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DETERMINATION OF THE SOLUBILITY OF OXYGEN IN LIQUID INDIUM

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Publication Date

1975-12-01

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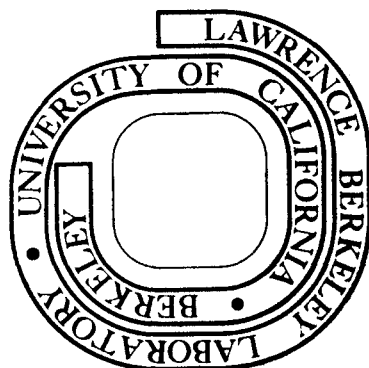
T. J. Anderson and L. F. Donaghey

December 1975

Prepared for the U. S. Energy Research and
Development Administration under Contract W-7405-ENG-48

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Determination of the Solubility of Oxygen in Liquid Indium

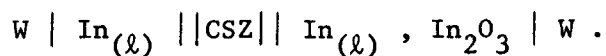
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December 1975

Abstract

The solubility and diffusivity of oxygen in liquid indium was studied by electrochemical titration of oxygen through calcia stabilized zirconia (CSZ), in the cell



The oxygen solubility was found to be 1.2×10^{-3} mole of $[O]_{\text{In}}$ per mole of In at 908°K.

A. Introduction

As a continued study of the properties of the Group III elements, the compounds formed with Group V materials, and their relationship with oxygen, the solubility and diffusivity of oxygen in liquid indium was determined.¹⁻³ The Group III element Al has received considerable attention with respect to its relation with oxygen as a result of the important ceramic applications. Foster and Scardefield¹ have measured the solubility of oxygen in liquid gallium over the temperature range from 900 to 1200°C by a gravimetric method while the diffusivity of atomic oxygen in gallium has been determined by Klinedinst and Stevenson⁴ with galvanostatic methods. To our knowledge no measurement of the solubility of oxygen in liquid indium has been performed while the only diffusivity determination is that of Klinedinst and Stevenson.⁴

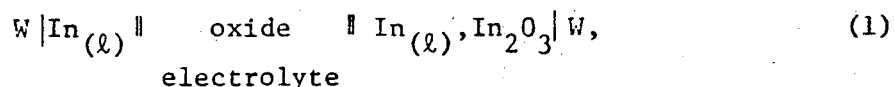
A solid state coulometric titration technique was first introduced by C. Wagner⁵ to study the dependence of the silver activity on the Ag/S ratio in silver sulfide. Several other investigators have employed solid oxide electrolytes to determine oxygen solubilities and diffusivities in liquid metals.⁶⁻¹¹ An oxygen ion conducting solid electrolyte has been used in this study to measure the oxygen diffusivity and solubility in liquid indium at a temperature of 908°K. The solubility was determined by coulometrically changing the dissolved oxygen content and measuring the resulting activity of atomic oxygen. By observing the cell potential response in a galvanostatic experiment, a diffusivity of oxygen could be determined.

B. Experimental

A schematic of the electrode arrangement used in this study is shown in Fig. 1. The electrolyte consisted of a flat closed one-end cylinder of calcia stabilized zirconia with an outside diameter of 0.95 cm. A pool of liquid indium was placed inside the electrolyte crucible which was dipped into the reference electrode mixture of indium and indium sesquioxide. The reference electrode material was contained inside an alumina crucible and electrical contact was made with tungsten wire. Once the cell was assembled it was placed in the peripheral apparatus discussed in Appendix I. Accurate data acquisition and precise timing were accomplished with the aid of a microcomputer. All other experimental equipment, procedures and materials were as summarized in Appendices I and II.

C. Theory

The electrochemical cell utilized in this study is the concentration cell,



where calcia-stabilized zirconia was the solid electrolyte. If the oxygen concentration in the liquid indium electrode is less than the saturation concentration, then oxygen will diffuse through the solid oxide electrolyte - as doubly negative ions - to the indium electrode from the $\text{In}_{(\ell)} + \text{In}_2\text{O}_3$ buffered electrode, whose oxygen activity is fixed by the two-phase equilibrium. The indium electrode thus becomes

progressively more negative as electronic charge accumulates until the diffusion of oxygen ions ceases. At equilibrium, the cell voltage is given by the Nernst equation,

$$\epsilon = \frac{RT}{4F} \ln \frac{P_{O_2}}{P_{O_2}^{eq}}, \quad (2)$$

where P_{O_2} and $P_{O_2}^{eq}$ are the oxygen partial pressures in the $In(\ell)$ and $In(\ell)+In_2O_3$ electrodes, respectively. Since the dependence of the equilibrium oxygen partial pressure is known, the measurement of the cell voltage is sufficient to determine the oxygen partial pressure in the liquid indium. The resulting partial pressure is

$$P_{O_2} = P_{O_2}^{eq} \exp\left(\frac{4F\epsilon}{RT}\right). \quad (3)$$

When the indium is undersaturated in oxygen, then ϵ is a negative quantity. On the other hand, when the liquid indium becomes saturated in oxygen, then the cell voltage becomes zero.

The partial pressure of diatomic oxygen in liquid indium can be established by considering the reaction for the dissolution of oxygen in liquid indium which is,



For this reaction, the equilibrium constant at one atmosphere total pressure and the temperature of interest is

$$K = \frac{a_{[O]}^2_{In}}{P_{O_2}} \quad (5)$$

where $a_{[O]}_{In}$ is the activity of dissolved oxygen in liquid indium. Combining Eqs. (3) and (5) results in the following expression for the dissolved oxygen activity,

$$a_{[O]}_{In} = \sqrt{K P_{O_2}^{eq}} \exp\left(\frac{2F\epsilon}{RT}\right) \quad (6)$$

Finally, the activity of oxygen can be expressed in terms of an activity coefficient, γ_o , and the oxygen mole fraction, x_o , to give

$$x_o = \frac{\sqrt{K}}{\gamma_o} \sqrt{P_{O_2}^{eq}} \exp\left(\frac{2F\epsilon}{RT}\right) \quad (7)$$

Provided the term \sqrt{K}/γ_o is known, the cell voltage is sufficient for determining the oxygen mole fraction in the indium electrode.

The term, \sqrt{K}/γ_o , can be determined as a function of oxygen content as follows. By applying a constant current for a known amount of time the composition of the indium electrode can be changed by an amount

$$\Delta n_o = \frac{Q}{2F} \quad (8)$$

where Q is the total charge passed. Assuming the number of moles titrated is small in comparison to the initial number moles of $[O]_{In}$ and In , Eqs. (7) and (8) combine to give

$$\frac{\sqrt{k}}{\gamma_o} = \frac{Q}{2Fn_{In}\sqrt{p_{O_2}^{eq}}} \left[\frac{1}{\exp\left(\frac{2F\varepsilon_1}{RT}\right) - \exp\left(\frac{2F\varepsilon_2}{RT}\right)} \right] \quad (9)$$

Here, ε_1 and ε_2 represents the equilibrium cell voltage before and after the titration is performed and n_{In} is the number of moles of indium liquid present in the electrode. Thus, the term \sqrt{k}/γ_o can be determined as a function of concentration in cell (1) and this value can be used to calculate the solubility of oxygen in liquid In .

Alternatively the solubility can be determined as follows.

The change in oxygen atom fraction produced by titration is given by

$$x_{O,1} - x_{O,2} \cong \frac{n_{O,1} - n_{O,2}}{n_{In}} = \frac{Q}{2Fn_{In}} \quad (10)$$

From Eq. (7) we find

$$x_{O,1}/x_{O,2} = \frac{\gamma_{O,2}}{\gamma_{O,1}} \exp\left[\frac{2F}{RT}(\varepsilon_1 - \varepsilon_2)\right] \quad (11)$$

Combining Eqs. (10) and (11) we obtain

$$1 - \frac{\gamma_{O,1}}{\gamma_{O,2}} \exp\left[\frac{2F}{RT}(\varepsilon_2 - \varepsilon_1)\right] = \frac{Q}{2Fn_{In}x_{O,1}} \quad (12)$$

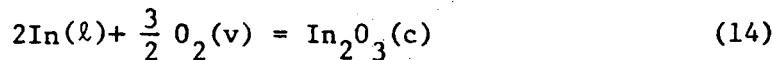
Assuming Henry's law is valid and letting state 1 represent the saturation condition Eq. (12) reduces to

$$1 - \exp\left[\frac{2F}{RT} \varepsilon_2\right] = \frac{Q}{2Fn_{\text{In}} x^{\text{sat}}} \quad (13)$$

Therefore a plot of $\exp\left(\frac{2F}{RT} \varepsilon_2\right)$ versus Q (or $I t$) should yield a straight line of slope $-1/(2Fn_{\text{In}} x^{\text{sat}})$ thus allowing the calculation of a saturation solubility.

D. Results

Electrochemical titrations were performed on the electrochemical cell (1). Listed in Table 1 are the equilibrium cell potentials measured before and after the titration of this cell operating at a temperature of 908°K . In each titration a constant current of $50 \mu\text{A}$ was put across the cell for a period of 30 min. Also given in Table 1 is the term \sqrt{K}/γ_0 , which was calculated from Eq. (9). The value of $P_{\text{O}_2}^{\text{eq}}$ was calculated from the Gibbs free energy of the reaction



The reference oxygen partial pressure is thus given by

$$P_{\text{O}_2}^{\text{eq}} = \exp\left(\frac{\Delta G^\circ(14)}{1.5 RT}\right) \quad (15)$$

where $\Delta G^\circ(14)$ was taken as

Table 1. Titration of oxygen into liquid indium.

Equilibrium emf (mV) before titration	Charge transferred into indium Electrode (Coulombs)	Equilibrium emf (mV) after titration	$\frac{\sqrt{K}}{Y_0} \times 10^{-9}$
- 0.99	+0.045	- 0.17	1.60
- 0.32	-0.045	- 1.04	1.82
-52.64	-0.09	-55.94	3.13
-55.94	-0.09	-60.44	2.53
-60.44	-0.09	-62.55	5.88
-62.55	-0.09	-64.80	5.83
-64.80	-0.09	-67.92	4.51
-67.92	-0.09	-72.12	3.67
-72.12	-0.09	-75.42	5.15
-75.42	-0.09	-79.23	4.88
-79.23	-0.09	-81.64	8.36
-81.64	-0.09	-85.30	5.95
-85.30	-0.09	-89.50	5.73

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$$\Delta G^{\circ}(14) = 223.16 + 7.947 \times 10^{-2} T, \text{ kcal}_{\text{th}} \text{ mol}^{-1}. \quad (16)$$

Shown in Fig. 2 is a typical response of the cell voltage to the applied current both during the actual titration and the following approach to the new equilibrium value.

E. Discussion

Upon examination of Table 1 it is observed that the term $\sqrt{K}/\gamma_{\text{O}}$ is nearly constant with respect to the dissolved oxygen content. Each titration resulted in oxygen mole fraction changes of $x_{[\text{O}]}_{\text{In}} = 5 \times 10^{-5}$. The fact that this term is constant implies that the oxygen activity varies linearly with the oxygen mole fraction or that Henry's law is applicable as is usual in most dilute metal solutions. This is especially apparent when the oxygen content is far from the saturation value. Using a mean value of 5×10^9 for $\sqrt{K}/\gamma_{\text{O}}$ allows the solubility of oxygen in liquid indium at 908 K to be calculated from

$$x_{[\text{O}]}_{\text{In}} = \frac{\sqrt{K P_{\text{O}_2}}}{\gamma_{\text{O}}} = 5 \times 10^9 \sqrt{P_{\text{O}_2}}. \quad (17)$$

The solubility of oxygen in indium at saturation was found to be $x_{[\text{O}]}_{\text{In}} = 1.2 \times 10^{-3}$, which was calculated using a value of $\sqrt{K}/\gamma_{\text{O}} = 1.6 \times 10^9$ since this was found when the cell voltage was nearest to zero or saturation. Unfortunately these measurements were performed at only one temperature thus not permitting the temperature dependence of $\sqrt{K}/\gamma_{\text{O}}$ to be found. It is possible to estimate the standard Gibbs free energy of reaction Eq. (4) with the data as found here. Expressing the equilibrium constant, K , in terms of its standard Gibbs free energy change and combining this with Eq. (7) gives

$$\Delta G^{\circ}(4) = 4FE - RT \ln \left[\frac{[\%O]}{p_{O_2}^{eq}} \right]^2 - 2RT \ln f_{O_2} \quad (18)$$

Here, the oxygen standard state is taken as 1 atm and the oxygen activity is given by the product of an activity coefficient, f_{O_2} , and the weight percent of dissolved oxygen, [% O]. In the limit that the oxygen weight percent goes to zero the oxygen activity coefficient goes to unity thus eliminating the last term in Eq. (18):

$$\Delta G^{\circ}(4) = \lim_{[\%O] \rightarrow 0} \left\{ 4FE - RT \ln \left[\frac{[\%O]}{p_{O_2}^{eq}} \right]^2 \right\} \quad (19)$$

Thus by plotting the bracketed term in the above equation versus the oxygen content, [% O], $\Delta G^{\circ}(4)$ can be found by extrapolation. The oxygen weight percent can be measured from the total titration current provided the titration was started at the onset of saturation (approach to zero cell voltage) and the saturation solubility is known. On the other hand, if Henry's law is assumed to hold at very small mole fraction the resulting plot will be horizontal at the value of $\Delta G^{\circ}(4)$ given by

$$\Delta G^{\circ}(4) = 2RT \ln \left[\frac{\sqrt{K} \text{ M.W.}(O)}{Y_{O_2} \text{ M.W.}(In)} \right] \quad (20)$$

where M.W.(O) and M.W.(In) are the molecular weights of atomic oxygen and indium, respectively. The small mass of the dissolved oxygen relative to the indium was neglected.

Using an average value of $\sqrt{K}/\gamma_o = 5.056 \times 10^9$ (obtained by averaging all data except the first two listings of Table 1) results in $\Delta G^{\circ}(4) = (73.5 \pm 2.4) \text{ kcal}_{\text{th}} \text{ mol}^{-1}$. For more concentrated solutions the oxygen activity coefficient will deviate from unity and can be calculated by using Eq. (18). When the value of K determined is combined with the average \sqrt{K}/γ_o , γ_o is found to be 0.138.

Shown in Fig. 3 is a plot of $\exp\left(\frac{2F\epsilon}{RT}\right)$ vs the differential charge titrated. If Henry's law is applicable the plot should be linear with a slope inversely proportional to the saturation solubility and have an intercept of unity. Good linearity was found in the less concentrated solutions with non-linearity at higher oxygen content. Thus either the Henry's law constant varies with [% O], or the first three titrations were in error. Assuming the latter to be true yields a saturation solubility of $x_o^{\text{sat}} = 3.3 \times 10^{-3}$. The x-axis in Fig. 3 is arbitrary because titration was not started at saturation. Thus the intercept is not useful to determine the accuracy of the early data. But an examination of the extrapolated intercept and the results of the titrations performed near saturation suggests that the data of the early titrations are in error. The value of x_o^{sat} found agrees well with that found by extrapolating with the response curve.

By monitoring the cell potential during a titration experiment it is possible to extract kinetic data. In this galvanostatic experiment charge-carrying oxygen ions are transferred across the solid electrolyte with oxidation occurring at the positive cell electrode and reduction at the negative electrode. Several mechanisms for oxygen transfer between the electrodes are operative while

usually one step is rate limiting. If the redox reaction rate is controlled by the adsorption or desorption of neutral oxygen atoms then the electrical potential is nearly independent of time² and in contradiction with our results. An assessment of other mechanisms indicates that the rate-limiting step is the diffusion of oxygen in liquid indium.^{3,4} Thus the diffusion coefficient of atomic oxygen in liquid indium can be ascertained from the data presented in Fig. 2.

During the passing of the constant current, I , the measured potential, ϵ is given by

$$\epsilon - \epsilon_0 + IR_0 = \frac{RT}{4F} \ln \left\{ \frac{P_{O_2}}{P_{O_2}^{eq}} \right\} \quad (21)$$

where ϵ_0 is the equilibrium cell voltage before the titration and R_0 is the ionic electrolyte resistance.

The solution of the diffusion equation for one dimensional oxygen diffusion out of a semi-infinite indium specimen with the initial condition

$$x_0 = x_0(t_0) \quad z \geq 0, \quad t = 0$$

and the boundary conditions

$$x_0 = x_0(t_0) \quad \text{for } z = \infty, \quad t > 0$$

$$\left(\frac{\partial x_0(z,t)}{\partial z} \right)_{z=0} = \frac{I V_{In}}{2FAD_0} \quad \text{for } t > 0$$

and evaluated at the electrode - electrolyte interface, $z = 0$, is given by

$$x_o(t) = x_o(t_o) - \frac{V_{In} I t^{1/2}}{FA\pi^{1/2} D_o^{1/2}} \quad (22)$$

Here, V_{In} is the indium molar volume, A the interfacial surface area and D_o the oxygen diffusivity. Eqs. (21), (22), and (5) can be combined to give

$$\varepsilon(t) + IR_o - \varepsilon_o = RT/2F \ln \left\{ \frac{\gamma_o}{\sqrt{K P_{O_2}^{eq}}} \left(x_o(t_o) - \frac{V_{In} I t^{1/2}}{FA\pi^{1/2} D_o^{1/2}} \right) \right\} \quad (23)$$

Therefore a plot of $\frac{\sqrt{K P_{O_2}^{eq}}}{\gamma_o} \exp\left[\frac{2F}{RT} (\varepsilon(t) + IR_o - \varepsilon_o)\right]$ versus $-It^{1/2}$ should yield a straight line of slope $V_{In}/FA\pi^{1/2} D_o^{1/2}$ and intercept $x_o(t_o)$.

Figure 4 shows such a plot from which an oxygen diffusivity of $2.2 \times 10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ was determined. This value is in good agreement with the value of Klinedinst and Stevenson⁽⁴⁾ of $(7.6 \pm 4.7) \times 10^{-7}$ who used the potentiostatic method with cylindrical geometry. The extrapolated value of $x_o(t_o)$ was 1.05×10^{-3} . The errors involved in these results include those associated with the measured emf, the determined \sqrt{K}/γ_o , and R_o , the fact that the electrode was not a semi-infinite medium, and the possibility of radial diffusion.

F. Conclusion

The results presented show that oxygen follows Henry's law when

dissolved in liquid indium at low concentrations. At concentrations more near to saturation it could not be shown that the solution is Henrian in nature. Further work on this system should involve both galvanostatic and potentiostatic measurements at several temperatures. The preferred geometry should be cylindrical because of ease of electrode separation and because an independent measurement of the diffusion coefficient can then be made which does not require solubility data.

Acknowledgment

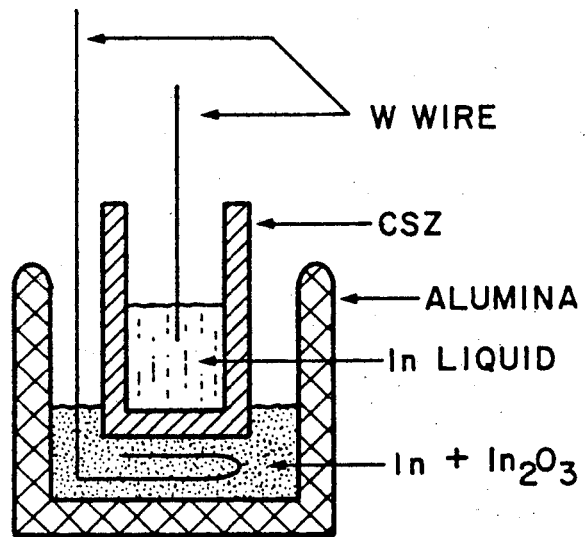
The financial support of the U.S. Energy Research and Development Administration is gratefully acknowledged.

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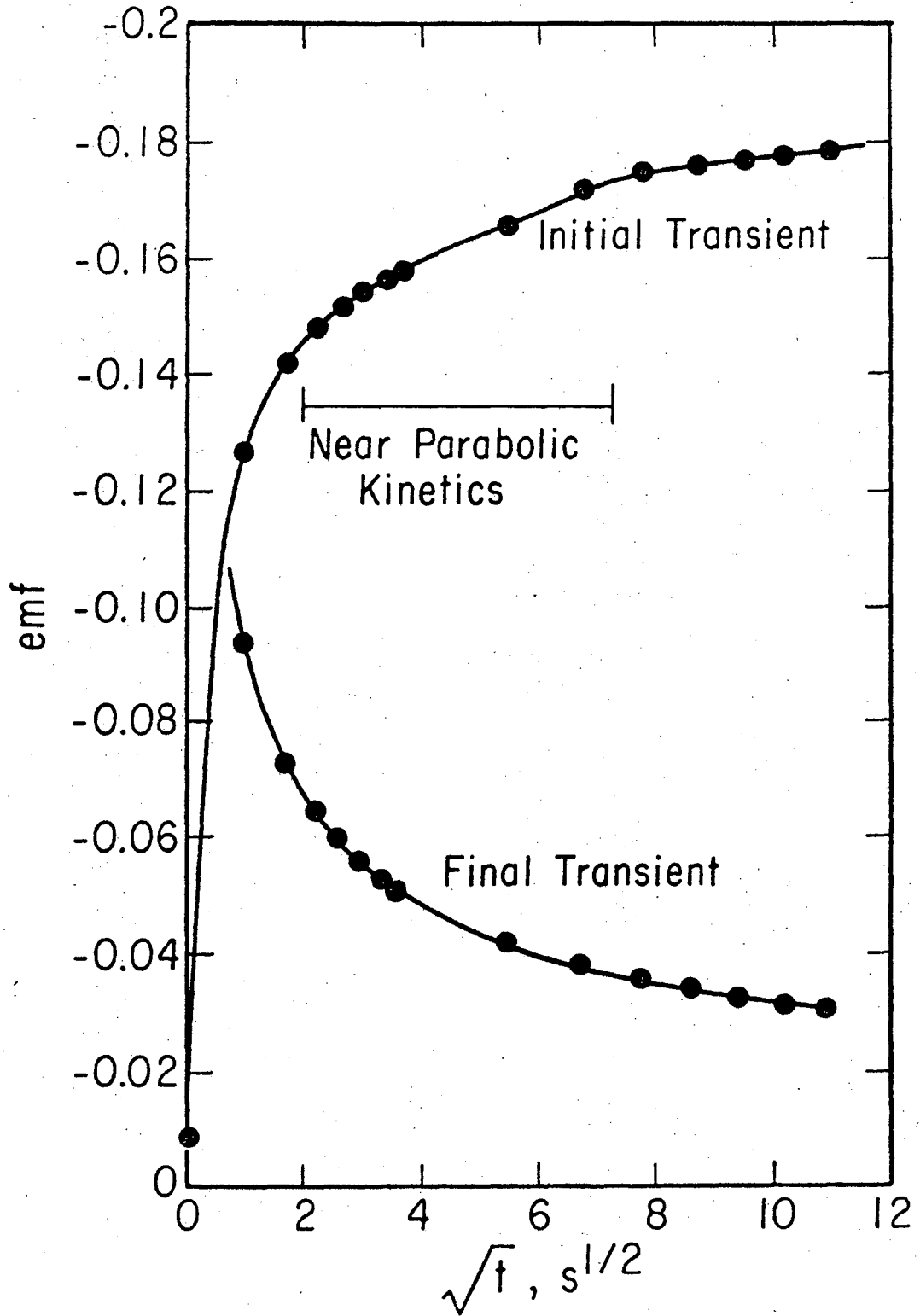
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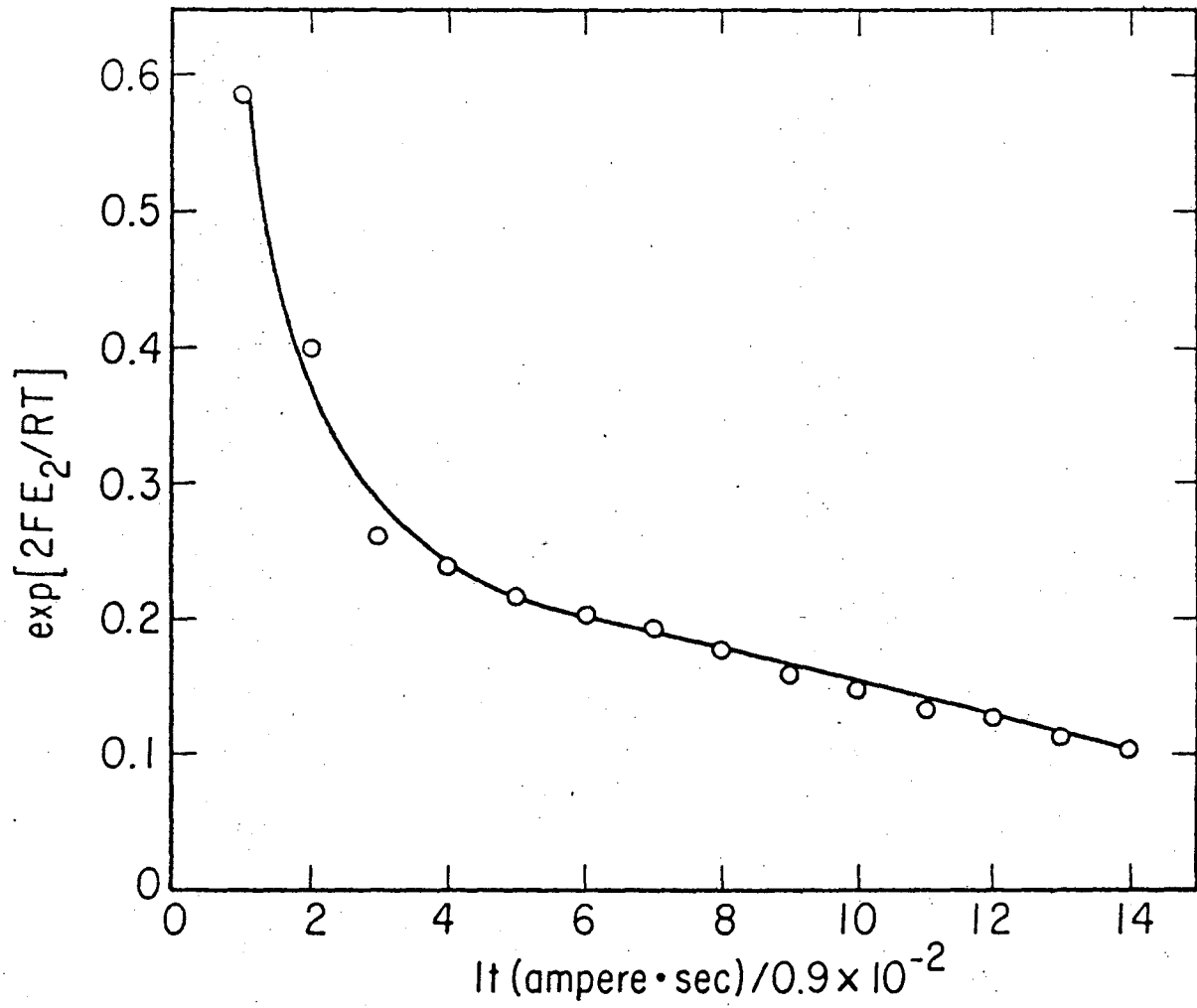
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Fig. 1.



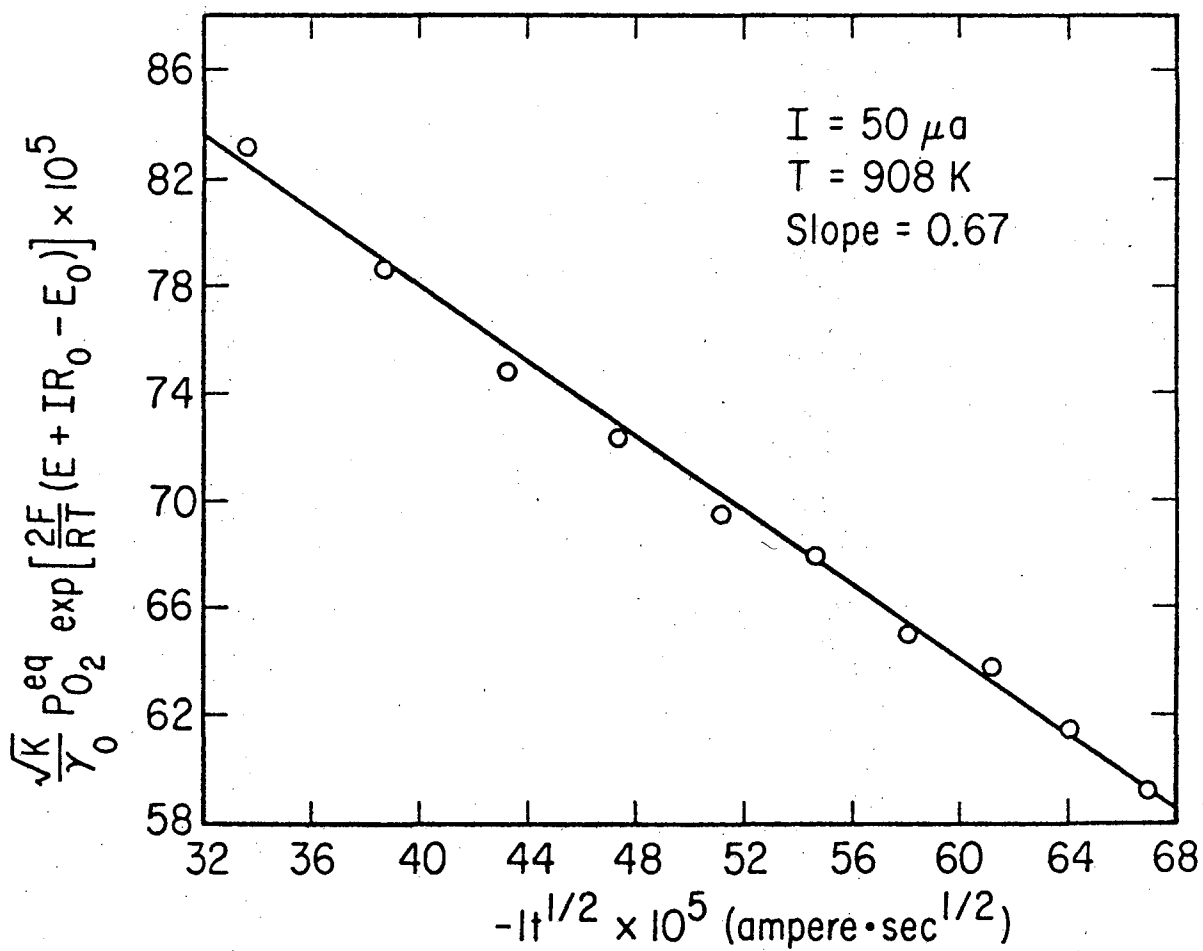
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Fig. 2.



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Fig. 3.



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Fig. 4.

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