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SOLID-STATE ELECTROCHEMICAL STUDY OF THE GIBBS ENERGY OF FORMATION OF B - GALLIUM SESQUIOXIDE USING A CALCIA-STABILIZED ZIRCONIA ELECTROLYTE

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Publication Date

1976-07-01

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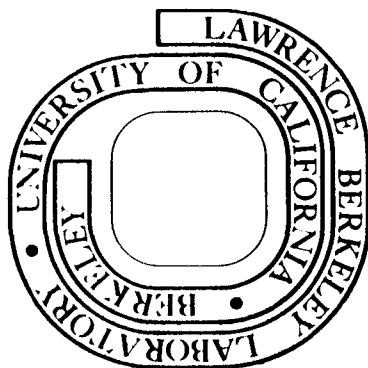
T. J. Anderson and L. F. Donaghey

July 1976

Prepared for the U. S. Energy Research and
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Solid-State Electrochemical Study of the Gibbs Energy of
Formation of β -Gallium Sesquioxide Using a
Calcium-Stabilized Zirconia Electrolyte

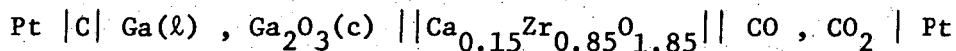
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July, 1976

Abstract

The Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3(\text{c})$ was determined with a high-temperature, solid-state electrochemical cell utilizing calcium-stabilized zirconia as the solid electrolyte and a $\text{CO} - \text{CO}_2$ gaseous mixture as the reference electrode. The Nernst voltage of the cell,



was measured over the temperature range from 775 to 1100 K. A linear regression analysis of the data showed that the Gibbs energy of formation can be represented by

$$G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, T) / \text{kcal}_{\text{th}} \text{mol}^{-1} = (-265.83 \pm 0.16) + (0.08345 \pm 0.00016)(T/K) .$$

A third law analysis of the data showed that the standard enthalpy of formation is given by

$$H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15) / \text{kcal}_{\text{th}} \text{mol}^{-1} = -261.0 \pm 0.1$$

which is in agreement with calorimetric results. The third-law results show a temperature dependence of $0.004 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$, which is most probably caused by an error in the estimated high temperature heat capacity of gallium rather than by electronic conduction in the solid electrolyte.

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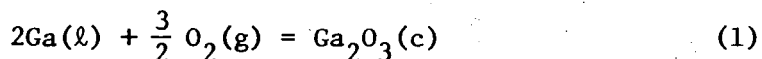
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Short Title: Gibbs Energy of Formation of Gallium Sesquioxide

Introduction

Gallium has become important in the semiconductor microelectronics industries as a component of compounds for electroluminescent and microwave devices. Gallium is also an important solvent for liquid-phase epitaxial crystal growth of compound semiconductors where oxygen is an electrically active impurity. Gallium sesquioxide added to Ga - GaP solutions has been used to achieve high electroluminescence efficiency in Zn-doped GaP light-emitting diodes.⁽¹⁻⁴⁾ Effective design of semiconductor device processes involving gallium should be aided by accurate thermodynamic data for gallium oxide.

The Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ by the reaction

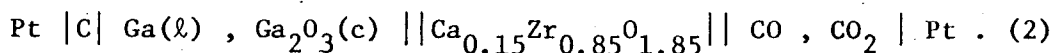


has been estimated by Coughlin⁽⁵⁾ and measured using solid-state electrochemical methods by Klinedinst and Stevenson⁽⁶⁾ and Smith and Chatterji.⁽⁷⁾ Pankratz and Kelley determined the high temperature heat content of $\beta - \text{Ga}_2\text{O}_3$ by calorimetric methods.⁽⁸⁾ More recently Mills measured the heat capacity of $\beta - \text{Ga}_2\text{O}_3$ by drop calorimetry.⁽⁹⁾ Unfortunately, the Gibbs energies of formation as determined in the previous studies show marked discrepancies, especially in the temperature dependence, i.e., the standard entropy of formation, and therefore, further experimentation and critical review of the data is appropriate. In this study the Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ was measured in a high-temperature, solid-state electrochemical cell with a $\text{CO} + \text{CO}_2$ gaseous mixture as the reference electrode. A microcomputer system was utilized for automated experimental control and for data acquisition, thereby providing continuous detection of any non-equilibrium conditions and of inconsistencies in experimental data.⁽¹⁰⁾

0 0 0 0 1 3 0 8 5 2 4

Theory

The solid-electrolyte galvanic cell employed in measuring the Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ can be represented schematically as



The equilibrium partial pressures of oxygen in the two electrodes are related to the cell potential E , by the Nernst equation:

$$E/mV = \{R/4F\}(T/K) [\ln \{p(\text{O}_2, \text{CO} + \text{CO}_2)/\text{atm}\} - \ln \{p(\text{O}_2, \text{Ga} + \text{Ga}_2\text{O}_3)/\text{atm}\}]. \quad (3)$$

In this equation, $p(\text{O}_2, \text{CO} + \text{CO}_2)$ indicates the oxygen fugacity of the $\text{CO} - \text{CO}_2$ gas mixture, $p(\text{O}_2, \text{Ga}, \text{Ga}_2\text{O}_3)$ represents that of the $\text{Ga} + \text{Ga}_2\text{O}_3$ mixture, R is the gas constant, T is the thermodynamic temperature and F is the Faraday constant.

The Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ is related to the oxygen partial pressure over the $\text{Ga} + \text{Ga}_2\text{O}_3$ mixture by the equilibrium constant for the formation reaction:

$$K_f(\text{Ga}_2\text{O}_3) = a(\text{Ga}_2\text{O}_3) a(\text{Ga})^{-2} p(\text{O}_2, \text{Ga}_2\text{O}_3, \text{Ga})^{-3/2} \quad (4)$$

or

$$K_f(\text{Ga}_2\text{O}_3) = \exp \left\{ -\Delta G_f^0(\text{Ga}_2\text{O}_3, \text{c}, T) / RT \right\} . \quad (5)$$

Equations 3 through 5 allow one to calculate $\Delta G_f^0(\text{Ga}_2\text{O}_3, \text{c}, T)$ from the measured experimental temperature and cell voltage:

$$\Delta G_f^0(\text{Ga}_2\text{O}_3, c, T) = 1.5 RT \ln p(\text{O}_2, \text{CO} + \text{CO}_2) - 6FE \quad (6)$$

Here, unit activities for Ga(l) and Ga₂O₃(c) in the mixture are assumed.

The reference oxygen partial pressure is established by the equilibrium reaction,



and is related to the Gibbs energy change for this reaction, ΔG(7), by:

$$p(\text{O}_2, \text{CO} + \text{CO}_2) = \left(\frac{p(\text{CO}_2)}{p(\text{CO})} \right)^2 \exp \{2\Delta G(7)/RT\} \quad (8)$$

where $\Delta G(7)/\text{cal}_{\text{th}} \text{mol}^{-1} = -68,270 - 0.18T \ln T - 0.34 \times 10^{-3} T^2 + 0.87 \times 10^5/T + 23.28T$, can be deduced from the equations given by Wicks and Block⁽¹¹⁾ for the Gibbs energies of formation of CO and CO₂.

Experimental

The Experimental Cell

The basic, solid-state galvanic cell design is depicted in figure 1. The cell consisted of a 5.08 cm diameter, closed-end alumina tube 45.7 cm in length secured by a Viton O-ring to a water-cooled, brass cell-head. Three 0.318 cm Cajon through-bore fittings were located on the cell head symmetrically around a 0.635 cm Cajon through-bore fitting. The thermocouple lead wires contained in

ceramic sheaths were passed through the 0.318 cm fittings. The larger, centered fitting was used to seal to a 0.634 cm diameter calcia-stabilized zirconia (CSZ) electrolyte tube, closed at the bottom.

Included in the brass head were bores for gas entrance and exit. The exit placement was such that the gas had to flow downward to the experimental cell, then through an alumina pushrod. Three spring-loaded tungsten wires provided support for a graphite chamber containing liquid gallium and $\beta - \text{Ga}_2\text{O}_3$ in contact with the CSZ tube.

The electrode materials were contained in a 5.08 cm diameter closed graphite crucible fitted with a screw cap containing a closely fitting hole through which the CSZ tube was inserted into the gallium electrode. Powdered graphite was added to seal the CSZ tube to the graphite lid. Details of electrode compartments are shown in cross-section in figure 2.

The cell was heated with a Marshall resistance-heated furnace 51 cm in length with a 6.35 cm bore. Excellent temperature control was furnished by an integrating, temperature-regulated, power supply designed and built at the Lawrence Berkeley Laboratory. Temperature uniformity and stability was held to within ± 0.5 K in the vicinity of the electrodes. Stray cell voltages induced by the temperature regulation circuit were eliminated by a metal ground shield placed around the 5.08 cm alumina tube. Type-S thermocouples (0.051 cm diameter, Pt - Pt 10%Rh) were calibrated in the cell under vacuum against a thermocouple calibrated at the National Bureau of Standards.

The calibration was performed with the standard thermocouple occupying the position normally that of the electrode, while the unknown thermocouple was placed in the normal operating positions. Each thermocouple emf was amplified using a X100 thermocouple amplifier calibrated with a Leeds and Northrup Type K-3 potentiometer facility.

The cell emf was measured with a Keithley 640 electrometer. High-isolation, triaxial cable was used to connect the experimental cell to the input head of the electrometer. The inner conductor of the triaxial cable was connected to the positive lead wire of the cell. The outer conductor was driven by the unity-gain feedback from the electrometer, thus acting as a driven guard. Leakage sources at the input head were negligible since the cable was guarded up to the sapphire insulated electrometer contact.

Materials

Gallium metal used in the study was semiconductor grade, 99.9999% pure, obtained from Cominco American. Gallium oxide was obtained from Alfa Products, and had a purity of 99.99%. The oxide was confirmed to be β - Ga_2O_3 and to show no detectable second phases by X-ray diffraction analysis.

The calcia-stabilized zirconia tubes containing 7.5 weight per cent calcia were obtained from the Zircoa Corporation of America. The tubes were confirmed to be leak tight both before and after the experiments. Spectroscopic-grade graphite was employed in the electrode compartment containing the liquid metal and a small amount of the oxide. Platinum lead wires were attached to the graphite

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compartment and to a platinum electrode made from Englehard unfluxed platinum paste (No. 6926) inside the CSZ tube end.

The CO + CO₂ reference electrode gas mixture was obtained from Matheson Gas Products. Chemical analysis showed the mixture to contain (25.29 ± 0.02) percent CO₂ and (2.45 ± 0.02) percent CO in high-purity argon. The ratio of the partial pressure of CO₂ to the partial pressure of CO in the primary standard gas was 10.322 ± .092.

Pure argon for use in purging the experimental cell was prepared by passing high-purity argon over Linde 4A molecular sieve at 195 K, then through a special, alumina-lined titanium-sponge purifier heated to 800 K. This gas was used as an inert purge gas for the metal-oxide electrode compartment, with the purge flow rate adjusted to 1 cm³ s⁻¹.

Reagent dibutyl phthalate was used in gas exhaust traps to prevent back-diffusion of oxygen into the experimental cell.

Microcomputer Control System

Operation of the electrochemical experiments and data acquisition were automated with a microcomputer system based on an Intel 8008 microprocessor. The facility is schematically shown in figure 3. The system had the capability of setting the cell operation temperature to a predetermined, cyclical sequence of values and monitoring the cell emf and thermocouple output voltages on a specified time base until equilibrium had been established, thus allowing continuous cell operation without operator assistance. A 4 1/2 digit panel meter

alternately displayed the cell voltage and temperature, while a permanent record was obtained on a teletype. The microcomputer was constructed from components stocked at the Lawrence Livermore Laboratory.

Procedure

In each of several experiments the cell compartments were leak-checked using a high vacuum system, then purged with high purity argon. The cell temperature was programmed to rise at 0.02 Ks^{-1} to the lowest measurement temperature, after which the reference gas flow was initiated. The cell temperature was then sequentially incremented and decremented throughout the experimental range, with the cell voltage measured and periodically recorded at each temperature until equilibrium was reached and confirmed. Reference gas and argon flow rates did not affect the cell voltage in the ranges selected. At the conclusion of each experiment the cell compartments were again checked for leaks and the metal electrode examined for evidence of oxidation. The electrode material was then analyzed by X-ray diffraction to confirm the absence of side-reaction products.

Results

Table 1 shows the measured cell potentials, the partial pressures of oxygen in the reference gas mixture, the calculated equilibrium partial pressures of oxygen in the $\text{Ga} + \text{Ga}_2\text{O}_3$ mixture, and the calculated values of the Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ over the experimental temperature.

0 6 0 0 4 3 0 8 5 2 7

Table 1 Summary of Experimental and Derived Data*

T/K	$E_{\text{measured}}/\text{mV}$	$\log_{10} \frac{p(\text{O}_2, \text{CO} + \text{CO}_2)}{\text{atm}}$	$\log_{10} \frac{p(\text{O}_2, \text{Ga} + \text{Ga}_2\text{O}_3)}{\text{atm}}$	$\frac{\Delta G_f^\circ (\text{Ga}_2\text{O}_3, \text{c}, \text{T})}{\text{kcal}_{\text{th}} \text{mol}^{-1}}$
776.9	421.1(±0.1)	-26.782(±.008)	-37.710(±.002)	-201.08(±.01)
815.1	418.4	-24.998	-35.347	-197.74
855.4	416.5	-23.288	-33.105	-194.36
902.3	415.4	-21.491	-30.773	-190.58
933.4	414.0	-20.400	-29.342	-187.98
967.9	412.4	-19.271	-27.861	-185.09
1004.4	410.9	-18.162	-26.410	-182.06
1039.9	409.1	-17.158	-25.090	-179.08
1044.7	408.5	-17.028	-24.911	-178.62
1048.8	408.5	-16.917	-24.770	-178.31
1051.1	407.9	-16.856	-24.680	-178.04
1059.5	408.0	-16.633	-24.397	-177.41
1091.2	406.9	-15.824	-23.342	-174.82

* atm = 101 325 Pa
 $\text{cal}_{\text{th}} = 4.184 \text{ J}$

A linear least-squares analysis of the experimental data obtained in the present study resulted in the following expression:

$$\Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T}) / \text{kcal}_{\text{th}} \text{mol}^{-1} = (-265.83 \pm 0.16) + (0.08345 \pm 0.00016) (\text{T}/\text{K}). \quad (9)$$

The uncertainties given in this expression are those computed from the standard errors of the mean values. The constant term appearing in equation 9 corresponds to the standard enthalpy change while the temperature coefficient represents the standard entropy change.

Discussion

A comparison of the data obtained in this study with data reported in previous studies is shown in figure 4. This figure shows the experimental values of $\Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T})$ plotted against temperature, with the least-squares straight line drawn through the data points for each study. Also shown are the estimated Gibbs energies of formation versus temperature of Coughlin,⁽⁵⁾ the calorimetric results of Pankratz and Kelley⁽⁸⁾ and the emf measurements of Smith and Chatterji⁽⁷⁾ and of Klinedinst and Stevenson.⁽⁶⁾

The $\Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T})$ values calculated from the experimental data of the present study showed excellent internal consistency with a standard error at 1000 K of only $\pm 0.31 \text{ kcal}_{\text{th}} \text{mol}^{-1}$. In comparison to the results of other studies, the magnitude of $\Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T})$ found in this study was more negative, except at temperatures above 1000 K. Since electronic conduction in the solid electrolyte tends to reduce the cell voltage, and thus the magnitude of the Gibbs energy

0 0 0 0 4 3 0 8 5 2 8

of formation, the higher magnitudes of $\Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T})$ are supportive of complete ionic conduction in the solid electrolyte with possible electronic conduction at temperature above 1000 K. The possibility of electrolyte failure suggested separate data analyses in the low and high temperature ranges of measurement.

In order to evaluate the internal consistence of the experimental results, and to facilitate comparison to calorimetric data, a third-law analysis was performed. The values of the standard enthalpy of formation of $\beta - \text{Ga}_2\text{O}_3$, $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$, were calculated from the following equation:

$$\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T}) = \Delta G_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T}) - \Delta_f\{\text{H}(\text{T}) - \text{H}(298.15)\} \\ + \text{T} \Delta S_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, \text{T}) + \Delta_f\{\text{S}(\text{T}) - \text{S}(298.15)\} .$$

The values of $\Delta_f\{\text{H}(\text{T}) - \text{H}(298.15)\}$ and $\Delta_f\{\text{S}(\text{T}) - \text{S}(298.15)\}$ for $\text{O}_2(\text{g})$ were taken from Hultgren et al.,⁽¹²⁾ although similar values are given by Wicks and Block,⁽¹¹⁾ that for $\text{Ga}(\ell)$ from Hultgren et al.,⁽¹²⁾ and that for $\beta - \text{Ga}_2\text{O}_3(\text{c})$ from Mills.⁽⁹⁾ The value $-72.87 \text{ cal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$ for $\Delta S_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ was determined from the data taken from Kelley⁽¹³⁾ for $\text{O}_2(\text{g})$ and from Adams, Johnston and Kerr⁽¹⁴⁾ for $\text{Ga}(\ell)$ and $\beta - \text{Ga}_2\text{O}_3(\text{c})$.

The results of the third-law analysis are presented in table 2. The overall mean value of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ and standard error of the mean were found to be -260.72 and $0.16 \text{ kcal}_{\text{th}}$, respectively, as indicated in analysis I. In this analysis, the cluster of data points near 1050 K were weighted so as to produce a uniform weighting of the

Table 2 Second-Law and Third-Law Analyses of the Experimental Data

T	Third-Law Analysis		Second-Law Analysis		
	$\Delta H_f^\circ(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ kcal _{th} mol ⁻¹	δ_1 kcal _{th} mol ⁻¹	Observed log K _p	Calculated log K _p	δ_2
776.9	-261.46	-.74	-56.565	-56.543	-.022
815.1	-261.19	-.48	-53.019	-53.038	0.019
855.4	-260.98	-.26	-49.657	-49.680	0.023
902.3	-260.90	-.19	-46.160	-46.150	-.010
933.4	-260.76	-.04	-44.014	-44.005	-.009
967.9	-260.58	0.14	-41.792	-41.786	-.006
1004.4*	-260.41	0.30	-39.614	-39.605	-.009
1039.9*	-260.21	0.51	-37.631	-37.631	-.005
1044.7*	-260.13	0.59	-37.366	-37.374	0.007
1048.8*	-260.13	0.58	-37.156	-37.156	0.000
1051.1*	-260.05	0.67	-37.018	-37.035	0.017
1059.5*	-260.07	0.64	-36.595	-36.597	0.002
1091.2*	-259.96	0.76	-35.013	-35.004	-.009
Analysis I: $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, \text{c}, 298.15)/\text{kcal}_{\text{th}} \text{mol}^{-1} = -260.7$			Analysis I: $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, \text{c}, 298.15)/\text{kcal}_{\text{th}} \text{mol}^{-1} = -265.2$		
Standard error/kcal _{th} mol ⁻¹ = 0.2			Standard error/kcal _{th} mol ⁻¹ = 0.1		
Analysis II: $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, \text{c}, 298.15)/\text{kcal}_{\text{th}} \text{mol}^{-1} = -261.0$			Analysis II: $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, \text{c}, 298.15)/\text{kcal}_{\text{th}} \text{mol}^{-1} = -265.5$		
Standard error/kcal _{th} mol ⁻¹ = 0.1			Standard error/kcal _{th} mol ⁻¹ = 0.1		

* Excluded from Analysis II

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data over the temperature range of measurement. The calculated values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ showed a small temperature dependence. This temperature dependence can be eliminated by adding $4.54 \text{ cal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$ to $\Delta S_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$.

It is interesting to note the effect of utilizing alternate sources of thermodynamic data in the third-law analysis. Glassner reports a high temperature heat capacity for liquid gallium which is 5% higher than that selected by Hultgren.⁽¹²⁾ Nevertheless, if Glassner's heat capacity data is used in the third-law calculation, the results are essentially unchanged from those given in table 2. Similarly, a third-law analysis with the thermodynamic data of Wicks and Block⁽¹¹⁾ for $\text{O}_2(\text{g})$ substituted for the selected data of Hultgren⁽¹²⁾ also gave results nearly equivalent to those shown in table 2. On the other hand, the selected thermodynamic data of Coughlin,⁽¹⁶⁾ when used in the third-law analysis gave a significantly different result for $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$, given by $-261.32 - 0.00196 T \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. Not only is the mean value of $-261.32 \pm 0.06 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ outside the standard error of the analysis shown in table 2, but the temperature dependence differs in sign. Other third-law analyses utilizing heat capacity data for Ga_2O_3 derived from Shchukarev et al.⁽¹⁷⁾ and from Pankratz and Kelley⁽⁸⁾ support the results shown in table 2. The temperature dependence of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ in the third-law analysis indicates either an error in the estimated heat capacity of gallium at high temperatures, or a measured cell-voltage error which increases with increasing temperature.

The values of $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, c, 298.15)$ calculated from the third-law analysis are compared in figure 5 to the data of Mah,⁽¹⁸⁾ determined by direct combustion calorimetry and to values derived from other studies. The value obtained by Shchukarev et al.⁽¹⁷⁾ from isothermal evaporation studies and the value derived from the present study are in close agreement with the calorimetrically determined value of $-261.05 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. Also shown in figure 5 are the results obtained from a third-law analysis of the data of Klinedinst and Steveson.⁽⁶⁾ The resulting values for $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, 298.15)$ exhibit a large temperature dependence with the average value lying somewhat above the calorimetrically determined value. Third-law analyses of the electrochemical results of Smith and Chatterji⁽⁷⁾ are shown by the dashed line in figure 5. Because the actual data were not available for this calculation, a data-fitted equation was used. This equation gave a nearly temperature-independent value of the standard heat of formation of $\beta - \text{Ga}_2\text{O}_3$, but shifted approximately $1.75 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ above the calorimetrically-determined value. Smith and Chatterji reported an error range of $0.8 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ with no apparent temperature dependence from their third-law analysis.

The values of $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, c, 298.15)$ calculated from the present experimental data show somewhat different temperature dependences in the low and high temperature ranges of measurement, as shown in figure 5. Below 970 K the calculated values of $\Delta H_f^\circ(\text{Ga}_2\text{O}_3, c, 298.15)$ have a temperature dependence of $4.2 \text{ cal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$, whereas above 970 K the temperature dependence is $5.4 \text{ cal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$. On the assumption that

the experimental results are in error in the high temperature range, an additional third-law analysis was performed on the experimental data in the range below 970 K. This analysis is denoted by analysis II in table 2. The average value of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ obtained from analysis II was $-260.98 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ with a standard error of $0.13 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. This result differs from the value obtained in analysis I by an amount only slightly larger than the standard error, indicating no significant systematic error in the high temperature range alone. Thus, the small temperature dependence in $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ obtained in the third-law analysis most probably indicates a systematic error in the thermodynamic functions, rather than an experimental error in the high temperature range alone.

A second-law analysis of the data obtained in the present study was also performed, and the results are shown in table 2. The least-squares value of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, T_m)$ at the mid-point experimental temperature, $T_m = 934.05 \text{ K}$ was found to be $-265.83 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. This value was corrected to 298.15 K by adding $-\Delta_f\{H(968.5) - H(298.15)\}$ to obtain $-265.15 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ for the standard heat of formation of $\beta - \text{Ga}_2\text{O}_3$ from solid gallium. This value is larger in magnitude than the third-law analysis (I) by $4.43 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$, which is larger than the standard error of the mean values from both second-law and third-law analyses. A second analysis (II), in which the high temperature data above 970 K was excluded, yielded a value of -265.54 for $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ within the standard error of the value obtained in analysis I. The difference between the values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ derived from second-law and third law methods is not surprising,

because of the limited range in temperature of the experimental measurements. A small difference in slope of the measured $\Delta G_f^{\circ}(T)$ can produce a large change in the value of $\Delta H_f^{\circ}(298.15)$ derived from the second-law analysis.

A comparison of the standard entropy and enthalpy of formation of $\beta - \text{Ga}_2\text{O}_3$ as derived from different sources is summarized in table 3. The enthalpy and entropy values reported by each source were corrected to the reference temperature. The values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, c, 298.15)$ obtained in previous electrochemical studies differ significantly from that obtained in the present study, and are more consistent with the value selected by Brewer,⁽¹⁹⁾ and by Rossini et al.,⁽²⁰⁾ $(-258 \pm 3 \text{ kcal}_{\text{th}})$, than with the more precise value obtained by Mah.⁽¹⁸⁾ The results of the present study show the highest consistency with the combustion-calorimetric data.

A potential source of error in the present study was electronic conduction in the CSZ electrolyte. Shown in figure 6 are conservative and liberal lower oxygen partial pressure limits to the electrolytic domain of CSZ as derived from the data of Schmalzreid⁽²¹⁾ and Patterson, Bogden and Rapp.⁽²²⁾ Also shown in figure 6 is the Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ and Ga_2O .⁽¹⁶⁾ The conservative limit places the $\text{Ga}_2\text{O}_3 - \text{Ga} - \text{O}_2$ equilibrium outside the ionic electrolytic domain at temperature above 880 K. The more recent and liberal limit places the most stable equilibrium of interest well within the limits of operation, however. In this study the working temperature was maintained below 1100 K in order to prevent conditions allowing electronic conduction in the solid

Table 3 Comparison of the Standard Enthalpy and Entropy of Formation of β - Ga_2O_3 from Different Sources

Method	$\Delta H_f^\circ(\text{Ga}_2\text{O}_3, c, 298.15) / \text{kcal}_{\text{th}} \text{mol}^{-1}$			$\Delta S_f^\circ(\text{Ga}_2\text{O}_3, c, 298.15) / \text{cal}_{\text{th}} \text{mol}^{-1}$		
	Experimental	Third Law	Second Law	Experimental	Second Law	Reference
Combustion Calorimetry	-261.05±0.3					18
Drop Calorimetry				-72.87		13,14
Isothermal Evaporation		-260.85±1.4				17
Electrochemical Cells						
coexistence electrode			-252.3		-65.1	6
coexistence electrode		-259.2	-258.8		-72.38	7
gas reference electrode			-252.1		-66.0	6
gas reference electrode		-260.7±0.2	-265.2±0.1		-77.60	This study (I)
gas reference electrode		-261.0±0.1	-265.5±0.1		-77.45	This study (II)

electrolyte. The results showed that while the emf data did not show a change in the temperature dependence at high temperature, the values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15 \text{ K})$ derived from the third-law analysis showed a small increase in the temperature dependence above 970 K. This result indicates possible electronic conduction in the solid electrolyte above 970. For this reason, the third-law analysis (II) is considered to be a more accurate test of the emf data.

The most probable cause of the variation of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ with temperature is that the thermodynamic data for gallium is incorrect. The specific heat data for O_2 should be very accurate, and the more recent calorimetric data of Mills⁽⁹⁾ for $\beta - \text{Ga}_2\text{O}_3$ agreed to within 1% with the data of Pankratz and Kelley.⁽⁸⁾ The most likely source of error is in the specific heat of gallium, for which a constant heat capacity was assumed above 700 K. Indeed, it appears that no measurements of the specific heat of gallium have been made above 720 K, and the assumption of a constant specific heat in this temperature range is probably in error. Nevertheless, the direct measurement of $\Delta G_f^{\circ}(\beta - \text{Ga}_2\text{O}_3)$ performed in this study showed much better consistency with the calorimetric data than did the data from earlier emf studies, as shown by the second-law and third-law analyses.

Conclusion

The Gibbs energy of formation of $\beta - \text{Ga}_2\text{O}_3$ was measured with high accuracy in an electrochemical cell utilizing a $\text{CO} + \text{CO}$ gaseous reference electrode. The use of a microcomputer system for automatic

control of the experiments proved exceptionally valuable for testing the reproducibility of the experimental data. The values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ determined from a third-law analysis were in close agreement with the calorimetrically determined value. A small temperature dependence of the derived values of $\Delta H_f^{\circ}(\text{Ga}_2\text{O}_3, \text{c}, 298.15)$ were attributed to errors in the predicted high temperature specific heat of gallium.

Acknowledgment

This work was supported by the U.S. Energy Research and Development Administration.

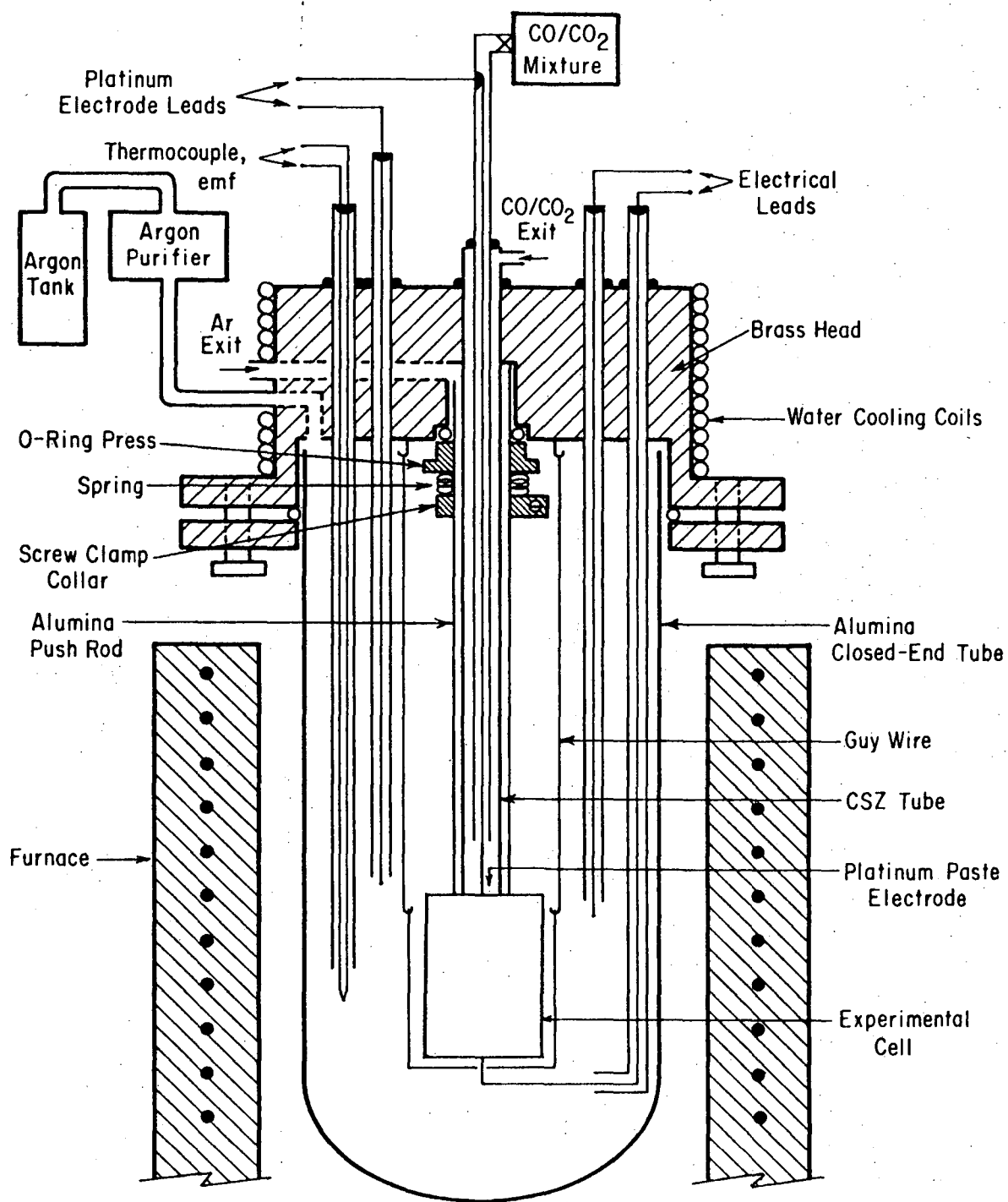
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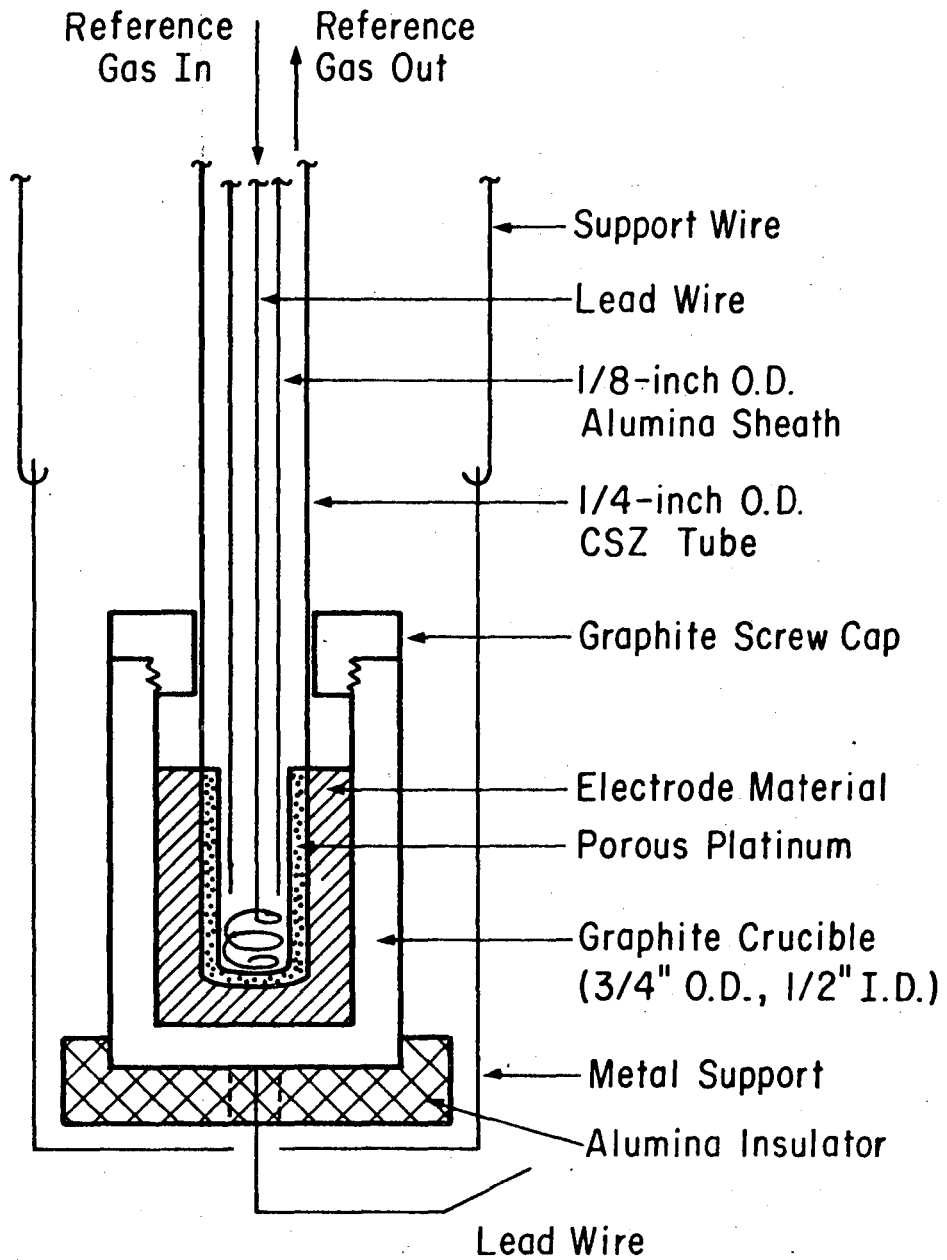
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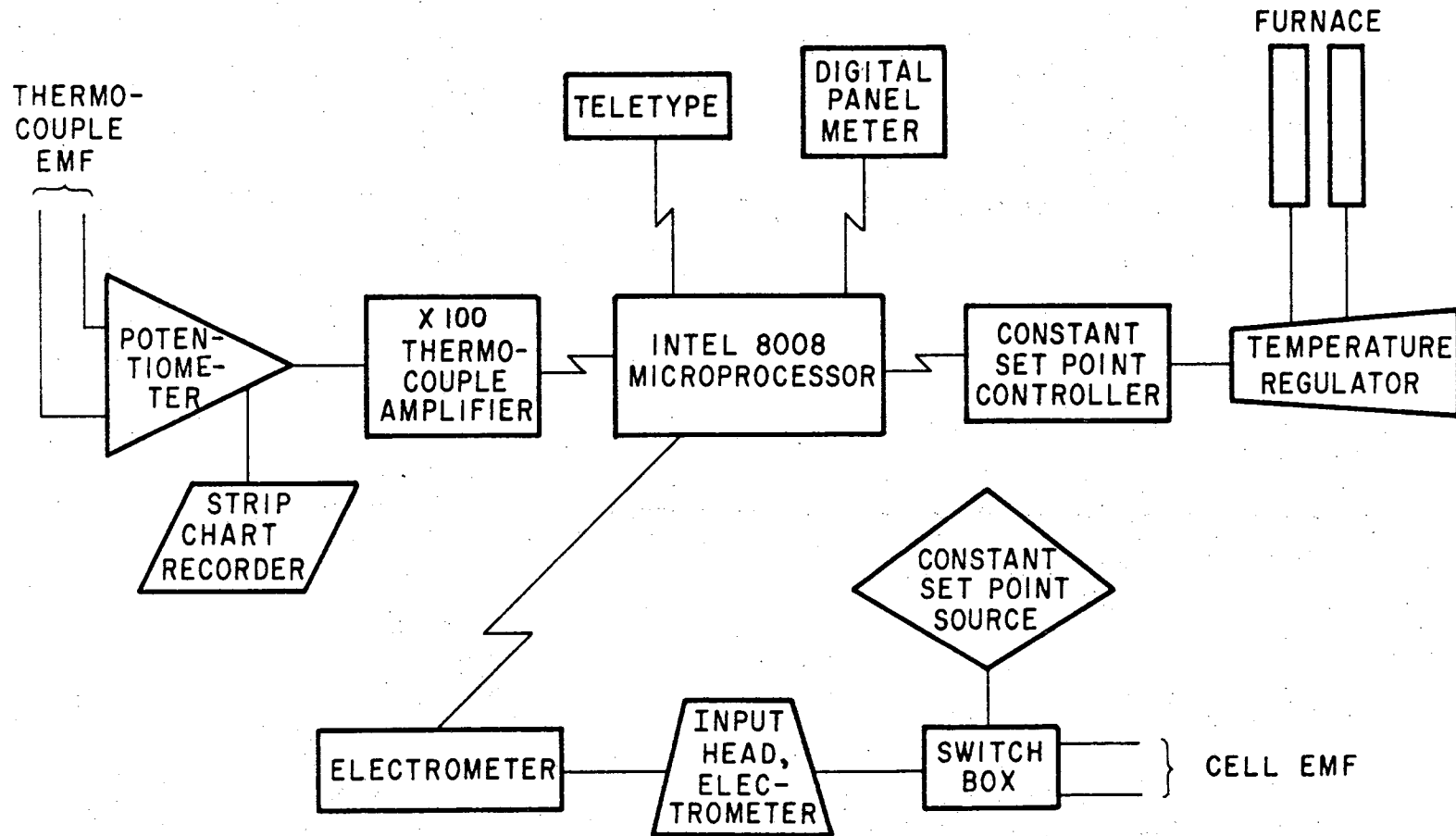
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Fig. 1 Schematic Diagram of the experimental cell.



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Fig. 2 Cross-section diagram of the electrode compartment.



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Fig. 3 Schematic of the microcomputer system utilized for experimental control and data acquisition.

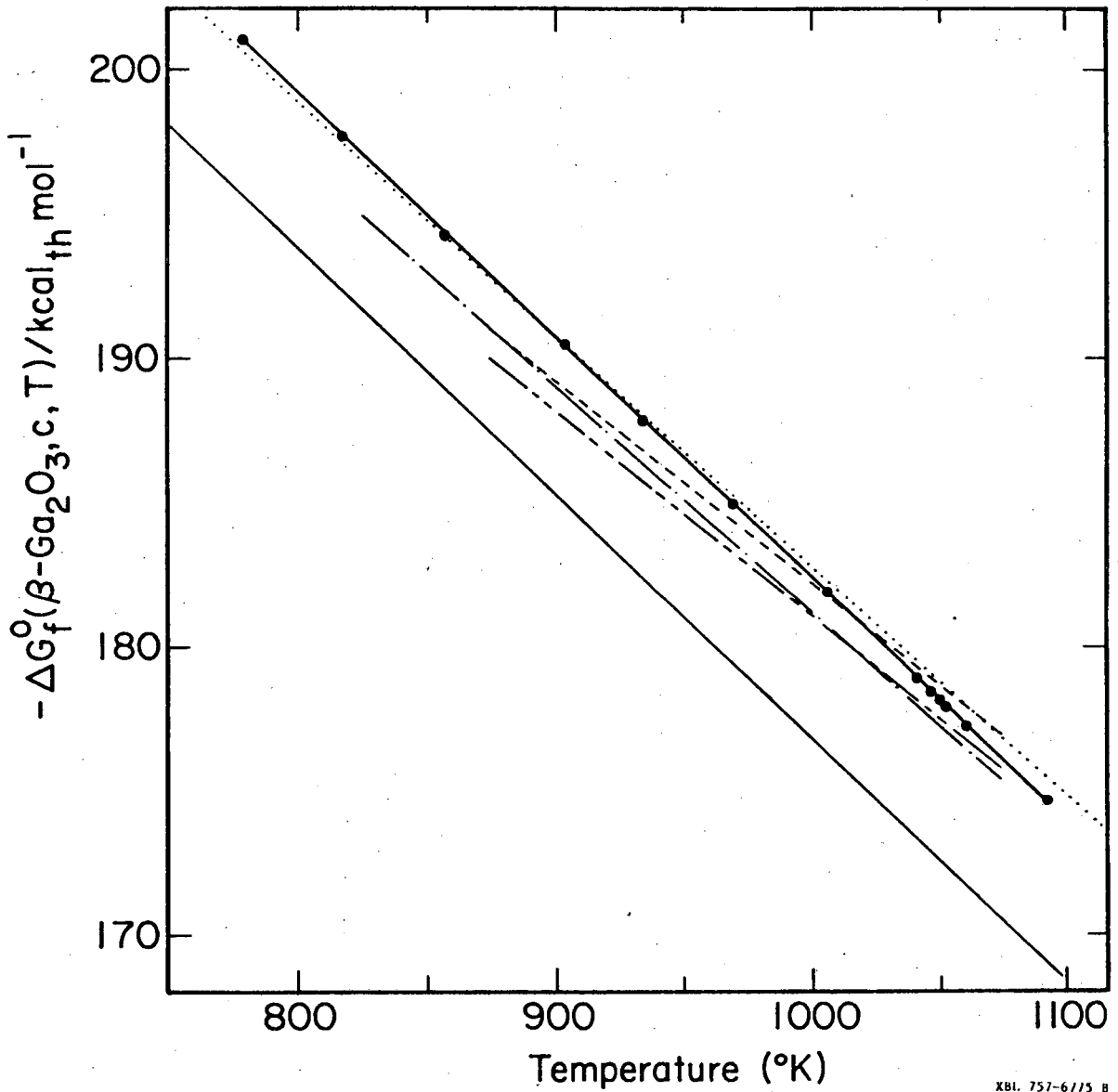
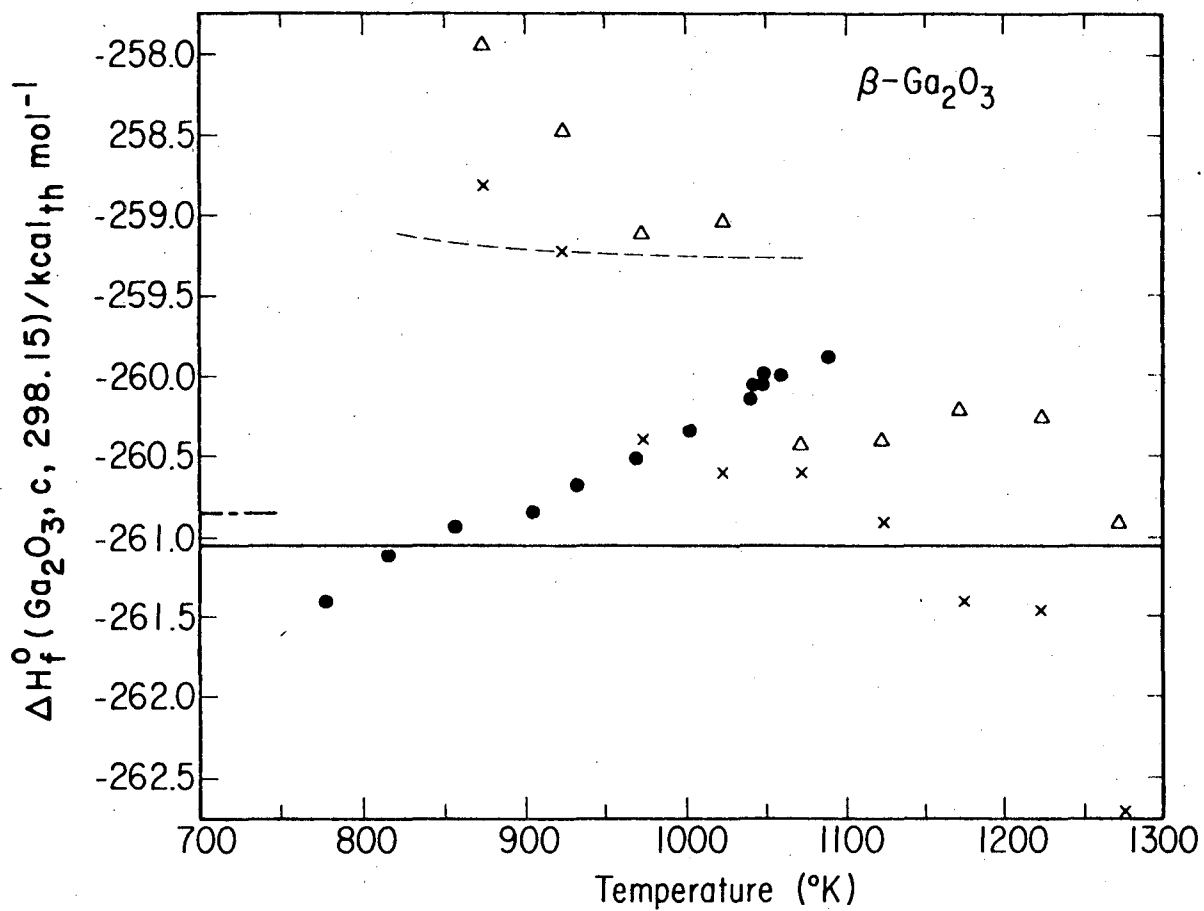


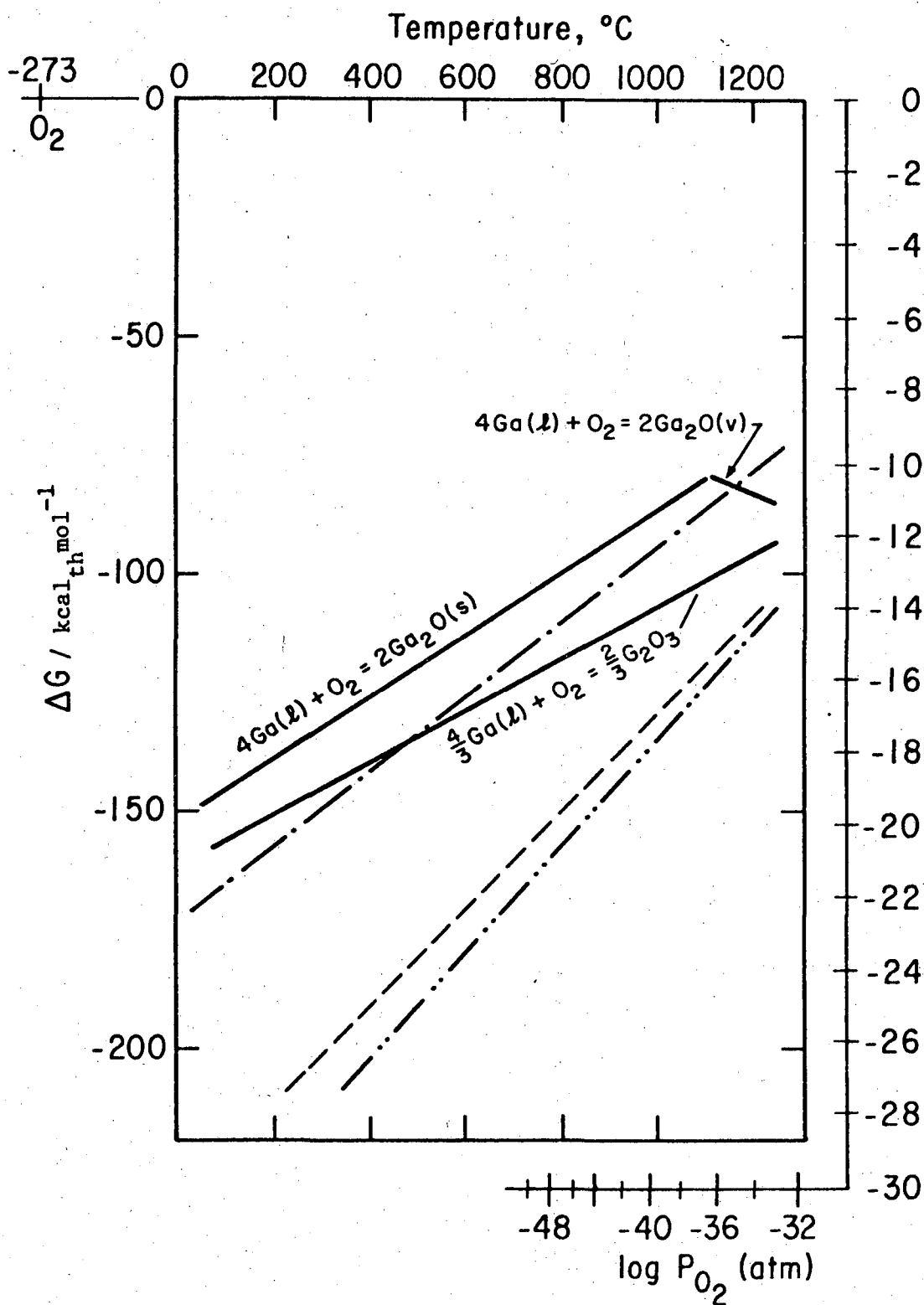
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0 0 0 0 4 3 0 8 5 3 6



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Fig. 5 Third-law calculation of $\Delta H_f^0(\text{Ga}_2\text{O}_3, c, 298.15)$ and comparison to the calorimetric data of (—) Mah, and to values derived from the data of (— - —) Shchukarev et al., (-----) Smith and Chatterji, and (x coulometric titration; Δ coexistence electrode Klinedinst and Stevenson.



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This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

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