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SOLID-STATE ELECTROCHEMICAL STUDY OF THE GIBBS ENERGY OF FORMATION OF INDIUM SESQUIOXIDE

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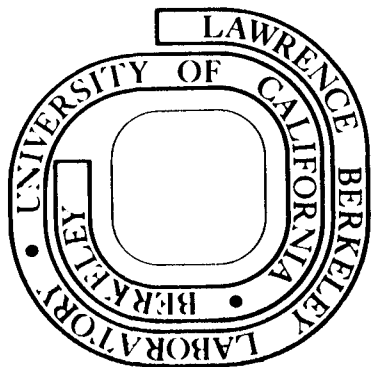
T. J. Anderson and L. F. Donaghey

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Solid-State Electrochemical Study of the Gibbs
Energy of Formation of Indium Sesquioxide

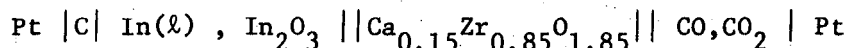
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August, 1976

Abstract

The Gibbs energy of formation of In_2O_3 was studied in the solid-state electrochemical cell,



over the temperature range from 950 to 1128 K, using calcia-stabilized zirconia as the solid electrolyte and a $\text{CO} + \text{CO}_2$ gaseous mixture as the reference electrode. The Nernst equation was used to derive data on the Gibbs energy of formation of indium oxide. A linear least-square regression analysis of the data gave

$$\Delta G_f^{\circ}(\text{In}_2\text{O}_3, \text{c}) / \text{kcal}_{\text{th}} \text{mol}^{-1} = (-223.67 \pm .14) + (8.044 \pm 0.014) \times 10^{-2} (T/\text{K}) .$$

A third-law analysis of the data showed that

$$\Delta H_f^{\circ}(\text{In}_2\text{O}_3, \text{c } 298.15) / \text{kcal}_{\text{th}} \text{mol}^{-1} = -222.09 \pm 0.01$$

in agreement with calorimetric determinations. Comparisons to results of other studies are presented. No evidence was found for the formation of $\text{In}_2\text{O}(\text{c})$ in the $\text{In}(\ell) + \text{In}_2\text{O}_3(\text{c})$ coexistence electrode.

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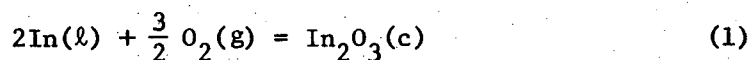
Short Title: Gibbs Energy of Formation of Indium Sesquioxide

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Introduction

Indium sesquioxide is an n-type semiconductor with a substantial electrical conductivity of $\sim 20 \text{ ohm}^{-1} \text{ cm}^{-1}$ and an electron mobility of $\sim 160 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temperature. These properties have made In_2O_3 useful as a material for processing thick film resistors. A review of its properties has been given by de Wit.⁽¹⁾ For the successful processing of In_2O_3 by chemical reactions involving oxidation, accurate information on the thermodynamic properties of In_2O_3 is important. This study was undertaken to provide accurate measurements of the Gibbs energy of formation of In_2O_3 using solid-state electrochemical methods under microcomputer control. A systematic method is applied to attain a level of accuracy not previously reported.

The Gibbs energy of formation of In_2O_3 by the reaction



has been measured using electrochemical methods by a number of authors.⁽²⁻⁶⁾ The Gibbs energy of formation has also been calculated from the equilibrium partial pressures of water and hydrogen over a mixture of In and In_2O_3 .^(7,8) Other studies on In_2O_3 from which thermodynamic data can be derived include vaporization studies,^(9,10) thermogravimetric analysis⁽¹¹⁾ and calorimetric combustion experiments.⁽¹²⁻¹⁴⁾ The values of the enthalpy of formation reported by these studies show a definite temperature dependence, and inconsistencies in the reported values of both the entropy and enthalpy of formation. These

discrepancies led us to re-examine the enthalpy and entropy functions chosen for data fitting, to explore a third-law analysis of the experimental data, and to examine in detail the consequences of side reactions.

In this study a solid-state electrochemical technique was used to measure the Gibbs energy of the reaction of In_2O_3 in the temperature range from 950 to 1128 K. A solid-state galvanic cell was employed, utilizing calcia-stabilized zirconia (CSZ) as the solid electrolyte, with experiments automated under microcomputer control. The results of these experiments are compared with other available data from the literature in a third-law calculation of the standard enthalpy of formation of In_2O_3 , and an analysis is presented for assessing the effect of equilibrium partial pressures of In_2O_3 over a mixture of $\text{In}(\ell) + \text{In}_2\text{O}_3(\text{c})$, based on the results of this study and on other available data. Finally, using the results of this study we propose an alternative explanation of the recent thermogravimetric data of de Wit. (11)

Experimental

An $\text{In} + \text{In}_2\text{O}_3$ coexistence electrode and a $\text{CO} + \text{CO}_2 + \text{Ar}$ gas electrode were used in the experimental cell whose structure was identical to that reported previously. (15) The coexistence electrode was prepared from 99.999% pure indium powder (Orion Chemical Co.) and 99.999% pure indium sesquioxide powder (Alfa Products). X-ray diffraction analysis showed the oxide powder to be pure In_2O_3 . Measured amounts of metal and oxide powders in the weight ratio of 10:1 were thoroughly mixed

and placed in a 2.54 cm O.D. tube of graphite (spectrographic grade) closed at one end. The graphite tube was fitted with a screw cap with a central hole through which a 0.635 cm O.D., closed-end calcia-stabilized zirconia (CSZ) tube containing the gas reference electrode and a platinum lead wire were inserted into the coexistence electrode. The CSZ tube (Zirconia Corporation of America) had a nominal composition of $\text{Ca}_{0.15}\text{Zr}_{0.85}\text{O}_{1.85}$. The closed end of the tube was coated inside with unfluxed platinum paste (Englehard No. 6926) to which a spiral platinum lead wire was attached.

The $\text{CO} + \text{CO}_2 + \text{Ar}$ reference gas mixture (Matheson Gas Products) was prepared from high purity gases. Chemical analysis showed the gas mixture to contain (25.29 ± 0.02) per cent CO_2 and (2.45 ± 0.02) per cent CO , with the balance consisting of high purity argon. The pressure in the experimental cell was maintained at 1 atm.*

The electrode assembly was contained within a 5.08 cm O.D. closed-end alumina tube sealed with a viton O-ring to a water-cooled brass cell head containing Cajon seals to alumina tubes supporting electrode leads and Pt, Pt + 10% Rh thermocouples calibrated to an NBS reference thermocouple. The coexistence electrode compartment was purged with argon purified by passing it over titanium sponge heated to 1123 K.

The cell was placed in a Marshall resistance-heated furnace and shielded from rf interference from the triac-controlled temperature

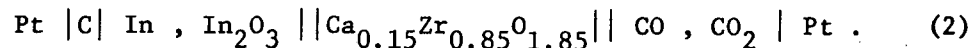
* In this paper the units used are related to SI units by $\text{atm} = 101.325 \text{ kPa}$, $\text{Torr} = 133.32 \text{ Pa}$, and $\text{cal}_{\text{th}} = 4.184 \text{ J}$.

regulator by a grounded platinum shield placed between the 5.08 cm O.D. alumina tube and the furnace winding. Temperatures could be maintained to within ± 0.5 K.

Cell emf was measured with a Keithley 640 electrometer which was connected to the cell leads with a triaxial cable containing a driven guard to reduce leakage currents. The electrometer output and amplified thermocouple output were monitored periodically by a microcomputer control system based on the Intel 8008 microprocessor. The control program was able to raise the cell temperature at $2 \times 10^{-2} \text{ K s}^{-1}$ to the operating temperature, monitor the cell temperature and emf and print the data on a teletype, test for equilibrium, and repeat the measurements at a series of fixed temperatures within the desired temperature range. The sequence of temperatures at which measurements were taken was chosen to test the reproducibility of the experiments and to eliminate systematic errors arising from thermal transients.

Results

The Gibbs energy of formation of indium sesquioxide was determined with the cell



The activity of oxygen in the coexistence electrode relative to that in the reference gas mixture was measured from the cell voltage E , and the Nernst equation,

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$$E = \frac{RT}{4F} \ln \left\{ \frac{p(\text{O}_2, \text{CO} + \text{CO}_2)}{p(\text{O}_2, \text{In} + \text{In}_2\text{O}_3)} \right\} \quad (3)$$

where R is the gas constant, T the absolute temperature, F is the Faraday constant, $p(\text{O}_2, \text{CO} + \text{CO}_2)$ the oxygen partial pressure over the $\text{CO} + \text{CO}_2$ mixture and $p(\text{O}_2, \text{In} + \text{In}_2\text{O}_3)$ that over the coexistence electrode.

The Gibbs energy of formation of In_2O_3 is related to the cell emf through the equilibrium constant of the reaction given in equation 1. Assuming unity activities for $\text{In}(\ell)$ and $\text{In}_2\text{O}_3(\text{c})$, $\Delta G_f^\circ(\text{In}_2\text{O}_3, \text{c}, T)$ is given by:

$$\Delta G_f^\circ(\text{In}_2\text{O}_3, \text{c}, T) = 1.5 RT \left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)^2 + 3\Delta G_{\text{ref}}^\circ - 6 FE . \quad (4)$$

The ratio of partial pressures of the reference gas components, $\left(\frac{P_{\text{CO}_2}}{P_{\text{CO}}} \right)$, was determined by chemical analysis to be (10.322 ± 0.092) . The term $\Delta G_{\text{ref}}^\circ$ in equation 4 is the Gibbs energy of reaction for the reference gas equilibrium,



and was calculated from the data of Wicks and Block⁽¹⁶⁾ to have the form,

$$\begin{aligned} \Delta G_{\text{ref}}^\circ / \text{kcal}_{\text{th}} \text{mol}^{-1} &= -68.27 - 1.8 \times 10^{-4} T \ln T \\ &- 3.4 \times 10^{-7} T^2 + 87./T + 0.02328(T/K) . \end{aligned}$$

Listed in table 1 are the temperatures of measurement, recorded cell emf, the partial pressures of oxygen in the reference and measured electrodes and the Gibbs energy of formation of In_2O_3 , as calculated from equation 4.

A linear least squares regression analysis of the $\Delta G_f^{\circ}(\text{In}_2\text{O}_3, c, T)$ data shown in table 2 gave the following equation:

$$\begin{aligned} \Delta G_f^{\circ}(\text{In}_2\text{O}_3, c, T) / \text{kcal}_{\text{th}} \text{mol}^{-1} = & -(223.67 \pm .14) \\ & + (8.044 \pm 0.014) \times 10^{-2} (T/K) . \end{aligned} \quad (6)$$

The error values given in this expression were obtained from the combined errors in the reference gas composition, the cell temperature and the deviation of the data from the least-squares line. The total error was found to be 0.25 kcal at 1000 K, which corresponds roughly to a 3 K error in temperature measurement or to a 1.8 mV error in cell emf measurement.

Discussion

The calculated values of $\Delta G_f^{\circ}(\text{In}_2\text{O}_3, c, T)$ obtained in this study are shown plotted in figure 1 as function of temperature and compared to data from the emf studies of Klinedinst and Stevenson⁽⁵⁾ (using an oxygen reference electrode), of Schaefer⁽²⁾ (using a Cu - Cu_2O reference electrode), of Newns and Pelmore⁽⁴⁾ (using a Ni - NiO reference electrode), of Chatterji and Vest⁽³⁾ (also using a Ni - NiO reference electrode), and of Bird et al.,⁽⁶⁾ (also using a Ni - NiO reference electrode). Also plotted in figure 1 are the values measured by Hochgeschwender and Ingraham employing a flowing gas equilibration technique.⁽⁷⁾

Table 1. Summary of Experimental and Derived Data

T/K	$E_{\text{measured}}/\text{mV}$	$\log_{10} \frac{p(\text{O}_2, \text{CO} + \text{CO}_2)}{\text{atm}}$	$\log_{10} \frac{p(\text{O}_2, \text{In} + \text{In}_2\text{O}_3)}{\text{atm}}$	$\frac{\Delta G_f^\circ(\text{In}_2\text{O}_3, \text{c}, \text{T})}{\text{kcal}_{\text{th}} \text{mol}^{-1}}$
950.8	128.9(± 0.1)	-19.820(± 0.008)	-22.553(± 0.002)	-147.18(± 0.01)
953.6	129.0	-19.729	-22.487	-146.98
986.1	128.4	-18.708	-21.716	-144.38
988.2	128.2	-18.644	-21.288	-144.19
1021.6	127.5	-17.667	-20.565	-141.52
1026.0	127.1	-17.543	-20.041	-141.12
1041.8	126.8	-17.107	-19.737	-139.86
1059.0	126.6	-16.646	-19.243	-138.51
1067.8	126.0	-16.417	-18.899	-137.75
1094.9	125.8	-15.732	-18.330	-135.64
1128.3	124.7	-14.935	-17.515	-132.91

In order to better ascertain the reliability of the experimental data, a third-law calculation was performed. The values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15)$ were calculated from the equation,

$$\begin{aligned} \Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15) = & \Delta G_f^\circ(\text{In}_2\text{O}_3, c, T) - \Delta_f^\circ\{H(T) - H(298.15)\} \\ & + T \left[\Delta S_f^\circ(\text{In}_2\text{O}_3, c, 298.15) + \Delta_f^\circ\{S(T) - S(298.15)\} \right]. \quad (7) \end{aligned}$$

The values of the entropy and enthalpy functions were taken from Coughlin.⁽¹⁷⁾ The value of $\Delta S_f^\circ(298.15)$ was taken to be $-0.0735 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ k}^{-1}$, as suggested by Hart.⁽¹⁸⁾ Component values were combined according to the stoichiometry of the formation reaction, equation 1, to determine the magnitudes of the terms in equation 7.

The results of the third-law analysis are summarized in table 2. A statistical study of the third-law results showed that

$$\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15) / \text{kcal}_{\text{th}} \text{ mol}^{-1} = -222.09 \pm 0.01 \quad (8)$$

with a surprisingly small standard error from the mean value. The derived values of the enthalpy of formation show a negligible temperature dependence of $0.00045 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ k}^{-1}$.

A comparison of the derived enthalpy of formation with calorimetrically determined values is presented in table 3. The value derived in the present study is within the error limits of the calorimetric results of Becker and Roth,⁽¹³⁾ but differs by twice the standard error from the more recent, and more accurate, results of Holley et al.⁽¹⁴⁾ Therefore, it is probable that the thermodynamic functions of Coughlin⁽¹⁷⁾ are in error by about 0.2%.

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

T/K	<u>Third-Law Analysis</u>		<u>Second-Law Analysis</u>		
	$\frac{\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15)}{\text{kcal}_{\text{th}} \text{mol}^{-1}}$	$\frac{\delta_1}{\text{kcal}_{\text{th}} \text{mol}^{-1}}$	Observed $\log K_p$	Calculated $\log K_p$	δ_2
950.8	-222.11	-.02	-33.830	-33.832	0.002
953.6	-222.14	-.05	-33.685	-33.681	-.004
986.1	-222.13	-.04	-31.998	-31.991	-.007
988.2	-222.12	-.03	-31.888	-31.886	-.002
1021.6	-222.11	-.02	-30.275	-30.269	-.006
1026.0	-222.07	0.02	-30.060	-30.064	0.004
1041.8	-222.07	0.02	-29.339	-29.341	0.002
1059.0	-222.10	-.01	-28.584	-28.579	-.005
1067.8	-222.04	0.05	-28.193	-28.199	0.006
1094.9	-222.10	-.01	-27.074	-27.065	-.009
1128.3	-222.04	0.05	-25.744	-25.744	0.000

Mean/ $\text{kcal}_{\text{th}} \text{mol}^{-1}$ -222.09

Standard error/ $\text{kcal}_{\text{th}} \text{mol}^{-1}$ = ± 0.01

$\frac{\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15)}{\text{kcal}_{\text{th}} \text{mol}^{-1}}$
= -222.53

Table 3 Comparison of Calorimetric Data with the
Derived Enthalpy of Formation of In_2O_3

$\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15)$ kcal _{th} mol ⁻¹	Source
-220.*	Ditte (12)
-222.5±0.7	Becker and Roth (13)
-221.27±0.40	Holley et al. (14)
-222.09±0.01	This work (third-law)

* As corrected by Becker and Roth (13)

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On the assumption that the third-law analytical results could be affected by an error in the estimated entropy of formation of In_2O_3 , entropy data were re-examined. The values of $S(\text{In}, \ell, 298.15)$ and $S(\text{O}_2, \text{g}, 298.15)$ have been very well determined by Kelley⁽¹⁹⁾ and are not expected to be in significant error. Becker and Roth⁽¹³⁾ estimated the entropy of cubic In_2O_3 at 298.15°K to be $0.0270 \pm 0.0025 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$ while Stubbs et al.,⁽⁸⁾ calculated a value of $0.0301 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$ from their phase equilibrium studies. Another alternative calculation of $\Delta S_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ is based on the assumption that $C_p(\text{In}_2\text{O}_3, \text{c}, T)$ is equal to $C_p(\beta\text{-Ga}_2\text{O}_3, \text{c}, T)$, where the coefficients for a linear temperature-dependent expression for $C_p(\text{In}_2\text{O}_3, \text{c}, T)$ are given by Glassner.⁽²⁰⁾ Using these values as extrema leads us to estimate a range from -0.07431 to $-0.07121 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$ for $\Delta S_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$. The variation of $\Delta S_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ within this range in the third-law calculation does not, however, change the resulting temperature dependence of the derived values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$, but does shift the magnitude of the enthalpy of formation by $\pm 1.6 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. An entropy of formation of $-0.726 \text{ kcal}_{\text{th}} \text{ mol}^{-1}$ is needed to give a temperature-independent value of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ which is in exact agreement with the calorimetric results of Holley et al.⁽¹⁴⁾

The results of the third-law analysis applied to the present experimental data and to that from other electrochemical studies are compared in Figure 2. The results obtained in this study exhibit the most temperature-independent values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ of all

the electrochemical studies conducted to date, with all calculated values falling between the calorimetric determinations of Becker and Roth⁽¹³⁾ and Holley et al.⁽¹⁴⁾ The values of $\Delta H_f^{\circ}(\text{In}_2\text{O}_3, c, 298.15)$ obtained from the other four emf studies (where actual data points were available) showed a definite temperature dependence of about $-0.0075 \text{ kcal}_{\text{th}} \text{ mol}^{-1} \text{ K}^{-1}$. It is interesting to note that all of the previous electrochemical studies utilized metal-metal oxide, reference electrodes, whereas a gaseous reference electrode was used in the present study. Polarization of the coexistence electrode would have the effect of raising the value of the derived enthalpy of formation. Thus, the negative temperature dependence of the third-law results could be explained if experimental measurements were made in the direction of decreasing temperatures while electrode polarization increased. In the present study, measurements were repeated several times as the cell temperature was cycled between chosen limits, so as to test for long-term, cell degradation effects.

The third-law analysis was repeated with other thermodynamic functions in order to test their effect on the derived values of $\Delta H_f^{\circ}(\text{In}_2\text{O}_3, c, 298.15)$. Values of $\{S(T) - S(298.15)\}$ and $\{H(T) - H(298.15)\}$ for gaseous oxygen were taken from the study of Wicks and Block⁽¹⁶⁾ from Hultgren,⁽²¹⁾ and from Kelley.⁽¹⁹⁾ Values for liquid indium were obtained from the selected values of Hultgren, and from Kelley. For indium sesquioxide values were calculated by integrating the heat capacity data of Shchukarev et al.⁽⁹⁾ In the latter calculation the heat capacity data was reduced to the form,

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$$C_p(\text{In}_2\text{O}_3, \text{c}, T) / \text{cal}_{\text{th}} \text{mol}^{-1} \text{K}^{-1} = 29.36 + 7.0 \times 10^{-3} T - 7.66 \times 10^{-5} (T/\text{K})^{-2}$$

by a least squares calculation. These analyses gave lower values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ with mean values in the range from -217.3 to -217.5 $\text{kcal}_{\text{th}} \text{mol}^{-1}$ with a temperature dependence of about 0.4 $\text{kcal}_{\text{th}} \text{mol}^{-1} \text{K}^{-1}$. These third-law analytical results are primarily influenced by the heat capacity data of Shchukarev et al.,⁽⁹⁾ and the lack of agreement of the derived enthalpy of formation with calorimetric data suggests possible error in their data.

A second-law test of the experimental data was also performed. These results are presented in table 2, and compared to values derived from other studies in table 4. The second-law test results are in fair agreement with the results of the third-law analysis, and differ by only 0.06%, well within the error in tabulated thermochemical data. The second-law test results of the data of News and Pelmore⁽⁴⁾ are in best agreement with the calorimetric results of Holley et al.,⁽¹⁴⁾ whereas other electrochemical studies gave higher second-law values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$.

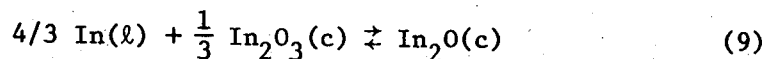
An important side reaction to consider at high temperatures is the decomposition of $\text{In}_2\text{O}_3(\text{c})$ to form $\text{In}_2\text{O}(\text{g})$. The existence of $\text{In}_2\text{O}(\text{c})$ above 1085 K has been suggested by Klinedinst and Stevenson⁽⁵⁾ to explain a discontinuity in the temperature dependence of the measured oxygen activity of a coexistence electrode containing $\text{In}(\ell)$ and indium oxides formed by electrochemical titration. No such discontinuity was found in the present study for a coexistence electrode containing $\text{In}(\ell)$ and $\text{In}_2\text{O}_3(\text{c})$. It is possible, therefore,

Table 4 Comparison of Enthalpy and Entropy of Formation of In_2O_3 from Second-Law Analyses

$\Delta H_f^\circ(\text{In}_2\text{O}_3, c, 298.15)$ kcal _{th} mol ⁻¹	$\Delta S_f^\circ(\text{In}_2\text{O}_3, c, 298.15)$ cal _{th} mol ⁻¹	Source
-222.53	-78.01	This work
-217.63	-72.91	Schaefer ⁽²⁾
-214.39	-70.2	Chatterji and Vest ⁽³⁾
-221.6	-75.7	Newns and Pelmore ⁽⁴⁾
-217.5	-73.2	Klinedinst and Stevenson ⁽⁵⁾
-219.5	-74.3	Bird et al. ⁽⁶⁾
-216.8	-68.4	Stubbs et al. ⁽⁸⁾
-221.27±0.4	-	Holley et al. ⁽¹⁴⁾ (calorimetric)
-	-73.5±2.5	Hart ⁽¹⁸⁾ (selected)

that $\text{In}_2\text{O}(\text{c})$ is produced by the titration of oxygen ions into $\text{In}(\ell)$ above 1085 K.

It is of interest to calculate the partial pressure of $\text{In}_2\text{O}(\text{g})$ that would exist in the $\text{In}(\ell) + \text{In}_2\text{O}(\text{c})$ electrode if equilibrium conditions prevailed. For the reaction,



the Gibbs energy change is found by subtracting $\frac{1}{3} \Delta G_f^0(\text{In}_2\text{O}_3, \text{c}, \text{T})$, obtained in this study, from that for $\text{In}_2\text{O}(\text{c})$ suggested by Klinedinst and Stevenson. (5) The result is

$$\Delta G(9)/\text{kcal}_{\text{th}} \text{mol}^{-1} = 20.56 - 0.01891 (T/\text{K}) . \quad (10)$$

The Gibbs energy change for this reaction is zero at 1087 K. Therefore above this temperature solid In_2O could form. The Gibbs energy of vaporization of In_2O by the reaction,



can now be found by combining the Gibbs energies of formation of the two species. (5) The result is

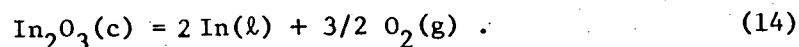
$$G(11)/\text{kcal}_{\text{th}} \text{mol}^{-1} = 32.0 - 1.8 \times 10^{-2} (T/\text{K}) . \quad (12)$$

Assuming ideal equilibrium conditions, the pressure of $\text{In}_2\text{O}(\text{g})$ over solid In_2O is then given by

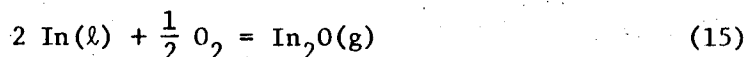
$$\log_{10} \{p(\text{In}_2\text{O})/\text{atm}\} = 3.9 - 6774 (T/\text{K})^{-1} . \quad (13)$$

This equation gives a value of 2.6 Torr at 1100 K.

If on the other hand, if $\text{In}_2\text{O}_3(\text{c})$ is present, the oxygen partial pressure is found from the equilibrium reaction,



Then, the reaction



is an additional source of In_2O in the gas phase. Combining the last two reactions, one obtains

$$\log_{10}\{p(\text{O}_2)/\text{atm}\} = 11.7 - 3.26 \times 10^4 (T/\text{K})^{-1} \quad (16)$$

$$\log_{10}\{p(\text{In}_2\text{O})/\text{atm}\} = 8.0 - 1.15 \times 10^4 (T/\text{K})^{-1} \quad (17)$$

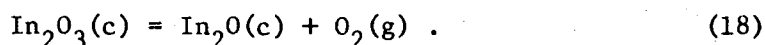
These expressions also give a value of 3.0 Torr for the partial pressure of $\text{In}_2\text{O}(\text{g})$ at 1100 K. Shchukarev et al.,⁽⁹⁾

found the pressure of $\text{In}_2\text{O}(\text{g})$ over a stoichiometric mixture of $\text{In}(\ell) + \text{In}_2\text{O}_3(\text{c})$ to be 0.631 Torr at 1101 K. Shown in figure 3

are the partial pressures of $\text{In}_2\text{O}(\text{g})$ established by a direct formation reaction in the presence of $\text{In}_2\text{O}_3(\text{c})$ or by vaporization of $\text{In}_2\text{O}(\text{c})$.

The mass spectrometer data is not sufficient for one to discern which mechanism is controlling, although the formation of $\text{In}_2\text{O}(\text{c})$ after vacuum sublimation of the $\text{In}_2\text{O}_3(\text{c}) + \text{In}(\ell)$ mixture has been reported.⁽⁹⁾

Also of importance to the present study is the equilibrium pressure of $\text{In}_2\text{O}(\text{g})$ over $\text{In}_2\text{O}_3(\text{c})$ produced by reaction 11, and



Reaction 18 has a Gibbs energy change given by

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$$\Delta G(18)/\text{kcal}_{\text{th}} \text{mol}^{-1} = 169.67 - 0.07254 (T/K) . \quad (19)$$

Combining this reaction with the Gibbs energy of vaporization for solid In_2O one can obtain an expression for the partial pressure of $\text{In}_2\text{O}(g)$, which is

$$\log_{10}\{p(\text{In}_2\text{O})/\text{atm}\} = 19.8 - 4.41 \times 10^4 (T/K)^{-1} - \log_{10}\{p(\text{O}_2)/\text{atm}\} . \quad (20)$$

This expression is somewhat different from that given by Van Dillen⁽²²⁾ which has the form

$$\log_{10}\{p(\text{In}_2\text{O})/\text{atm}\} = 17.7 - 42,189(T/K)^{-1} - \log_{10}\{p(\text{O}_2)/\text{atm}\} . \quad (21)$$

The formation of $\text{In}_2\text{O}(c)$ as a reaction product during $\text{In}_2\text{O}_3(c)$ decomposition is suggested by the thermogravimetry studies of de Wit⁽¹¹⁾ who found a small ($0.017 \mu\text{gs}^{-1}$) linear weight loss of $\text{In}_2\text{O}_3(c)$ over the temperature range from 1173 to 1473 K. De Wit attributed this result to a defect reaction involving either the formation of oxygen vacancies or indium interstitials in $\text{In}_2\text{O}_3(c)$, however, rather than to the formation of an $\text{In}_2\text{O}(c)$ surface reaction product. In our study of the $\text{In}(l) + \text{In}_2\text{O}_3(c)$ coexistence electrode, no discontinuities in cell emf with temperature were observed, in spite of some vaporization of $\text{In}(l)$. Therefore, we conclude that $\text{In}_2\text{O}(c)$ could be produced by a rapid dissociative decomposition reaction from $\text{In}_2\text{O}_3(c)$ above 1173 K, but that $\text{In}_2\text{O}(c)$ is not present in the $\text{In}(l) + \text{In}_2\text{O}_3(c)$ coexistence electrode. This conclusion also is supported by X-ray diffraction analysis on our coexistence electrodes following high-temperature studies.

Finally, it is important to determine whether electronic conduction in the solid electrolyte could have introduced an error in the cell emf. Shown in figure 4 are the ionic-conduction domain limits for CSZ, as determined by Schmalzreid⁽²³⁾ and by Patterson et al.,⁽²⁴⁾ along with the Gibbs energy of formation of the various oxides of indium plotted as a function of temperature. The Gibbs energy of formation of $\text{In}_2\text{O}_3(\text{c})$ is well within the conservative limit for the ionic-conduction domain, over the entire temperature range used in the present study. The experimental data was tested for evidence of electronic conduction by statistically examining the second derivative of the cell emf as a function of temperature. The resulting second derivative was found to be essentially zero, indicating that the magnitude of the cell emf was not reduced by partial electrolyte failure at the higher experimental temperatures.

Conclusion

The Gibbs energy of formation of In_2O_3 was readily measurable utilizing a solid-state electrochemical cell with a $\text{CO} + \text{CO}_2$ reference electrode. The microcomputer automation of the study proved exceptionally beneficial for automatic testing of thermodynamic equilibrium and of the reproducibility of the data. The results of the study gave the most temperature-independent values of $\Delta H_f^\circ(\text{In}_2\text{O}_3, \text{c}, 298.15)$ of all the emf studies of the $\text{In}_2\text{O}_3(\text{c})$ formation reaction, and in close agreement with calorimetric data. No evidence was found for the formation of $\text{In}_2\text{O}(\text{c})$ over an $\text{In}(\text{l}) + \text{In}_2\text{O}_3(\text{c})$ coexistence electrodes.

Acknowledgment

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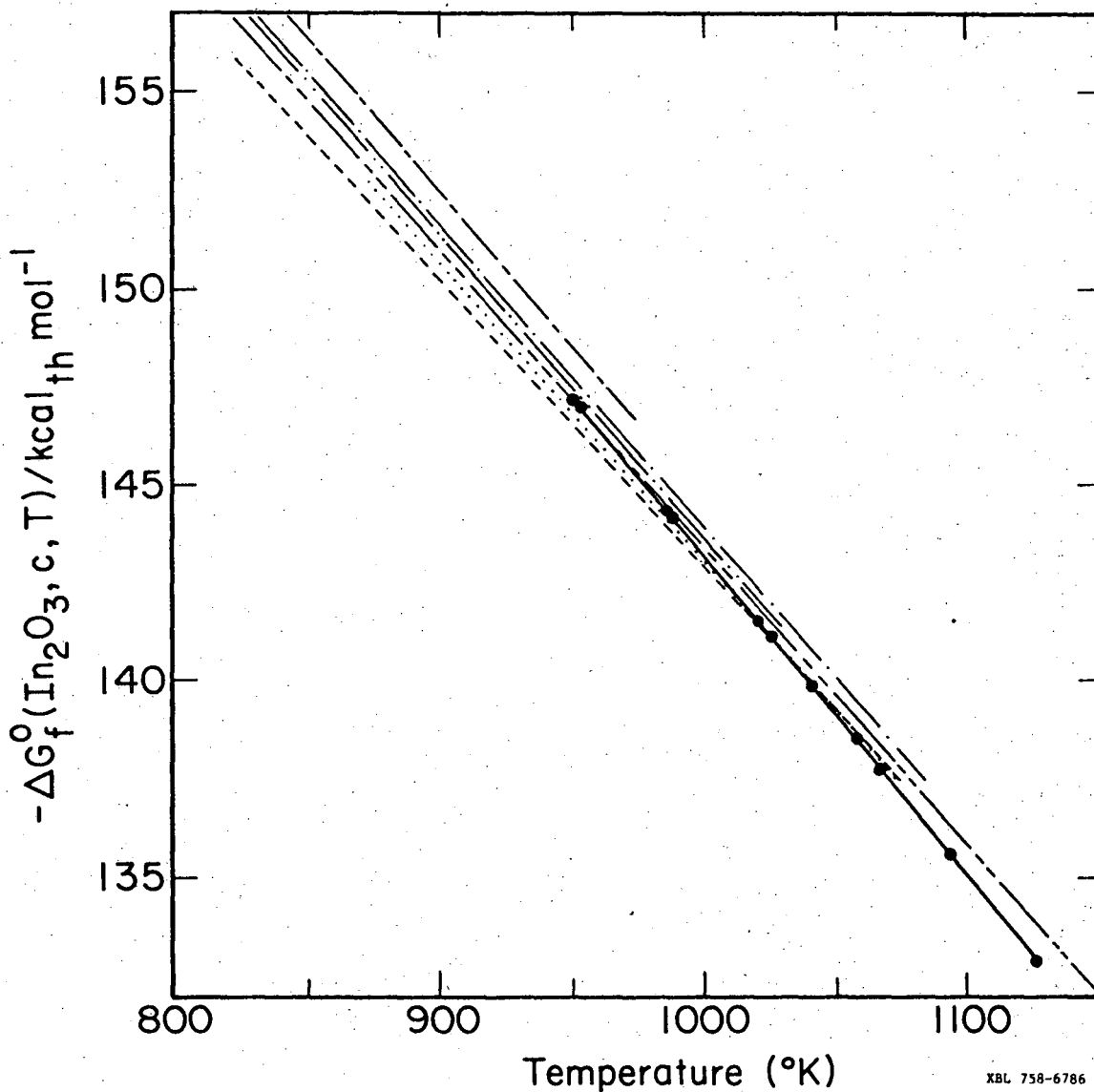
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- Fig. 2 Standard enthalpy of formation of $\text{In}_2\text{O}_3(\text{c})$ obtained by a third-law analysis of the experimental data: (•) This work; (x) Schaefer; (Δ) Klinedinst and Stevenson; (---) Chatterji and Vest; (— - —) News and Pelmore; (— • —) Bird et al.; (—) Holley, Huber and Neierkord; (— -- —) Becker and Roth.
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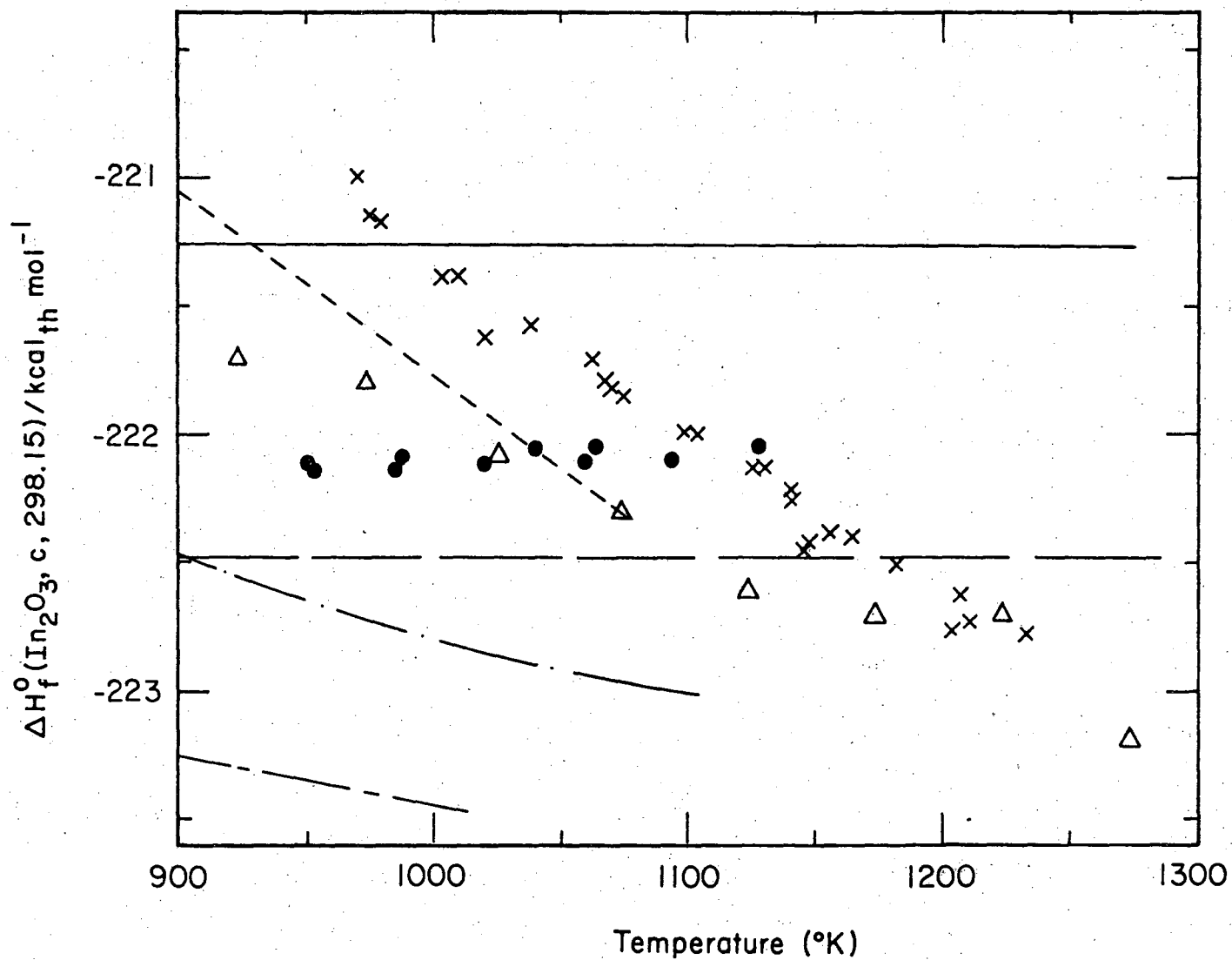
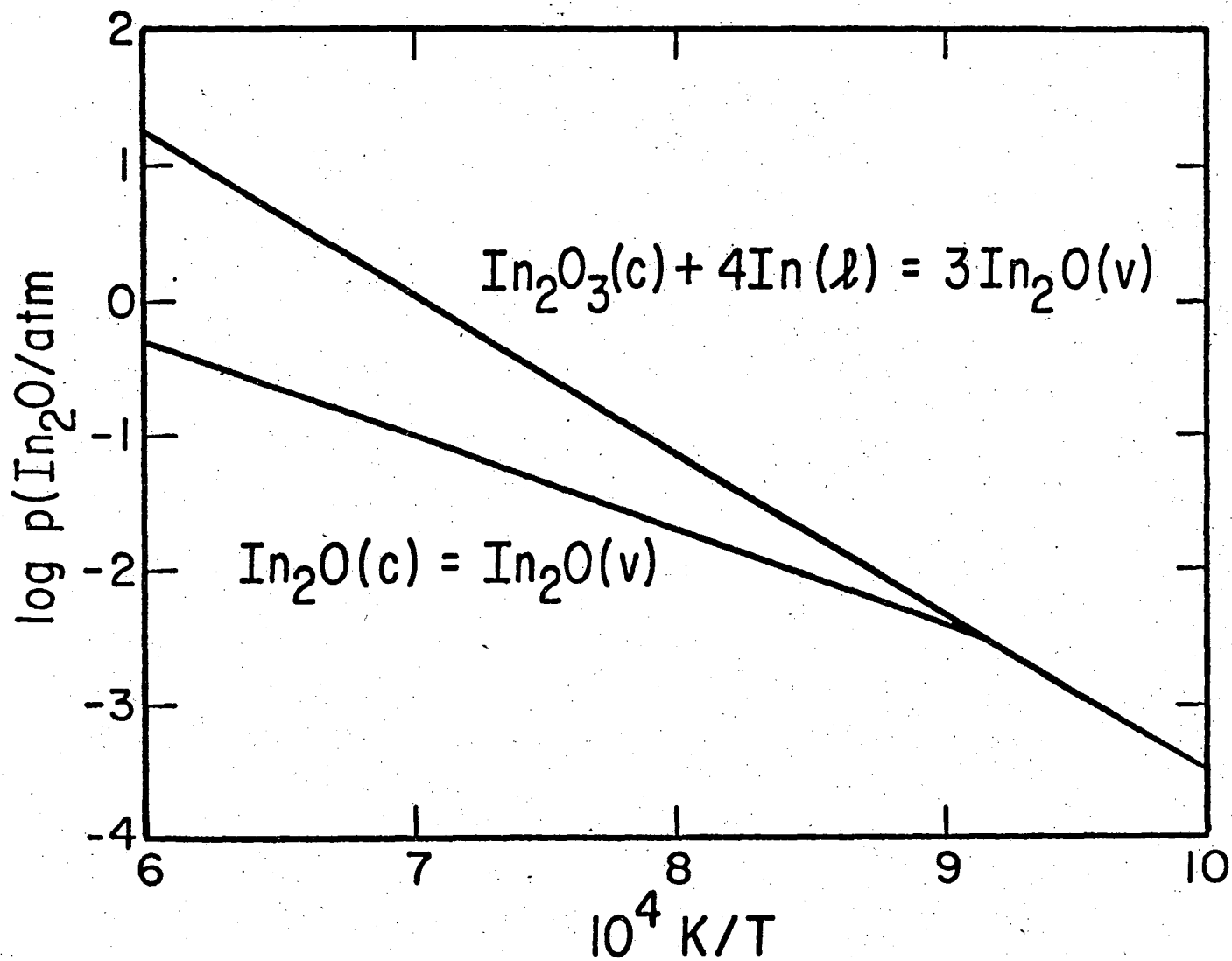


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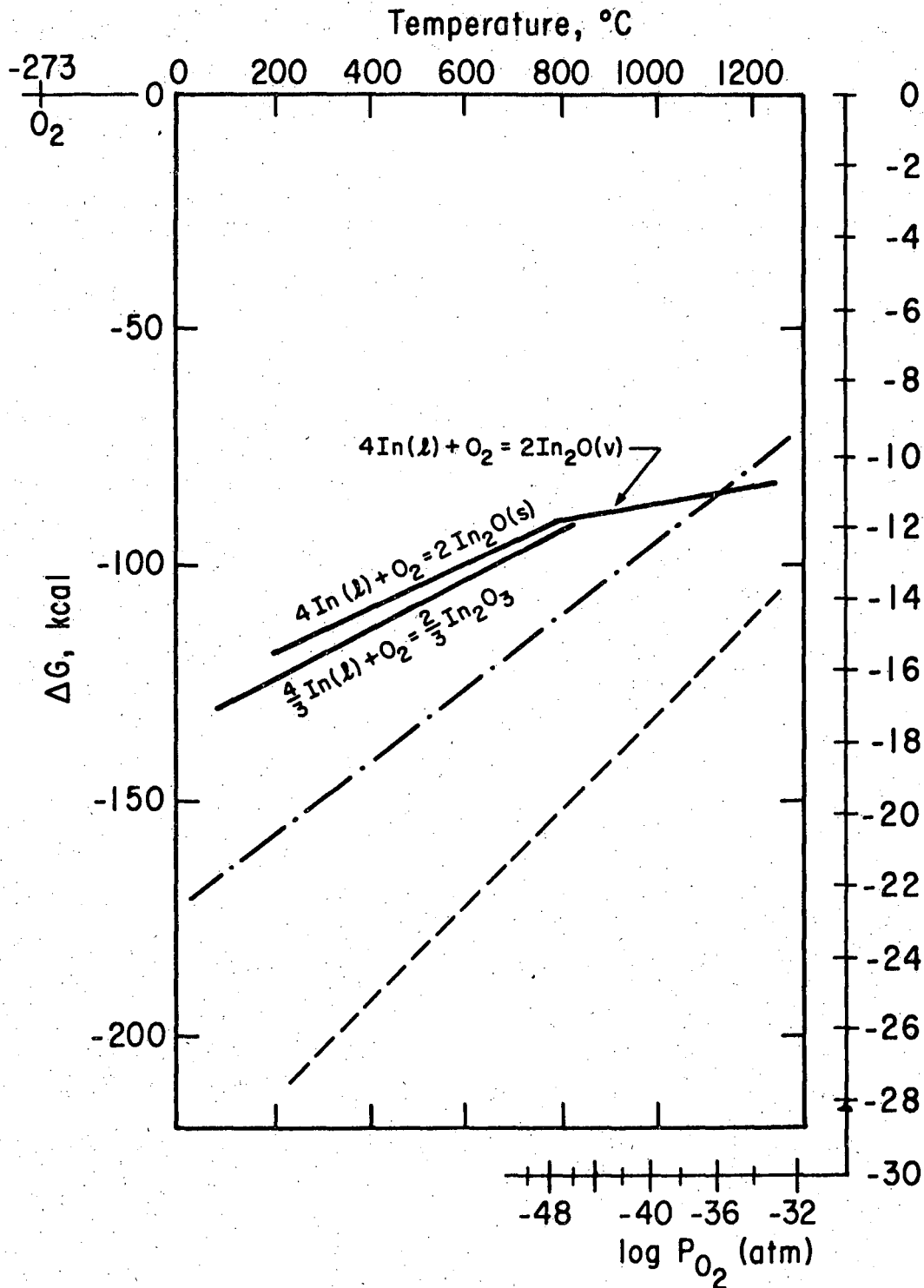
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Fig. 3 Partial pressure of $\text{In}_2\text{O}(\text{g})$ as a function of temperature for two possible formation reactions.



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Fig. 4 Gibbs energies of formation of the oxides of indium on a molar O_2 basis compared to the ionic-conduction domain limits of calcia-stabilized zirconia after Schmalzreid, (— · —) and Patterson et al., (---).

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