_f(glass) values (ref 35, 36, 53, 113, 126, 130, 172), with the heat of formation values ranging from −280 to −368 kcal/mol. More definitive values for the heat of formation of boric oxide have been obtained from (a) solution experiments for boric oxide to form boric acid (ref 44, 89, 132, 156, 177, 180); solution experiments involving the heat of pyrolysis of diborane to its elements[121] combined with the heat of hydrolysis of diborane;[122] the hydrolysis of BCl_3 (ref 64, 84, 155); and (b) the heat of combustion of B_2O_3(c) in fluorine.[83]

Published values of the various heats of combustion and heats of solution experiments are listed in Table I. In order to obtain the ΔH_f of B_2O_3(c) from the ΔH_f(glass) values, it is necessary to have the enthalpy of reaction for the change in phase. The $\Delta H_f°_{298}$(l) is calculated from $\Delta H_r°$(298 K) = 4.44[83] for B_2O_3(c) = B_2O_3(glass). The value of $\Delta H_r°$ was determined as the difference in the solution heats of crystalline and glassy B_2O_3. The heat of solution of B_2O_3 (amorphous)[89,132,180] was combined with $\Delta H_r°$(298 K) = 4.44 kcal/mol to obtain a $\Delta H°_{soln}(B_2O_3(c))$. No correction was applied to the tabulated heat of solution data, since the heat of dilution of H_3BO_3 is relatively small.[24] The auxiliary value of $\Delta H_f°_{298}(H_3BO_3(c)) = -261.5 \pm 0.2$ kcal/mol[167] is used in the calculation. A recent fluorination experiment[83] yielded a measured $\Delta H_c°$ of −239.12 kcal/mol for $B_2O_3(c) + 3F_2(g) = 2BF_3(g) + \frac{3}{2}O_2(g)$. This becomes −238.8 ± 0.4 kcal/mol when adjusted to be consistent with the JANAF value of $\Delta H_f°_{298}(BF_3(g)) = -271.4 \pm 0.4$ kcal/mol.[167]

The value recommended is −304.0 ± 0.4 kcal/mol (also adopted by the JANAF Tables)[167] obtained from the direct fluorination of B_2O_3(c)[83] since it does not require the number of corrections necessary in solution experiments. The solution calorimetric measurements,[64,84,121,122,155] which involved the hydrolysis of diborane and BCl_3(l), led to heats of formation of B_2O_3(c) with a relatively large uncertainty since the techniques were indirect and many auxiliary data were employed in the derivation. The direct combustion experiments of boron in oxygen are unreliable because of incomplete combustion or ill-defined states of combustion products.

The recommended value for $\Delta H_f°_{298}(B_2O_3(l))$ is -299.5 ± 0.5 kcal/mol which is calculated from $\Delta H_r°$ = 4.44,[83] using $\Delta H_f°_{298}(B_2O_3(c)) = -304.0 \pm 0.4$ kcal/mol.

The melting point 450 ± 2 °C (723 ± 2 K) was determined by Kracek et al.[98] The heat of fusion was not directly measured but was obtained from the $\Delta H_r°$ value of 4.44 kcal/mol for $B_2O_3(c) \rightarrow B_2O_3$(amorphous)[83] and the heat contents of the two forms at the melting point. This yielded $\Delta H_m° = 5.8 \pm 0.1$ kcal/mol.

The adopted C_p of 14.96 gibbs/mol for B_2O_3(c) was derived from the C_p data of Kerr, Hersh, and Johnston[92] and Shmidt,[152] which were obtained in the temperature regions 18–296.6 and 303–703 K, respectively. These sets of data were plotted and joined smoothly at 298 K.[167] The derived entropy, $S°_{298}$ = 12.90 gibbs/mol, was obtained from Kerr, Hersh and Johnston,[92] based on $S°_{18}$ = 0.025 eu. Low-temperature specific heat data were also reported for crystalline B_2O_3 by Kelley.[90] Southard[161] measured the heat content above room temperature to the melting point. The C_p values reported by these authors are in good agreement with the adopted value.

The heat capacities, 59.6-295 and 306.7-910 K, for B_2O_3(glass) were measured adiabatically by Turdakin and Tarasov[173] and Shmidt,[152] respectively. Specific heats to 620 K for quenched, annealed, and slowly cooled samples were reported by Thomas and Parks.[170] The specific heats of the three samples in their experiments differed markedly, especially in the 500-600 K range, depending upon the previous thermal history of the sample. Heat content measurements have also been reported by Southard[161] and Krasovitskaya et al.[99] They determined the heat content by dropping into the calorimeter a sample from a known high temperature in a sealed container. In this process the final state of the sample can vary from run to run, depending upon how well the initial state has reached equilibrium and how fast the sample changes during the experiment into a stable form at room temperature. Lasjaunias et al.[199] and Stephens[209] measured the specific heat in the range 0.05–1 K and reported that it did not vary according to the linear law generally observed.

The recommended value of 15.01 gibbs/mol[167] for the C_p of the glass was derived from the C_p data of Turdakin and Tarasov[173] (60-295 K) combined with those of Shmidt[152] (307-600 K). The $S°_{298}$ value of 18.75 gibbs/mol was obtained in a manner analogous to that for the heat of formation. A constant C_p = 31.0 gibbs/mol was chosen above the melting point.[167]

B. Aluminum Oxides

Al_2O_3 has been reported in many crystalline forms. The stable crystalline form is corundum (α-alumina). δ-, γ-, and κ-aluminas are structurally related, metastable forms. Recently, Lippens and Steggerda[103] summarized the various forms of Al_2O_3, their crystal structures, and conditions of formation by dehydration. α- and κ-aluminas belong to the "nearly anhydrous", high-temperature classification[103] based on their formation temperatures of 600-900 and 900-1000 °C, respectively. Cubic γ-Al_2O_3, which is often formed upon the oxidation of aluminum or the dehydration of hydrous aluminum oxide at temperatures not exceeding 600 °C, has a spinel structure with vacant spaces in the aluminum lattice. Upon heating all the metastable forms change irreversibly to the α-alumina.[5,103,118,186]

Although several new references are cited for the condensed phases of alumina, the adopted ΔH_f values are in agreement with those of the JANAF Tables.[167]

1. *Alpha* (α-Al_2O_3)

The heat of formation of α-alumina was determined by means of calorimetric heats of combustion of aluminum and from equilibrium studies. The calorimetry investigation yielded $\Delta H_f^\circ{}_{298}$ values of -400.5 ± 0.25,[105] -400.5 ± 0.3,[75] -399.2 ± 0.3,[157] and -400.6 ± 1.4[144] kcal/mol.

Fischer and Gewehr[45] reported the equilibrium data for the reaction $Al_2O_3(c) + 6HCl(g) \rightarrow 2AlCl_3(g) + 3H_2O(g)$. Third-law analyses of the data give $\Delta H_r^\circ{}_{298} = 81.4 \pm 1.0$ kcal/mol. Mashovets and Yudin[109] studied the reaction $2AlF_3(c) + 3H_2O(g) \rightarrow Al_2O_3(c) + 6HF(g)$ and reported a $\Delta H_r^\circ{}_{298} = 99.3 \pm 0.6$ kcal/mol. When combined with auxiliary JANAF values,[167] the $\Delta H_f^\circ{}_{298}$ resulted in -401.8 ± 1.5 and -405.2 ± 1.5 kcal/mol for the data involving gaseous $AlCl_3$[45] and crystalline AlF_3,[109] respectively.

The recommended value for the $\Delta H_f^\circ{}_{298}$ of α-$Al_2O_3(c)$ is -400.5 ± 0.3 kcal/mol based on the excellent agreement between the calorimetric measurements.[75,105] The other results[45,144] confirm this value with a somewhat larger uncertainty. Earlier equilibrium data involving crystalline AlF_3[109] may be in error due to the formation of aluminum oxyfluoride.[141]

The recommended $C_p^\circ{}_{298}$ value of 18.88 gibbs/mol for α-$Al_2O_3(c)$ was taken from Ditmars and Douglas[31] who tabulated functions from 0 to 1200 K. These functions were obtained from earlier C_p data in the temperature region 13–380 K involving the Calorimetry Conference Sample.[51] The specific heat of Al_2O_3 has also been recently determined at low temperature[198] and in the range 1500–2300 K.[205] The $S^\circ{}_{298}$ value of 12.17 gibbs/mol was derived from a C_p based on $S^\circ{}_{13} = 0.0016$ gibbs/mol. The adopted values have been confirmed by more recent studies.[47,49,62,153,168]

2. *Kappa* (κ-Al_2O_3)

Yokokawa and Kleppa[186] reported the results of a calorimetric study of the heats of solution of κ-alumina in a lead–cadmium–borate melt at 978 K. A $\Delta H_r^\circ{}_{978} = -3.6$ kcal/mol was reported for the irreversible process $\kappa \rightarrow \alpha$. This yields $\Delta H_r^\circ{}_{298} = -3.2$ kcal/mol based on JANAF free energy functions.[167] When combined with $\Delta H_f^\circ{}_{298}$ (α-$Al_2O_3(c)$) $= -400.5 \pm 0.3$, a $\Delta H_f^\circ{}_{298}$ (κ-$Al_2O_3(c)$) of -397.3 kcal/mol was calculated; Yamada et al.[185] derived $\Delta H_f^\circ{}_{298} = -397 \pm 1$ kcal/mol from the same data.

Based on these results a $\Delta H_f^\circ{}_{298}$ value of -397.3 ± 1 kcal/mol is recommended.

3. *Delta* (δ-Al_2O_3)

Calorimetric study of the heats of solution in an oxide melt resulted in a $\Delta H_r^\circ{}_{978} = -2.7$ kcal/mol for the irreversible process $\delta \rightarrow \alpha$.[186] This value becomes $\Delta H_r^\circ{}_{298} = -2.2$ kcal/mol based on the established JANAF functions.[167] The heat of solution of α-alumina in the solvent used was 7.6 ± 0.2 kcal/mol,[186] considered to be fairly well established. DTA studies by Gani and McPherson[54] gave $\Delta H_r^\circ = -2.8 \pm 0.5$ kcal/mol. Assuming that the irreversible transition occurs at an approximate temperature of 1300 K, one derives $\Delta H_r^\circ{}_{298} = -2.0$ kcal/mol.

The calculated $\Delta H_f^\circ{}_{298} = -378.3 \pm 0.6$ kcal/mol is from a calorimetric study.[186] DTA studies confirm this value.

4. *Gamma* (γ-Al_2O_3)

γ-Al_2O_3 shows much variability, depending on its thermal history. Yokokawa and Kleppa[186] derived the heat of transformation of γ-metastable modification to the α form. They reported a $\Delta H_r^\circ{}_{978} = -5.3$ kcal/mol from their calorimetric study. This yields $\Delta H^\circ{}_{298} = -4.5$ kcal/mol.[167] Using $\Delta H_f^\circ{}_{298}(\alpha$-$Al_2O_3(c))$ $= -400.5$ kcal/mol, a value of -396.0 ± 1.5 kcal/mol is derived for $\Delta H_f^\circ{}_{298}(\gamma$-$Al_2O_3)$. The DTA results of Gani and McPherson[54] gave $\Delta H^\circ{}_{978}(\gamma \rightarrow \alpha) = -5.8 \pm 1.6$ kcal/mol. Yamada et al.[185] used dynamic, adiabatic calorimetry to measure $\Delta H_r^\circ{}_{773} = 12.6 \pm 1.0$ kcal/mol for the reaction $Al_2O_3{\cdot}H_2O$(c, boehmite) $\rightarrow Al_2O_3(\gamma) + H_2O(g)$. Using enthalpy data from the JANAF Table[167] and $\Delta H_f^\circ{}_{298}$(boehmite) $= -472.0$ kcal/mol,[114] one derives $\Delta H_r^\circ{}_{298} = 17.5 \pm 1.3$ kcal/mol and $\Delta H_f^\circ{}_{298}(\gamma$-$Al_2O_3) = -396.7 \pm 2$ kcal/mol. Other values for the transformation of $\gamma \rightarrow \alpha$ are ΔH_r°, -7.7,[63] -11.0,[97] and -7.8[129] kcal/mol.

Excellent agreement between the two calorimetric experiments[185,186] supports the recommendation of $\Delta H_f^\circ{}_{298}(\gamma$-$Al_2O_3)$ $= -396.0 \pm 1.5$ kcal/mol. Recent DTA results[54] confirmed this value with a larger uncertainty. Other reported values[63,97,129] correspond to less stable samples, presumably with more residual water and less well-developed crystal structure.

5. *$Al_2O_3(l)$*

The melting point, $T_m = 2054 \pm 6$ °C (2327 ± 6 K), was recommended by Schneider[139] as a result of a cooperative measurement of the melting point by nine groups in seven countries. It has been confirmed by several recent studies.[47,136,154] These were all determined in inert atmospheres. Nelson and Richardson[203] and Yanagida and Kroeger[211] found a depression of approximately 30 °C in the melting point when melting occurred in oxygen atmospheres.

The heat of melting, ΔH_m°, is the difference at T_m between the enthalpy of $Al_2O_3(l)$ and $Al_2O_3(\alpha,c)$. Reported calorimetric values of ΔH_m° are 25.7 ± 1.3,[7,153] 25.9,[151] and 28.3 ± 0.6[46,86] kcal/mol. The recent studies[7,153] are the most extensive. The excellent agreement of these three ΔH_m° experiments[7,151,153] yields the recommended value of -25.8 ± 1 kcal/mol which, when reduced with the adopted C_p°, results in 26.5 ± 1 kcal/mol. The recent studies[7,153] have satisfactorily resolved the discrepancy in the ΔH_m° which was earlier reported as 28.3 kcal/mol.[86]

A value of $\Delta H_f^\circ{}_{298}(Al_2O_3(l)) = -383.7 \pm 1.2$ kcal/mol is calculated from that of the crystalline α form by adding the ΔH_m° and the difference in $(H^\circ{}_{2327} - H^\circ{}_{298})$ for crystal and liquid.

Data on the specific heat of liquid alumina include those of Shpil'rain et al.[7,153] at 2323–3100 K, Sheindlin et al.[151] at 2350–2800 K, and Fomichev and co-workers[46,86] at 2337 to 2480 K. The latest studies[7,153] where the specific heats of liquid alumina were determined with the aid of an evaporating liquid calorimeter satisfactorily resolved the discrepancy in the value for the C_{pm}° which was reported earlier to be either 47.7[151] or 34.6[86] gibbs/mol. The JANAF Tables,[167] in an analysis of the new data,[7,153] applied a temperature correction which yielded $C_{pm}^\circ = 46.0$ gibbs/mol, assuming C_p° is independent of temperature. We adopted $C_p^\circ = 46.0$ gibbs/mol. The $S^\circ{}_{298}$ value of 18.54 gibbs/mol is calculated in a manner similar to the ΔH_f° of $Al_2O_3(l)$.

C. Gallium Oxides

1. *$Ga_2O_3(c)$*

Several polymorphic forms of Ga_2O_3 are known to exist;[134,197] however, the only stable modification is commonly referred to as β-gallia. Early combustion calorimetry investigations by Klemm and Schnick[95] yielded -258 ± 3 kcal/mol for the $\Delta H_f^\circ{}_{298}$ of $Ga_2O_3(c)$, in fair agreement with the value of -255.8 kcal/mol obtained by Roth and Becker.[131] A subsequent combustion study by Mah[106] yielded -261.05 kcal/mol. The National Bureau of Standards[114] summarized the literature and adopted -260.3 kcal/mol for the $\Delta H_f^\circ{}_{298}$ of $Ga_2O_3(c)$. Hart[68] in a survey of the periodicity of chemical thermodynamic functions gave the $\Delta H_f^\circ{}_{298}$ of $Ga_2O_3(c)$ as -258 kcal/mol. Another survey by

Veryatin and Mashirov[179] concluded a value of −259 kcal/mol.

The value reported by Mah[106] appears to be the most precise (−261.0 ± 1 kcal/mol). A recent electrolysis experiment by Anderson and Donaghey[188] confirms this value. The early measurements[95,131] are considered to be biased by 3 to 5 kcal.

The heat capacity of Ga_2O_3(c) over the temperature range 298 to 1800 K was measured by Mills[111] using differential scanning calorimetry, and by Adams and Johnston[3] and King,[94] who employed adiabatic calorimetry. The recommended value of 22.42 gibbs/mol[111] is within 1% agreement with the other two values.[3,94] An $S°_{298}$ value of 20.31 gibbs/mol was reported by Kelley and King.[91]

Goldschmidt and co-workers[56] estimated the melting point of Ga_2O_3 to be approximately 1900 °C; von Wartenberg and Reusch[178] reported a value of 1740 °C; and Hill et al.[74] obtained 1725 ± 15 °C. The latest melting point determination on Ga_2O_3 was that of Schneider and Waring,[145] who determined a value of 1795 ± 15 °C in a quenching furnace. Temperatures in the quenching furnace were measured with both an optical pyrometer and a Pt–Rh thermocouple. We recommend a value of 1795 ± 15 °C (2068 ± 20 K) for the melting point of Ga_2O_3 based on these recent precise experiments. The determination of Hill et al.[74] was made employing a strip furnace, which is generally subject to considerable random errors.

Heat of melting data for Ga_2O_3 have not been reported in the literature.

D. Indium Oxides

1. $In_2O_3(c)$

Although indium is known to form two oxides, In_2O_3 and In_2O,[12] relatively little data are available to prove the existence of In_2O. Indium sesquioxide, In_2O_3, has the cubic c-type structure.[108] There is considerable discrepancy on its volatilization. Brewer[12] reported it to volatilize predominantly by decomposition to the gaseous elements at temperatures of 677 °C. However, Schneider[143] has shown that volatilization of In_2O_3 does not become significant until temperatures in excess of 1350 °C are reached and maintained for several hours. In_2O_3 can also be crystallized with a corundum structure under high pressures and temperatures.[19,124] Broch and Christensen[14] attempted to prepare In_2O by the procedure of Brauer.[11] X-Ray analysis of the products of these preparations always showed the presence of only In and cubic In_2O_3. They concluded that unambiguous proof for the existence of crystalline In_2O has not yet been presented. Recently, Klinedinst and Stevenson[96] interpreted the results of their electrochemical measurements at temperatures between 1123 and 1273 K to yield the standard Gibbs energy of formation of crystalline In_2O, corresponding to the equation $2In(l) + \frac{1}{2}O_2(g) = In_2O(c)$. However, no identification of the solid In_2O has been reported.

The enthalpy of In_2O_3(c) was found by Becker and Roth[8] to be $\Delta H_f°_{298} = -222.5 \pm 0.7$ kcal/mol from the combustion of In in oxygen.[8] Holley et al.[76] obtained a value of −221.3 ± 0.4 kcal/mol by calorimetric determinations. Stubbs et al.[166] obtained −216.8 kcal/mol using an equilibrium method in a dynamic system. Based on the results of Knudsen mass spectrometer experiments, Burns et al.[17] reported a value of $\Delta H_f°_{298}(In_2O_3(c)) = -216 \pm 7$ kcal/mol, using Coughlin's[23] values for the free energy functions. These authors[17] studied the reaction $In_2O_3(c) = In(g) + O_2(g)$ in the temperature range 1265–1540 K. The standard Gibbs energy has recently been derived, using electrochemical cells, by Klinedinst and Stevenson.[96] When combined with Couglin's thermodynamic functions,[23] their value agrees well with the value of $\Delta H_f°_{298}(In_2O_3(c)) = -222.2 \pm 1.1$ kcal/mol derived from emf measurements of Newns and Pelmore.[117]

The calorimetric[8,76] and electrochemical[96,117,189] values were chosen for recommending a $\Delta H_f°_{298}$ value. Four experiments[76,96,117,189] confirmed the results of Becker and Roth.[8] However, the recent measurements of Anderson and Donaghey[189] were of greater precision and therefore their value of −222.1 ± 0.01 kcal/mol is recommended. The value obtained by Stubbs et al.[166] was considered less accurate than the recommended value since their method was an indirect one. The mass spectrometer experiments[17] cast serious doubt on the reaction studied, since at temperatures above 1123 K it has been reported that In_2O_3 is an unstable oxide.[96]

Goldschmidt et al.[56] estimated the melting point of In_2O_3 to be over 2000 °C. Schneider[143] determined the melting point to be 1910 ± 10 °C (2183 K) in an induction furnace having an iridium crucible as the heating element. This value is recommended. X-Ray patterns of In_2O_3 heated to 1905 and 1915 °C showed only the diffraction peaks identifiable with cubic In_2O_3.[143] No data on the heat of melting have been reported in the literature.

Values for the $C_p°_{298}$ and $S°_{298}$ of In_2O_3(c) were reported by Stubbs et al.[166] and Nilson and Pettersson.[213] The National Bureau of Standards[114] adopted 22.0 and 24.9 gibbs/mol for the $C_p°_{298}$ and $S°_{298}$, respectively, from these studies.

E. Thallium Oxides

Tl_4O_3, Tl_2O_3, and Tl_2O are the only definitively established oxides of thallium.[12,202,206-208] The high-temperature chemistry of all these oxides is greatly influenced by the volatility of thallous oxide, whose vapor pressure reaches about 1 mm at 850 K.[24] Marcel and Bouaziz[107] detected α-Tl_2O form at temperatures above 354 °C. A structural analysis has been reported for Tl_4O_3(c); however, no thermodynamic data have been reported.[188,189]

1. $Tl_2O_3(c,l)$

Cubicciotti[24] determined the enthalpy of formation as $\Delta H_f°_{298}(Tl_2O_3(c)) = -94.3 \pm 0.8$ kcal/mol by solution calorimetry. There are no prior literature reports of the direct determination of the enthalpy of formation of Tl_2O_3. The results of Duncan's[34] study of the oxygen pressure over molten mixtures of Tl_2O_3 and Tl_2O have been used to derive values of the enthalpy of formation of Tl_2O_3;[23] however, these values are essentially estimates. Brewer[12] remarked on this problem in his review.

The melting point and heat of melting of Tl_2O_3(c) have been determined as 989 ± 2 K and 3.5 ± 1 kcal/mol, respectively, by Shchukarev et al.[147] Duncan[34] reported 990 ± 5 K as the melting temperature. A $\Delta H_f°_{298}(Tl_2O_3(l))$ value of −69.8 ± 2 kcal/mol is calculated from that of crystal by adding the $\Delta H_m°$ and the difference in $(H°_{989} - H°_{298}) = 21.0$ kcal/mol.[26]

The heat capacity of Tl_2O_3(c) was measured by Mills[111] in the temperature range 298 to 800 K using differential scanning calorimetry and drop calorimetry. The smoothed curve correlating the data yielded a $C_p°_{298}$ of 25.86 joules/mol, which was 2% lower than the values reported by Cubicciotti and Eding.[26] The more recent study by Mills[111] was the most extensive, and therefore the results of this investigation are recommended. The $S°_{298}$ value of 38.0 gibbs/mol was derived from the measurement of Cubicciotti.[25]

2. $Tl_2O(c,l)$

The enthalpy of formation of Tl_2O by solution calorimetry of the oxide and the metal in H_2SO_4 has been reported as −43.2 kcal/mol by Roth and Meischsner;[133] recalculation of their data yielded a value 1 − 2 kcal less negative.[12] Cubicciotti[24] reported −40.4 ± 1.4 kcal/mol from solution calorimetry experiments. The difference between the two values has been attributed to the method of preparation of the Tl_2O sample.[24] The more recent value of Cubicciotti[24] is recommended for $\Delta H_f^\circ{}_{298}(Tl_2O(c))$.

Drop calorimetry experiments have determined the melting point and heat of melting of Tl_2O as 852 K and 7.24 kcal/mol, respectively.[26] A value of 8.6 kcal/mol for the heat of fusion of Tl_2O has also been reported.[107] This difference in the heat of fusion may, again, be attributed to the method of preparation of Tl_2O. We recommend the values of $T_m = 852 \pm 20$ K and $\Delta H_m^\circ = 7.24 \pm 1$ kcal/mol. The heat of formation value of -21.8 ± 3 kcal/mol for $Tl_2O(l)$ is derived from that of $Tl_2O(c)$ by adding ΔH_m° and the enthalpy increment $(H^\circ{}_{852} - H^\circ{}_{298}) = 11.4$ kcal/mol given in ref 26.

A $C_p^\circ{}_{298}$ value of 19.30 gibbs/mol for $Tl_2O(c)$ was derived from the heat content measurements by Cubicciotti and Eding.[26] A very early study of the entropy was conducted by Bahr.[200] However, the recommended $S^\circ{}_{298}$ value is 34.7 gibbs/mol obtained by Cubicciotti.[25] No reliable values for the heat capacity of $Tl_2O(l)$ could be obtained by drop calorimetry since Tl_2O reacted with the platinum container at higher temperatures.[26]

IV. Heats of Formation of Gaseous Oxides

Five general techniques—calorimetry, flame photometry, transpiration, effusion, and mass spectrometry—have been employed to establish the experimental heats of formation of the gaseous group 3 oxides. These techniques, in addition to spectroscopic data, have been employed to determine the dissociation energies or the heats of formation of the suboxides within a very narrow degree of uncertainty. Ion bombardment techniques have enabled accurate measurement of the appearance potential (AP) and the ionization potential (IP) of the suboxides, and resulting heats of formation have been calculated. The electron affinities of the suboxides have been obtained by means of charge exchange experiments with the well-known Cl^- and F^- ions and neutral suboxides, and through H_2/O_2 flame studies.

Results obtained from these various measurements are discussed in this section.

A. Boron Oxides

1. $B_2O_3(g)$

Calculation of a correct heat of vaporization of B_2O_3 is heavily dependent upon the molecular structure and vibrational frequencies of the gaseous species since this uncertainty affects third-law thermochemical investigations. Early spectroscopic evidence[4,159,183] was interpreted as supporting a bent C_{2v} configuration for the gaseous B_2O_3 molecule. In 1965, Hanst et al.[66] reported new infrared and mass spectroscopic results which were inconsistent with a C_{2v} configuration. Instead, they suggested a D_{3h} symmetry for this molecule. The structure of $B_2O_3(g)$ has now been resolved and the V-shaped symmetry has been confirmed by electric deflection[85] and electron diffraction[37] studies. This structure has been used to calculate the free energy functions of $B_2O_3(g)$.[167]

The vapor pressure over $B_2O_3(l)$ was measured by several investigators using the techniques of mass spectrometry,[10,15,38,158] Knudsen effusion,[115,162] torsion effusion,[73,137] transpiration,[61] and effusion-weight loss.[21,140,160] The vapor pressure data of Sommer[158] superseded those values obtained by White et al.,[184] who revised their values because of errors in some of the temperatures. Second- and third-law analyses of these data are presented in Table II. The derived $\Delta H_f^\circ{}_{298}$ values based on third-law analyses, using $\Delta H_f^\circ{}_{298}(B_2O_3(l)) = -299.5$ kcal/mol, are also given.

TABLE II. Proposed ΔH_f° Values for $B_2O_3(g)$

method	$\Delta H_v^\circ{}_{298}$, kcal/mol 2nd law	$\Delta H_v^\circ{}_{298}$, kcal/mol 3rd law	$\Delta H_f^\circ{}_{298}$, kcal/mol	ref
mass spectrometry	95.7 ± 1.5			38
	100.5 ± 3			15
	92.3 ± 1	99.2 ± 1.5	−200.4	158
effusion–mass spectrometry	93.1 ± 1.5	99.1 ± 1.0	−200.5	10
Knudsen effusion	82.6 ± 3	98.5 ± 2.0	−201.0	115
	89.6 ± 1.7	99.1 ± 1.5	−200.5	162
Torsion effusion	101.0 ± 1.5	100.0 ± 0.5	−200.0	73
	95.5 ± 1.0	101.5 ± 0.5	−198.0	137
transpiration	92.5 ± 2.5	102.8 ± 2.0	−197.0	61
effusion	101.7 ± 12	98.3 ± 1.0	−201.2	140
effusion–carrier gas	66.2 ± 8	98.0 ± 5	−201.5	160
	73.3 ± 2.3	87.4 ± 1.5	−212.2	21

In recommending a value for $\Delta H_f^\circ{}_{298}$ for $B_2O_3(g)$, the greatest weight was given to the third-law investigations. The carrier gas experiments[21,160] were considered to be unreliable since the initial rate of evaporation of B_2O_3 was obtained by graphical extrapolation, which generally leads to vapors which are considerably too high. Three torsion and effusion experiments[73,140,162] yielded excellent second and third-law agreement (within ±1 kcal/mol of each other). The recommended value is 100.0 ± 0.5 kcal/mol for the ΔH_v, leading to -200.0 ± 1 kcal/mol for the $\Delta H_f^\circ{}_{298}(B_2O_3(g))$. Other reported values, with the exception of ref 21 and 160, are in good agreement with this recommended value for the heat of formation. Apparently no attempt was made in the mass spectrometer experiments[15,38] to perform calibration experiments which would have allowed the ion intensity data to be converted to absolute partial pressures, thus precluding a third-law analysis.

2. $B_2O_3(g)^+$

The ionization potential of B_2O_3 was reported as 14.0 ± 0.5 eV by Blackburn et al.[10] in a study of the gaseous reactions of Al with B_2O_3 and Al_2O_3. Inghram et al.[78] obtained 13.5 eV from reactions in the B + B_2O_3 system. We recommend a value of 14.0 ± 0.5 eV (323 kcal) since the measurement in this system[10] is more reliable because the study involving B and $B_2O_3(l)$[78] had a rapidly changing activity of boron in the presence of $B_2O_3(l)$.[138,176] Using this value in conjunction with $\Delta H_f^\circ{}_{298}(B_2O_3(g)) = -200 \pm 1$ kcal/mol, a $\Delta H_f^\circ{}_{298}$ $B_2O_3(g)^+$ value of 123 ± 12 kcal/mol is obtained.

3. $B_2O_2(g)$

It has been demonstrated that under reducing conditions B_2O_2 is an important vapor species in the B–O system. Inghram et al.[78] and Scheer[138] identified the species and measured its partial pressure in the system B(c) + $B_2O_3(l)$, the former by mass spectrometer and the latter by torsion effusion techniques. Searcy and Myers[140] and Rentzepis et al.[125] measured the effusion of B_2O_3 vapors from mixtures of MgO and B, and B_2O_3 and C, respectively. Blackburn et al.[10] and Farber et al.[39] measured the ion currents corresponding to BO^+ and $B_2O_2^+$ as a function of temperature in a mass spectrometer.

The results of all these experiments are summarized in Table III. The values are adjusted to be consistent with the JANAF[167] auxiliary data.

As can be seen from Table III, there is a range from −105 to −113 kcal/mol in the values for the $\Delta H_f^\circ{}_{298}$.

The experiments involving $B_2O_3(l)$ and B(c) have resulted in a changing activity of boron in the presence of $B_2O_3(l)$.[176] Therefore, the attainment of equilibrium in the experiments of ref 78 and 138 might have been impeded by the formation of a condensed polymer, with the result that observed pressures of B_2O_2 may be lower than the equilibrium pressures. In the experiments of Searcy and Myers[140] poor contact between the solid reactants resulted in a lowering of the partial pressures of the gaseous products. Therefore, all these investigations possibly have led to an upper limit for the heat of formation of $B_2O_3(g)$. Also, investigations where equilibrium reactions between $B_2O_3(l)$

TABLE III. Proposed $\Delta H_f°$ Values for $B_2O_2(g)$

method	reaction[a]	$\Delta H_f°_{298}$, kcal/mol	ref
mass spectrometry	A	-110.8 ± 1.8[b]	39
mass spectrometry	A	-113.2 ± 1.9[b]	10
mass spectrometry	B	-105.5 ± 0.7	78
	C	-109.0 ± 0.5	78
effusion	D	-102.6 ± 10	140
torsion effusion	B	-110.2 ± 0.9	138
effusion	E	-108.5 ± 1.5[c]	125

[a] (A) $\frac{1}{2}B_2O_2(g) = BO(g)$; (B) $\frac{2}{3}B(c) + \frac{2}{3}B_2O_3(l) = B_2O_2(g)$; (C) $\frac{2}{3}B(c) + \frac{2}{3}B_2O_3(g) = B_2O_2(g)$; (D) $2MgO(c) + 2B(c) = 2Mg(g) + B_2O_2(g)$; (E) $B_2O_3(l) + C(c) = B_2O_2(g) + CO(g)$. [b] Derived from second-law values. [c] The value of $\Delta H_f°_{298}$ was obtained from derived log $K_f(B_2O_2,g)$ values by the third-law method.

and B(c) were involved were not considered definitive. However, the experiments involving the reaction of B(c) with gaseous B_2O_3 did not have the loss in activity that was found with liquid B_2O_3–solid B reactions. Thus $\Delta H_f°_{298}(B_2O_2(g)) = -109 \pm 2$ kcal/mol is recommended.[78] Second-law mass spectrometric and effusion experimental results are in agreement.[10,39,125]

4. $B_2O_2^+(g)$

The heat of formation, $\Delta H_f°_{298}(B_2O_2^+(g)) = 213.8 \pm 14$ kcal/mol, was calculated from the ionization potential of 14.0 ± 0.5 eV (323 ± 12 kcal/mol) for $B_2O_2(g) \rightarrow B_2O_2^+(g) + e^-(g)$[10] using $\Delta H_f°_{298}(B_2O_2(g)) = -109 \pm 2$ kcal/mol. Inghram et al.[78] reported the appearance potential as 13.5 eV.

5. $BO_2(g)$

The BO_2 molecule has been identified by spectroscopy[82,159,191] and by mass spectrometry.[176] The literature values for its heat of formation vary over a wide range from −66 to −84 kcal/mol (see Table IV).

Kaskan and Millikan[87] made observations on the green bands in trimethyl borate-air flames and gave an estimate of about −83 kcal for $\Delta H_f°_{298}(BO_2(g))$. The same authors[88] later reported a spectroscopic value of −75.3 kcal/mol. The recent mass spectrometric results[176] support this value and indicate a serious systematic error in the values of Greene[60] and Rusin and Tatevskii.[135]

Considering the spectroscopic value[88] and the second- and third-law agreement (within 2.5 kcal/mol) obtained in the recent mass spectrometric studies,[176] a value of -77.0 ± 3 kcal/mol for the $\Delta H_f°_{298}(BO_2(g))$ is recommended. This leads to an atomization energy, $D°(BO_2) = 327$ kcal/mol.

6. $BO_2^+(g)$

The heat of formation of $BO_2^+(g)$, $\Delta H_f°_{298}(BO_2^+(g)) = 245 \pm 25$ kcal/mol, is derived from the recommended value of $\Delta H_f°_{298}(BO_2(g)) = -77.0 \pm 2.5$ kcal/mol and an appearance potential $(BO_2^+(g) = 14 \pm 1$ eV) from $BO_2(g)$.[176] Wada and Kiser[181] gave a value of $\Delta H_f°_{298}(BO_2^+(g)) = 121$ kcal/mol which was derived from $AP(BO_2^+) = 17.3 \pm 0.3$ eV from $B(OCH_3)_3(g)$, in which the dissociative process was postulated to be $B(OCH_3)_3(g) + e = BO_2^+(g) + CH_3O(g) + 2CH_3(g) + 2e$. If this process were correctly assigned, the ionization potential of $BO_2(g)$ should be 8.6 eV; however, this is considered unlikely in view of the appearance potential comparison for BO_2 and BO^+ (AP = 12.8 eV), $B_2O_3^+$ (AP = 13.5 eV), and $B_2O_2^+$ (AP = 13.5 eV).

7. $BO_2^-(g)$

The electron affinity (EA) of $BO_2(g)$ was calculated as 82.3 ± 3 kcal/mol based on equilibrium data for $BO_2(g) + Cl^-(g) = BO_2^-(g) + Cl(g)$ obtained by means of effusion mass spectrometry by Srivastava et al.[164] Their second- and third- law results agreed within 3 kcal/mol, indicating the absence of any serious systematic errors in the measurements and in the molecular constants used for the free energy functions.[167] Using this value and $\Delta H_f°_{298}(BO_2(g)) = -77 \pm 3$, one derives $\Delta H_f°_{298}(BO_2^-(g)) = -159.3 \pm 3$ kcal/mol. This may be compared with $\Delta H_f°_{298}(BO_2^-(g)) = -162.7 \pm 4$ kcal/mol reported by Jensen[80] who used $H_2/N_2/O_2$ flames to study the reaction:

$$HBO_2(g) + e^- = H(g) + BO_2^-(g)$$

TABLE IV. Proposed Values for $\Delta H_f°_{298}(BO_2(g))$

method	reaction[a]	$\Delta H_f°_{298}$, kcal/mol[b]	ref
Knudsen mass spectrometer	A	-77 ± 2.5	176
spectroscopy	B	-68.4 ± 2	60
spectroscopy	B	-75.3	88
flame photometric	A	-83.6	87
calorimetric	A	-66.2 ± 4	135

[a] (A) $HBO_2(g) + OH(g) = H_2O(g) + BO_2(g)$; (B) $\frac{1}{2}B_2O_3(l) + \frac{1}{4}O_2(g) = BO_2(g)$. [b] The auxiliary data $\Delta H_f°_{298}$ [$HBO_2(g) = -134$, $B_2O_3(l) = -299.5$, $OH(g) = 9.43$, $H_2O(g) = -57.8$ kcal/mol] are used in the calculation.

8. $BO(g)$

Early literature values for the $D°$ of the molecule BO extended over a range of about 41 kcal/mol: 209.3,[70] 184,[9] 175,[55] and 168.[104] However, during the last decade, several workers determined $D°$ of BO values which were in close agreement. de Galan[29] from flame photometric measurements reported a $D°(BO) = 191.4$ kcal, corresponding to $\Delta H_f°_{298}(BO(g)) = -0.1$ kcal/mol. The mass spectrometer experiments of Blackburn et al.[10] and Farber et al.[39] resulted in second-law $\Delta H_r°_{298}$ values of 56.6 ± 1.8 and 55.0 ± 1.9 kcal/mol, respectively, for the reaction $\frac{1}{2}B_2O_2(g) \rightarrow BO(g)$. These yielded $\Delta H_f°_{298}(BO(g)) = 2.1 \pm 2.8$[10] and 0.9 ± 2.9 kcal/mol,[39] using the present $\Delta H_f°_{298}(B_2O_2(g)) = -109 \pm 2$ kcal/mol. Coppens et al.,[22] from a Knudsen mass spectrometer study of three isomolecular exchange reactions, concluded $D°(BO) = 191.2 \pm 2.3$ kcal or $\Delta H_f°_{298}(BO(g)) = 0.1 \pm 2.3$ kcal/mol. The value of $\Delta H_f°_{298}(BO(g)) = 0.1 \pm 1$ kcal/mol, or $D°(BO) = 191.3 \pm 1$ kcal, is recommended and is closely supported by the second-law mass spectrometer study[39] which yielded 0.9 ± 2.9 kcal/mol for the $\Delta H_f°_{298}$.

9. $BO^+(g)$

The heat of formation of $BO^+(g)$, $\Delta H_f°_{298} = 311.3 \pm 23$ kcal/mol, is derived from the present value of $\Delta H_f°_{298}(BO(g)) = 0.1 \pm 1$ kcal/mol and the appearance potential $(BO^+(g)) = 13.5 \pm 1$ eV).[10,164] Other reported appearance potentials include 12.8[175] and 19 eV.[78] The BO^+ ion observed in the experiments of Inghram et al.[78] was clearly a fragment ion. The adopted appearance potential of 13.5 eV compares well with the result of self-consistent field calculations, which gave a value of 13.24 eV for the ionization potential of BO.[79]

10. $BO^-(g)$

The electron affinity (EA) of BO was determined by Srivastava, Uy, and Farber,[164] based on effusion mass spectrometer data for the reaction $BO(g) + Cl^-(g) = BO^-(g) + Cl(g)$. Their second- and third-law results agreed within 2 kcal/mol, which indicated the absence of any serious systematic errors in the measurements and in the molecular constants used for the free energy functions of $BO^-(g)$. The average third law yielded $\Delta H_f°_{298}(BO^-(g)) = -71.9 \pm 2.0$ kcal/mol. This leads to an electron affinity value of 71.9 ± 2.0 for BO(g), using $\Delta H_f°_{298}(BO(g)) = 0.1 \pm 1$ kcal/mol. Jensen,[80] by means of re-

TABLE V. Proposed $\Delta H_f°$ Values for $Al_2O_2(g)$

method	reaction[a]	$\Delta H_f°_{298}$ kcal/mol	$D°$ kcal/mol	ref
effusion–mass	A	−106.4 ± 5	383.6	43
spectrometry	B	−103.0 ± 6	380.2	43
effusion–mass	A[b]	−99.1 + 9	376.3	33
spectrometry	A[c]	−95.9 ± 9	373.1	33
	C[b]	−99.3 ± 9	376.5	33
	C[c]	−97.8 ± 9	375.0	33
	D[b]	−113.7 ± 8	390.2	190
evaporation	D	−99.8 ± 10	377.0	196

[a] Reactions: (A) $Al_2O(g) + AlO(g) = Al(g) + Al_2O_2(g)$; (B) $Al_2O(g) + AlO_2(g) = AlO(g) + Al_2O_2(g)$; (C) $2AlO(g) = Al_2O_2(g)$; (D) $Al_2O_2(g) = 2Al(g) + 2O(g)$. [b] Using a tungsten effusion cell. [c] Using a molybdenum effusion cell.

TABLE VI. Proposed Values for $\Delta H_f°_{298}(Al_2O(g))$

method	reaction[a]	$\Delta H_f°_{298}$ kcal/mol	$D°$ kcal/mol	ref
Knudsen–mass	A	−33.2 ± 3	247.0	72
spectrometry	B	−32.0 ± 3	246.0	43
	C	−31.6 ± 1	245.0	30
	A[b]	−41.8 ± 4	256.0	33
	A[c]	−40.2 ± 6	254.0	33
	D	−35.7 ± 1	249.5	171
	E	−42.8 ± 3	259.8	190
vaporization–mass	A	−35.0	248.8	16
spectrometry	E	−34.7 ± 5	248.7	196
Knudsen effusion	D	−31.0	244.7	123
	D	−35.1 ± 2	248.5	101
	D	−31.4 ± 2	245.0	69

[a] (A) $2AlO(g) = Al_2O(g) + O(g)$; (B) $Al(g) + AlO(g) = Al_2O(g)$; (C) $\frac{4}{3}Al(g) + \frac{1}{3}Al_2O_3(c) = Al_2O(g)$; (D) $\frac{4}{3}Al(l) + \frac{1}{3}Al_2O_3(c) = Al_2O(g)$; (E) $Al_2O(g) = 2Al(g) + O(g)$. [b] Using molybdenum cells. [c] Using tungsten cells.

actions in flames, reported a lower limit of approximately 58.5 kcal/mol for the electron affinity.

B. Aluminum Oxides

The composition of the vapor over solid and liquid aluminum oxide has been the subject of wide disagreement for many years. Most of these determinations have been reviewed by Farber, Srivastava, and Uy.[43] It has been concluded that the major species effusing from alumina were Al_2O_2, Al_2O, AlO_2, and AlO along with the elements. A discussion of the individual oxides follows.

1. $Al_2O_3(g)$

Although positive identification of $Al_2O_3(g)$ has not been reported, it is possible that the molecule exists. From weight-loss experiments it has been determined that the other species over alumina account for approximately 75% of the vapor.[23] Thus it is desirable to consider the possibility of $Al_2O_3(g)$ accounting for 25% of the vapor concentration over the liquid phase. This would mean that $Al_2O_3(g)$ has a partial pressure of approximately 2×10^{-5} atm at 2600 K, which corresponds to a value of −198 kcal/mol for the $\Delta H_f°_{298}$ of $Al_2O_3(g)$ and 175 kcal/mol for the heat of vaporization. Bond energy calculations with four equal Al–O bonds of 120 kcal/mol result in a $\Delta H_f°_{298}$ of approximately −150 kcal/mol. If this value is correct, then $Al_2O_3(g)$ would not be seen in the mass spectrometer experiments reported to date although the weight loss experiments would indicate that the $Al_2O_3(g)$ would have sufficient intensity for mass spectrometer identification. However, as stated previously, positive identification of $Al_2O_3(g)$ has not been made. Additionally, an attempt was made by Farber et al.[43] to identify the $Al_2O_3^-$ ion mass spectrometrically. No species corresponding to the Al_2O_3 mass peak was observed over a range of electron energies from 0 to 70 eV. If one postulates that $Al_2O_3(g)$ exists, the parent molecular ion would have to undergo fragmentation as evidenced by the absence of $Al_2O_3^+$. (Examples of molecules for which the parent ion undergoes fragmentation are CF_4, BF_3, and MgF_2.) A criterion for a molecule to ion-molecule transition is that the transfer take place within the potential energy wells. It is possible, although not a common occurrence, that in some systems the potential energy curve of the ionic species is so displaced that the vertical drawn from the potential energy trough of the molecular species will intersect the curve at the ionic species above its potential energy trough. In such an event the ion is formed above its dissociation limit and the molecular ion will dissociate upon its first vibration.[43]

2. $Al_2O_2(g)$

Recently, Farber, Srivastava, and Uy[43] identified species effusing through an elongated orifice from an alumina cell, using a mass spectrometer. Their data are analyzed along with an earlier study by Drowart et al.,[33] who used tungsten and molybdenum cells (Table V). Results are based on the newly established free-energy functions[167] and on the auxiliary data of $\Delta H_f°_{298}$ [$AlO(g) = 16.5 \pm 2$, $Al_2O(g) = -32.0 \pm 3$ kcal/mol, and $AlO_2(g) = -44.9 \pm 3$ kcal/mol]. The uncertainty includes a large contribution from the use of the auxiliary data. Data in the table are presented for reactions involving these molecules.

The metal cells used by Drowart et al.[33] caused reduction of the vapor species which contributed to the variation in $\Delta H_f°$ values derived from different reactions. Their values are biased by ~6 kcal/mol. The effect of tungsten and molybdenum cells on the partial pressures of the aluminum suboxides have been discussed in detail previously.[43,92] Tungsten cells were also employed by Chervonnyi et al.[190]

Recently the Al_2O_2 molecule was observed by Fu and Burns[196] in an evaporation experiment and was assumed to be in virtual equilibrium with the condensed phase. On this basis they assigned a value of 0.325 for the evaporation coefficient. Their observed partial pressure of Al_2O_2 was approximately 60 times smaller than the equilibrium partial pressure.[167]

A value of −106.4 ± 6 kcal/mol for the $\Delta H_f°_{298}$ of $Al_2O_2(g)$ is recommended from reaction (A) of Farber et al.[43] This corresponds to $D° = 383.6 \pm 6$ kcal/mol for the dissociation to the elements.

3. $Al_2O_2^+(g)$

The appearance potential of Al_2O_2 was reported as 9.9 ± 0.5 eV (228.3 ± 12 kcal/mol) by Drowart et al.[33] Their value has been confirmed by Farber et al.[43] and Fu and Burns,[196] who measured 10 ± 1 and 9.9 eV, respectively. The $\Delta H°_{298} = 121.9 \pm 15$ kcal/mol is derived from the ionization potential and 228.3 ± 12 kcal/mol for $Al_2O_2(g) \rightarrow Al_2O_2^+(g) + e(g)$, using $\Delta H_f°_{298}(Al_2O_2(g)) = -106.4 \pm 6$ kcal/mol.

4. $Al_2O(g)$

The heat of formation of $Al_2O(g)$ has been measured by mass spectrometry (ref 16, 30, 33, 43, 72, 171, 190, 196) as well as by weight-loss effusion techniques (ref 69, 101, 123). Recent results are presented in Table VI. These values have been adjusted to the newly established free-energy functions of $Al_2O(g)$.[167]

Discrepancies in the ΔH_f values have been fairly well resolved, excluding mass spectrometer investigations in metal cells.[33,190] These may be dismissed for the reason that Al_2O reacted with molybdenum or tungsten cells, causing reduction in the vapor species. Assessing these values, it would appear reasonable to recommend $\Delta H_f°_{298}(Al_2O(g)) = -32.0 \pm 3$ kcal/mol, or $D° = 246 \pm 3$ kcal/mol, since these data resulted from a study of the vapor species over $Al_2O_3(c)$ in an alumina effusion cell.[43] This value includes almost the whole range of values and also reproduces the approximate proportions of $Al_2O(g)$ and $AlO(g)$ reported[16,43] over Al_2O_3. This recommended value is also in agreement with a second-law value of $\Delta H_f°_{298}(Al_2O(g)) = -30.5 \pm 3$ kcal/mol obtained from a separate mass spectrometer study involving reactions of $Al(l) - AlF_3$ in alumina effusion cells.[163] Porter et al.[120] had previously reported a heat of dissociation of 256 ± 7 kcal/mol for Al_2O from a second-law mass spectrometer study of $Al(l)–Al_2O_3(c)$.

Other weight-loss measurements[1,2,13,20] led to heats of formation of $Al_2O(g)$ with a relatively large uncertainty since the techniques were indirect and many questionable auxiliary data were employed in the derivation.

5. $Al_2O^+(g)$

The values reported for the appearance potential for Al_2O^+ include 8.20 ± 0.15,[72] 8.5 ± 1,[43] 7.7 ± 0.5,[16,171,196] and 7.9 ± 0.3 eV.[30] Although these values are consistent, the value of 8.2 ± 0.15 (189.1 ± 3.5 kcal/mol) is recommended because of its high precision. Using this value in conjunction with $\Delta H_f°_{298}(Al_2O(g)) = -32.0 \pm 3$ kcal/mol, one obtains $\Delta H_f°_{298}(Al_2O^+(g)) = 157.1 \pm 5$ kcal/mol.

6. $AlO_2(g)$

The existence of the AlO_2 molecule has been reported in five thermochemical effusion–mass spectrometer investigations.[40-43,165] In a nonequilibrium mass spectrometer study[201] involving a flow tube reaction of a large excess of O_2 with Al vapor, fairly large concentrations of $AlO_2(g)$ were reported. Recently, a spark source study of the aluminum oxide vapor species employing a very high-precision mass spectrometer definitely confirmed the AlO_2^+ ion in varying concentrations as a function of the spark temperature.[212] From enriched O^{18}-labeling experiments these authors[212] concluded that the AlO_2 was formed from the reaction of the single atoms present in the spark source plasma.

Several chemiluminescence experiments involving the release of aluminum compounds in the upper atmosphere indicate a continuum superimposed over the AlO bond structure attributable to the emission from AlO_2 formed from the reaction of AlO with O.[58,59,127] This continuum was also observed in chemiluminescence experiments of Al with oxidants.[57,128] The formation of AlO_2 from laser induced fluorescence of a fast flow reaction has also recently been reported.[193,194]

The AlO_2 molecule was not observed in a recent Langmuir evaporation mass spectrometer investigation[204] nor in an effusion–mass spectrometer study[190] employing a tungsten cell. However, as reported previously,[43,192] this would not be unexpected in experiments of this type. Langmuir-type evaporation experiments do not generally yield equilibrium data.[196] For example, Paule's observed partial pressures for the evaporated species from $Al_2O_3(c)$[204] were all lower than the reported equilibrium values,[43,167] in one case by as much as 50 times. The reaction of aluminum oxide vapor species with tungsten cells precludes the formation of AlO_2.[43,192] The JANAF Tables[167] analysis excludes the data for aluminum oxide species which were obtained employing such metal cells.

In an experiment to obtain thermodynamic data for the AlO_2 species Farber, Srivastava, and Uy[42] performed effusion–mass spectrometric studies of the vapor species over the system Al(l) and $Al_2O_3(c)$ with gaseous O_2 also being admitted into the effusion cell. From the equilibrium data a $\Delta H°_{298}$ value of −0.25 ± 3.6 kcal/mol was obtained for the isomolecular reaction $AlO_2(g) + Al(g) = 2AlO(g)$. A subsequent study of the vapor species over neutral Al_2O_3[43] yielded −0.35 ± 0.2 kcal/mol for the ΔH_{298} of this reaction. The corresponding ΔH_{f298} of $AlO_2(g)$ was determined as −44.9 ± 3 kcal/mol. Two mass spectrometer studies of Al additive compositions in H_2/O_2 atmospheric flames confirmed this value.[40,41] Farber et al.[41] reported a $\Delta G°$ of 7.4 kcal/mol for the reaction $AlO(g) + H_2O(g) = AlO_2(g) + H_2(g)$ at 2250 ± 100 K, leading to −42.5 ± 5 kcal/mol for the ΔH_{f298} of $AlO_2(g)$. The JANAF Tables[167] derived −44 kcal/mol from an analysis of various Al–O bond strengths for molecules containing aluminum and oxygen.

Fontijn et al.[193,194] in a fast flow reaction, studied the kinetics of the reaction $AlO + O_2 = AlO_2 + O$ via laser-induced fluorescence from 300 to 1400 K and found that the reaction had no measurable activation energy. Fontijn et al. concluded that the use of $D(O–AlO) = D(Al–O) = 120 \pm 2$ kcal/mol obtained from the mass spectrometer results of Farber et al.[42,43] leads to a ΔH_{298} value of −2 ± 2 kcal/mol for the above reaction, easily consistent with the lack of an activation energy.

Thus the existence of the AlO_2 molecule and its heat of formation have been definitely established from seven mass spectrometric and seven spectroscopic and chemiluminescence investigations, whereas no valid experimental evidence to the contrary has been presented in other studies. The value of −44.9 ± 3 kcal/mol by Farber et al.[43] is recommended for the ΔH_{f298} of $AlO_2(g)$.

7. $AlO_2^+(g)$

A $\Delta H_f°_{298}(AlO_2^+(g))$ value of 195.7 ± 25 kcal/mol is calculated from $\Delta H_f°_{298}(AlO_2(g)) = -44.9 \pm 3$ kcal/mol using Farber et al.'s appearance potential of 10.0 ± 1 eV (230.6 ± 23 kcal/mol).[42,43,165] The appearance potential of AlO_2^+ is comparable to that of $Al_2O_2^+$ (AP = 9.9 eV), indicating that AlO_2^+ is the product from the direct ionization of the neutral AlO_2 molecule. Moreover, the bond energy, $D°(AlO_2–Al)$, should be approximately $D°(AlO) = 5.20$ eV based on bond energies derived by assuming either the square-planer[33] or symmetric linear structure for $Al_2O_2(g)$. Thus, for AlO_2^+ to be a fragment ion of $Al_2O_2(g)$, it would be necessary for the ionization potential of AlO_2 to have an anomalously low value of 5 ± 1 eV, which is considered very unlikely.

8. $AlO_2^-(g)$

Srivastava et al.[165] studied the isomolecular reaction $AlO_2(g) + Cl^-(g) = AlO_2^-(g) + Cl(g)$, using effusion–mass spectrometry. Their second- and third-law studies resulted in $\Delta H_r°_{298} = -8.8 \pm 8$ and -11.0 ± 1.0 kcal/mol, respectively, when adjusted to be consistent with JANAF[167] auxiliary data. Placing a higher degree of confidence in the third-law data, a $\Delta H_f°_{298}(AlO_2^-(g)) = -141.0 \pm 5$ kcal/mol is derived. The corresponding electron affinity, EA (AlO_2) = 96.1 ± 3 kcal/mol (4.1 ± 0.1 eV), is 14 kcal greater than the EA of BO_2, 82.3 ± 3 kcal/mol.

9. $AlO(g)$

The $D°$ of AlO had been controversial for 20 years. However, during the last 4 years the discrepancy in the bond energy values for AlO has been resolved, and it is now possible to recommend a $D°$ value for AlO within 2 kcal. Recently proposed values for $D°(AlO)$ are summarized in Table VII.

A wide discrepancy exists regarding the results of two groups of experiments: (1) Knudsen effusion, evaporation, spectroscopic and mass spectrometric; and (2) combustion and flame spectroscopy. The bond energy differs by a maximum of only 5 or 6 kcal among the various types of experiments in group 1, which in turn differ by as much as 20 kcal with those of group 2.

Farber and Srivastava[40,41,165] have reported that the discrepancy between the dissociation energy values for AlO obtained from flame experiments[65,81,116] and those from other thermochemical and spectroscopic methods was likely due to the unreliability of calculating absolute AlO concentrations from the intensity measurements. Drowart[32] and Frank and Krauss[48] have also cited reasons to reject these flame-photometric values.

Excellent agreement between the results of three different experimental techniques, effusion-mass spectrometric,[43,72] spectroscopic,[110] and chemiluminescent,[28] suggests that $D^\circ = 120 \pm 1$ kcal/mol, or $\Delta H_f{}^\circ{}_{298}(AlO(g)) = 16.5 \pm 2$ kcal/mol from the neutral cell experiments.[43] The recent flame-mass spectrometric results[40,41] confirm this value. Earlier mass spectrometric data[33] were unreliable owing to the reaction between Al(l) and the metal effusion cell (tungsten and molybdenum), which caused reduction of the vapor species. Other reported D° values have been summarized by Farber et al.[43] and Dagdigian et al.[28]

10. $AlO^+(g)$

The ionization potential of AlO has been reported as 9.5 eV (219.5 kcal/mol). The uncertainties include 0.5,[33] 1.0,[43,165] and 0.15 eV.[72] Using this value in conjunction with $\Delta H_f{}^\circ{}_{298}(AlO(g)) = 16.5 \pm 2$ kcal/mol, one obtains $\Delta H_f{}^\circ{}_{298}(AlO^+(g)) = 236.3 \pm 5$ kcal/mol.

11. $AlO^-(g)$

The electron affinity of AlO has been obtained using effusion-mass spectrometry by Srivastava, Uy, and Farber.[165] They studied the charge exchange reaction $AlO(g) + Cl^-(g) = AlO^-(g) + Cl(g)$ in the temperature range 2080–2222 K. When combined with the present value of $\Delta H_f{}^\circ{}_{298}(AlO(g)) = 16.5 \pm 2$ kcal/mol, a $\Delta H_f{}^\circ{}_{298}(AlO^-(g)) = -64.0 \pm 4$ kcal/mol is calculated. The corresponding electron affinity, EA(AlO) = 80.5 ± 4 kcal/mol (3.5 eV), is 8.6 kcal/mol more than the present EA(BO) = 71.9 kcal/mol. Gaines and Page[52] predicted the electron affinity of AlO to be 11 kcal/mol higher than that of BO based on valence-state promotion energy considerations.

C. Gallium Oxides

1. $Ga_2O(g)$

The pressures of Ga_2O over Ga(l) and H_2O vapor in the temperature range 1200–1300 K and over Ga(l) and $Ga_2O_3(c)$ in the temperature range 1073–1273 K were measured by Chaplygin[18] and by Frosch and Thurmond,[50] respectively, using the transport method. Burns[16] studied the rate of evaporation from Ga_2O_3 at the melting point employing evaporation-mass spectrometric techniques. The three experiments yielded 213.1 ± 1,[18] 213 ± 5,[50] and 208.9 ± 7[16] kcal/mol for the D° when adjusted to be consistent with the auxiliary data of $Ga_2O_3(c)$ and $Ga_2O(g)$ given in ref 119 and 6, respectively.

The D° of Ga_2O has also been investigated by Shchukarev et al.,[150] using mass spectrometer techniques; however, the derived reaction enthalpies are unreliable because of high fragmentation of the gaseous species at 70 eV, the ionizing electron energy used in their experiments.

Burns[16] obtained data at only one temperature (2068 K). From his data the partial pressure of GaO is approximately 1% of the partial pressure of Ga_2O_3. Therefore, the transport experiments, assuming the products to be only Ga_2O, would have a negligible error (less than 0.1 kcal/mol). A value of $D^\circ = -213.1 \pm 3$ is recommended, which corresponds to $\Delta H_f{}^\circ{}_{298}(Ga_2O(g)) = -23.6 \pm 3$ kcal/mol obtained by two transport experiments.[18,50] The mass spectrometer experiments of the metal oxide system employing tungsten cells have shown the D° to be lower by 5 to 6 kcal/mol. The tungsten cell caused reduction of the vapor species.

2. $Ga_2O^+(g)$

The $\Delta H_f{}^\circ{}_{298}(Ga_2O^+(g)) = 170.1 \pm 17$ kcal/mol is derived from the ionization potential of 8.4 ± 0.6 eV (193.7 ± 14 kcal/mol) for $Ga_2O(g) \rightarrow Ga_2O^+(g) + e(g)$. It is assumed that the ionization potential is equal to the appearance potential measured by Burns[16] and Fu and Burns.[196] A value of 8.0 is also reported in the literature.[150]

TABLE VII. Proposed Values for $\Delta H_f{}^\circ{}_{298}$ and D° of AlO(g)

method	reaction[a]	$\Delta H_f{}^\circ{}_{298}$ kcal/mol	D° kcal/mol	ref
effusion-mass spectrometry	A	16.5 ± 3	119.9	43
	B	18.5 ± 3	117.8	72
	C	17.8 ± 3	118.6	72
	A[b]	21.5 ± 7	113.5	33
	A[c]	22.9 ± 7	114.8	33
	A	19.2 ± 3	117.2	190
vaporization-mass spectrometry		20.5 ± 4	115.9	16
		16.0 ± 2	120.4	196
flame mass spectrometry		18.5 ± 5	117.8	40, 41
chemiluminescence		14.8 ± 1	121.5	28
spectroscopy		≥14.4 ± 0.6	≤122.1	174
		16.6	120.0	110
flame spectroscopy		−5 ● 10	141.5	81
		−3.5 ± 18	140.0	116
		−0.6	137.0	65
		17.3 ± 7	119.1	195
effusion	D	>9.3	<127.1	13

[a] (A) $AlO(g) = Al(g) + O(g)$; (B) $Al(g) + O_2(g) = AlO(g) + O(g)$; (C) $Al(g) + SO(g) = AlO(g) + S(g)$; (D) $Al_2O_3(c) = 2AlO(g) + O(g)$. [b] Using molybdenum cells. [c] Using tungsten cells.

3. $GaO(g)$

The values for the dissociation of GaO have been determined as 117 kcal/mol by Gurvich and Veits[65] using the flame spectroscopic technique and as 92.1 ± 3.5 kcal/mol by Burns[16] by means of vaporization studies and mass spectrometer identification at the melting point of Ga_2O_3 (2068 K). A recent evaporation experiment reported $D_0 = 86.5$ kcal/mol.[196] A linear Birge–Sponer extrapolation gives a D° of 70 kcal/mol.[55] The discrepancy between the dissociation energy values for GaO obtained from flame experiments[65] and vaporization studies[16] was likely due to the unreliability of calculating absolute GaO concentrations from the intensity measurements.[65] Hildenbrand[71] has shown that improved values from Birge–Sponer extrapolation of the ground state can be obtained by correcting the extrapolation for the ionicity of the state.

In the absence of supporting data, and bearing in mind that the mass spectrometer data[16] were obtained at a single temperature, a value of $D^\circ = 92.1 \pm 6$ is recommended, which corresponds to $\Delta H_f{}^\circ{}_{298}(GaO(g)) = 32.4 \pm 6$ kcal/mol. The error limit has been extended since only one temperature point was reported and no second law corroboration was obtained.

4. $GaO(g)^+$

Burns[16] and Fu and Burns[196] measured an appearance potential of 9.4 ± 0.5 eV (216.8 ± 12 kcal/mol) for GaO on the assumption that it was identical with the ionization potential for $GaO(g) = GaO(g)^+ + e(g)$. We calculated a $\Delta H_f{}^\circ{}_{298}$ of $GaO(g)^+$ of 249.2 ± 18 kcal/mol using a $\Delta H_f{}^\circ{}_{298}(GaO(g))$ value of 32.4 ± 6 kcal/mol.

D. Indium Oxides

1. $In_2O(g)$

Brewer[12] suggested that In_2O_3 vaporizes mainly to the element. Earlier, in a study of In_2O_3, it was concluded that the gaseous oxide, In_2O, was a product of its vaporization.[169] Shchukarev et al.[146] performed transport experiments and postulated that the predominant gaseous species was In_2O_3. In the vapor pressure study of Khvorostukhina,[93] it was assumed that the dissociation products were InO and O_2. In contrast to the results of these experiments, no In_2O_3 was seen in the mass spectrometer experiments, and the intensity of InO was too small for any meaningful measurements.[16,17,150] The pressures of In_2O over In(l) and H_2O vapor in the temperature range 1100–1300 K were measured by Chaplygin,[18] using the transport method. These studies yielded $D°$ values of 191.4 ± 1 and 190.3 kcal/mol by third and second laws, respectively. Recently, Valderrama and Jacob[210] measured the pressures of In(g) and In_2O(g) by effusion and Langmuir free evaporation of the reaction $4In(g) + In_2O_3(c) = 3In_2O(g)$ and calculated a $D°$ of 180 ± 1 kcal/mol for In_2O(g).

The Knudsen effusion[17] and vaporization[16] mass spectrometer experiments resulted in identical $D°$ values, In_2O = 182.0 ± 4 kcal/mol. The other mass spectrometer investigation[150] of the evaporation of indium oxides yielded $D°$ values of 185.5 and 193.5 kcal/mol by second and third laws, respectively.

The partial pressure of the InO was too small for accurate measurements;[17] therefore, the transport experiment, assuming the products to be only In_2O, should be more reliable than the condensed phase mixture of In + In_2O_3.[210] We therefore recommend a value of $D°(In_2O(g))$ = 191.4 ± 5 kcal/mol.[18] When combined with the $\Delta H_f°$ of In(g),[100] this corresponds to $\Delta H_f°_{298}(In_2O(g)) = -15.7 \pm 5$ kcal/mol. The mass spectrometer experiment,[150] although performed at 70 eV, supports this value. Ionization voltages of 70 eV would not contribute to the concentration of In_2O since it is the gaseous species with the highest molecular weight. The tungsten cell possibly caused reduction of the vapor species in the other two mass spectrometer experiments.[16,17] Thus, the $D°$ values may be biased by 5 to 6 kcal/mol. The pressure measurements[93,146] must be reinterpreted in terms of In and In_2O.

2. *$In_2O^+(g)$*

A $\Delta H_f°_{298}(In_2O^+(g)) = 168.8 \pm 17$ kcal/mol is derived from the ionization potential 8.0 ± 0.5 eV (184.5 ± 12 kcal/mol) for $In_2O(g) \rightarrow In_2O^+(g) + e^-(g)$. It is assumed that the ionization potential is equal to the appearance potential measured by Burns et al. in two separate mass spectrometer investigations.[16,17] A value of 9 ± 0.5 eV[129] has also been reported. The $\Delta H_f°_{298}$ of In_2O^+ is based on $\Delta H_f°_{298}(In_2O(g)) = -15.7 \pm 5$ kcal/mol, which includes the uncertainties inherent in the properties of this species.

3. *InO(g)*

Spectra attributed to the molecule InO have been reported by Haraguchi and Fuwa[67] and by Watson and Shambon.[182] From the data of Watson and Shambon,[182] Howell[77] derived $D°$(InO) = 25 kcal/mol. In contrast, thermochemical measurements in flames resulted in $D°$(InO) = 103 kcal/mol.[65] Burns et al.,[17] employing Knudsen-mass spectrometer techniques, identified the molecule InO, but the intensity was too small to measure. They gave an upper limit for $D°(InO) \leq 76$ kcal/mol. Shchukarev et al.[150] also performed Knudsen–mass spectrometer experiments; however, no meaningful results could be derived from their data since the studies were performed at an ionizing energy of 70 eV, resulting in extensive fragmentation.

There appears to be no reliable chemical data to settle the $D°$ of InO. The flame value of 103 kcal/mol appears to be too high. The spectroscopic value of 25 kcal/mol is, however, too low by comparison with the other oxides; $D°$ = 120 (AlO), 191.2 (BO), and 92.1 (GaO) kcal/mol.

E. Thallium Oxides

The only definitely established gaseous oxide of thallium identified mass spectrometrically is Tl_2O.[6,24,149] No other thallium-containing ions have been observed.

1. *$Tl_2O(g)$*

Although, four mass spectrometer studies have been performed to study Tl_2O(g),[6,24,25,149] no reaction enthalpies could be derived because of the substantial oxygen peaks from the background gases. Also, the measurements were made between 40 and 70 eV, resulting in extensive fragmentation.

Two transpiration studies[27,148] involving solid Tl_2O_3 have been performed. Cubicciotti and Keneshea[27] reported the enthalpy of vaporization of $Tl_2O_3(c) = Tl_2O(g) + O_2(g)$ as 90 ± 0.5 kcal/mol at 1000 K. When combined with $\Delta H_f°_{298}(Tl_2O_3(c)) = -94.3 \pm 0.8$ kcal/mol, and reducing it to 298 K,[24] one obtains a $\Delta H_f°_{298}(Tl_2O(g))$ value of 1.2 ± 1.3 kcal/mol. Shchukarev et al.[148] assumed (incorrectly) that the vapor species under 1 atm of oxygen was Tl_2O_3. Recalculation of their results gave pressure data approximately two orders of magnitude greater than the transpiration data of Cubicciotti and Keneshea.[27]

The effusion method has been employed in three studies of the vapor pressure of thallous oxide.[25,112,142] Cubicciotti[25] used the mass spectrometer to identify the effusion species and reported the enthalpy of sublimation at 700 K to be 42.5 ± 0.3 kcal/mol. When combining this value with $\Delta H_f°_{298}(Tl_2O(c)) = -40.4 \pm 2$ kcal/mol, and reducing it to 298 K,[24,25] one derives a $\Delta H_f°_{298}(Tl_2O(g))$ value of 4.9 ± 3 kcal/mol. The vapor pressures obtained by Mulford[112] were somewhat higher than those of Cubicciotti.[25] Shakhtakhtinskii and Kuliev[142] used a radiotracer effusion method to study the sublimation of thallium from Tl_2O_3. Because their vapor pressures were too high, they presumed that the Tl_2O_3 had decomposed to Tl_2O and therefore reported their results as vapor pressures of Tl_2O. Their vapor pressures were several orders of magnitude higher than those of Cubicciotti.[25]

Cubicciotti's recent effusion study[25] appears to be precise and is therefore recommended as providing the best value [$\Delta H_f°_{298}(Tl_2O(g)) = 4.9 \pm 3$, and $D° = 0.9 \pm 3$ kcal/mol], although no mass spectrometric identification has confirmed the reaction. The agreement with his other value of 1.2 kcal/mol is quite adequate considering the two separate experimental techniques involved. In the transpiration experiments of Shchukarev et al.,[148] the material used was contaminated with bromide, resulting in a bromide species more volatile than the oxide; therefore, their results were dominated by a bromide impurity. Mulford's results[112] exhibited a considerable degree of scatter, apparently from the chemical analysis for effusate. Shakhtakhtinskii and Kuliev[142] were unsure of the composition of their solid.

2. *$Tl_2O^+(g)$*

The ionization potential of Tl_2O has been reported as 7.5 ±

TABLE VIII. Recommended Values for the Thermodynamic Properties of the Oxides (c,l)

oxide	$\Delta H_f°_{298}$, kcal/mol	T_m, K	$\Delta H_m°$, kcal/mol	$S°_{298}$ gibbs/mol	$C_p°_{298}$ gibbs/mol
B_2O_3(c)	−304.0 ± 0.4	723 ± 2	5.8 ± 0.3	12.90	14.96
B_2O_3(l)	−299.5 ± 0.5			18.75	31.00 (723 K)
α-Al_2O_3(c)	−400.5 ± 0.3	2327 ± 6	26.5 ± 1.0	12.17	18.88
κ-Al_2O_3(c)	−397.3 ± 1.0				
δ-Al_2O_3(c)	−378.3 ± 1.0				
γ-Al_2O_3(c)	−396.0 ± 1.5				
Al_2O_3(l)	−383.7 ± 1.2			18.54	46.00 (2327 K)
Ga_2O_3(c)	−261.0 ± 1.0	2068 ± 20		20.31	22.42
In_2O_3(c)	−222.1 ± 0.1	2183 ± 10		24.90	22.00
Tl_2O_3(c)	−94.3 ± 1.0	989 ± 2	3.5 ± 1	38.00	25.86
Tl_2O_3(l)	−69.8 ± 2.0				
Tl_2O(c)	−40.4 ± 2.0	852 ± 20	7.24 ± 1	34.70	19.30
Tl_2O(l)	−21.8 ± 3.0				

TABLE IX. Recommended Values for the Thermodynamic Properties of Gaseous Oxides

	$\Delta H_f^\circ{}_{298}$	$S^\circ{}_{298}$	$C_p^\circ{}_{298}$
oxide	kcal/mol	gibbs/mol	
B_2O_3(g)	−200.0 ± 1.0	67.79	15.98
$B_2O_3^+$(g)	123.0 ± 12.0		
B_2O_2(g)	−109.0 ± 2.0	57.96	13.69
$B_2O_2^+$(g)	213.8 ± 14.0		
BO_2(g)	−77.0 ± 3.0	54.90	10.34
BO_2^+(g)	245.0 ± 23.0		
BO_2^-(g)	−159.3 ± 3.0	51.58	9.35
BO(g)	0.1 ± 1.0	48.60	6.98
BO^+(g)	311.3 ± 23		
BO^-(g)	−71.9 ± 2.0	47.53(164)	7.00(164)
Al_2O_2(g)	−106.4 ± 6.0	66.04	15.25
$Al_2O_2^+$(g)	121.9 ± 15.0	68.07	15.64
Al_2O(g)	−32.0 ± 3.0	61.41	12.51
Al_2O^+(g)	157.1 ± 5.0	63.57	12.71
AlO_2(g)	−44.9 ± 3	58.61	11.68
AlO_2^+(g)	195.7 ± 25		
AlO_2^-(g)	−141.0 ± 5	54.85	11.09
AlO(g)	16.5 ± 2	52.17	7.38
AlO^+(g)	236.3 ± 5	55.18	7.92
AlO^-(g)	−64.0 ± 4	50.83	7.48
Ga_2O(g)	−23.6 ± 3		
Ga_2O^+(g)	170.1 ± 17		
GaO(g)	32.4 ± 6	53.86[187]	7.66[187]
GaO^+(g)	249.2 ± 18		
In_2O(g)	−15.7 ± 5		
In_2O^+(g)	168.8 ± 17		
Tl_2O(g)	4.9 ± 3.0	75.85[25]	12.47[25]
Tl_2O^+(g)	177.8 ± 9		

0.3 eV (172.9 ± 7 kcal/mol) by Cubicciotti.[24] Using this value in conjunction with $\Delta H_f^\circ{}_{298}(Tl_2O(g)) = 4.9 \pm 3$ kcal/mol, one obtains $\Delta H_f^\circ{}_{298}(Tl_2O^+) = 177.8 \pm 9$ kcal/mol.

V. Recommended Values

Recommended values for the heats of formation, $\Delta H_f^\circ{}_{298}$, melting temperatures, T_m°, and heats of melting, ΔH_m°, for the condensed species, including error limits illustrating the present uncertainties, together with their entropies, $S^\circ{}_{298}$, and heat capacities, are summarized in Table VIII. Similarly, recommended values for the heats of formation, entropies, and heat capacities of gaseous oxides and ionic species are presented in Table IX.

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