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A POLAROGRAPHIC TECHNIQUE

FOR THE INVESTIGATION
OF V_2O_5 - B_2O_3 SYSTEM

A Thesis
Submitted to the Faculty of Graduate Studies
Through the Department of Engineering Materials
In Partial Fulfilment of the Requirements
for the degree of
Master of Applied Science
at the University of Windsor

by

Anthony G. Meszaros

Windsor, Ontario
1970

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ABSTRACT

A polarographic technique for use at high temperature has been developed for the examination of metal oxides in molten borates under atmospheric conditons.

Vanadium pentoxide (V_2O_5) in boric oxide (B_2O_3) has been investigated at $850^{\circ}C$. using the method. Although the kinetics of the reaction could not be determined, the polarographic waves are of interest. The activation energy of diffusion current is between 25-35 Kcal.mole⁻¹ indicating a highly complex system with relatively slow-moving ions. The technique shows that, structurally, the melt is similar to those produced by alkali metal oxides in boric oxide. Since a linear relationship exists between the mole fraction of solute and the diffusion current, the proposed method could prove to be a valuable analytical procedure.

ACKNOWLEDGEMENT

I gratefully acknowledge the assistance given to me by Professor R. G. Billingham, my advisor, and by Dr. R. Vilenchich, for translating a pertinent publication. The assistance of the Chemical Engineering Department, in allowing me to use their facilities, is greatly appreciated. I would also like to extend my gratitude to the National Research Council of Canada for their financial assistance during this study.

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I. INTRODUCTION

The electro-winning of metals from their oxides is of increasing interest in the light of the growing importance of hydrometallurgical processes. The oxide form of most metals is found in nature, therefore, increasing attention is being devoted to extraction processes involving molten salt solvents. It has been shown that alkali metal borates are good solvents for oxides (1).

This study is concerned with the polarographic investigation of high temperature borate melts, which it is felt, could assist in solving various problems which exist in oxide-solvent systems, eg. with respect to kinetics of electrode processes, analytical determination of ions, electrochemical characterization and structure of fused salts (2).

Since the borate melts are very corrosive, it is of primary importance to construct an operational cell and electrode system.

Thus the objectives of this project were to construct an operational cell and electrode system, and subsequently to develop a technique for the investigation of vanadium pentoxide (V_2O_5) in boric oxide (B_2O_5) in the temperature range 800-850°C.

The feasibility of working with metal oxides in molten sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and the potential relationships between similar electrochemical behaviour of oxides in aqueous and fused salt media were also investigated.

II. LITERATURE SURVEY

The new material requirements by space and nuclear reactor technology assure an increasingly important role for molten media. Some real and potential applications for molten salts are listed by Inman (1).

To study the electrochemical behaviour in molten solvents, one of the most reliable methods available is polarography. According to Kemula (3), over 20,000 papers, to date, have been published in this discipline and further applications of the method continue to be investigated. Although the polarographic method really refers to the use of a dropping mercury electrode system (4), the voltammetric studies of fused salts are very commonly found in "Polarography in Molten Salts" or in other reference literature (5, 6, 7, 8, 9).

In the experimental work it is very important that the initial melt be of high purity. The purity of a system is indicated by a small polarographic residual current and a wide decomposition potential span up to the point of the electrolysis of the solvent itself.

The first publication on the polarography of fused salts appeared in 1948 (9). It was shown that for Ni (II), Cu(II), Bi(III) in the $\text{NH}_4\text{NO}_3\text{-LiNO}_3\text{-NH}_4\text{Cl}$ system the Ilkovic Equation

was applicable. The advantages of high temperature polarography attracted many investigators. In addition to the work of many American workers, a considerable amount of work was done by the Russian scientists (5). Rapid advances were made also in Japan (10), where the Committee of Fused Salt Chemistry was inaugurated within the Electrochemical Society of Japan in 1958.

Borate systems, specifically, would be of interest in the field of metal electro-winning, since intermediate steps such as chlorination of the oxide ores could be eliminated due to high solubilities of oxides in borates (1). An excellent compendium of high temperature investigations up to 1967 is presented in the "Molten Salts Handbook" (11).

Russian and Japanese workers have carried out extensive polarographic investigations in high temperature borate systems (2, 12, 13).

The electrodes (reference and indicator) used are most important in high temperature polarographic studies. The different designs used so far in high temperature (800-1000°C) borate melts have been made of platinum since virtually nothing else would withstand the strong oxidizing media. In a general statement, however, Laitinen (14) raises the objection against ill-defined electrodes, stating: "Not only is the reference electrode potential poorly reproducible from experiment to experiment, but appreciable and variable polarization can occur due to the passage of a variable current during a single experiment, rendering an uncertainty in the slopes of

current-voltage curves".

Other investigators have obtained data which contradict the above statement (7, 13).

An interesting reference electrode for high temperature work has been described in the literature (15). The quasi-reference electrode (Q.R.E.), as it is described, is a bright platinum wire or other inert conductor immersed directly in the solution. It may have a very small area, and must be used with potentiostatic or other circuits that prevent the drawing of cell current through the Q.R.E.; therefore, it has a constant value of potential for the duration of an experiment. Q.R.E. was used successfully in a number of cases (16, 17). The justification for the use of Q.R.E. was established by Manning (16) when the known redox behaviour of silver was studied. The reduction of Ag^+ to Ag^0 proceeded reversibly, the observed half-wave potentials were reproducible and the limiting current was proportional to the concentration of silver so that the current-voltage curves were analytically useful.

The structural aspects of fused electrolytes are of great importance, and polarography can be an aid in solving related problems. It is well known (18) that glasses rich in alkali invariably are relatively good conductors. B_2O_3 and V_2O_5 are both considered to be glass formers, and this explains why polarographic examination has not been carried out in the past in such a complex system ($\text{V}_2\text{O}_5\text{-B}_2\text{O}_3$). The

structure of B_2O_3 and V_2O_5 glasses is still controversial (19, 20).

In general, the basic chemistry of common oxyanion salts in the molten state is not well known (21).

III. THEORETICAL CONSIDERATIONS

A. Current, diffusion and concentration relationships (22).

The polarographic investigation of molten systems at stationary solid electrodes is diffusion-controlled when the electrochemical processes are rapid. The diffusion process brings the material to the electrode surface, and thus may be described as a mass transfer process.

Essentially, three factors may contribute to this process:

a. Migration, which is an electric field effect and depends upon the charge in the species and is thus operative only with ions. In such cases its effect depends upon the concentration of the ion, its charge and its mobility under a field force.

b. Diffusion, which depends upon the natural diffusion to the electrode. The diffusion is temperature - and concentration - dependent, and is independent of applied voltage. If the concentration of the species in the bulk of the solution is greater than the concentration at the electrode surface, the species will tend to diffuse from the bulk of the solution toward the electrode surface. The potential gradient, caused by the difference in concentration at the electrode surface and in the bulk of the solution, is called "concentration

polarization".

c. Convection, which could arise from thermal and concentration gradients. In classical polarography the effect of convection is minimized to such an extent that it becomes insignificant.

The addition of sufficient electrolyte eliminates the problem of migration and convection. In effect, therefore, the only mass transport process of significance is diffusion.

1. Derivation of diffusion current

If we consider a plane electrode of surface area A across which a current i passes, due to an externally impressed emf., the current density is then $I = \frac{i}{A}$. Assuming that Fick's First Law of Diffusion holds, then

rate of diffusion \propto concentration gradient

Since diffusion is the rate-controlling step, therefore,

rate of diffusion = rate of electrode reaction

$$D \left(\frac{\partial c}{\partial x} \right)_{x=0} = \frac{I}{nF}$$

where, n = the number of electrons involved in reaction

F = Faraday (96,494 coulombs)

$\left(\frac{\partial c}{\partial x} \right)_{x=0}$ = concentration gradient

c = concentration

x = distance from the electrode surface

D = diffusion coefficient

By rearrangement and substitution,

$$i = nFAD \left(\frac{\partial c}{\partial x} \right)_{x=0}$$

If the decrease of concentration across the diffusion layer is $C_0 - C_e$, and the thickness of diffusion layer is l , then

$$\frac{\partial c}{\partial x} = \frac{C_0 - C_e}{l}$$

where, C_0 = concentration of bulk solution

C_e = concentration at electrode

$$\text{By substitution, } i = nFAD \frac{C_0 - C_e}{l}$$

when, $C_0 \gg C_e$ the current reaches a maximum value, called the diffusion current (i_d).

$$i_d = \frac{n FAD C_0}{l}$$

It is, therefore, not possible to increase the current further with an increase in voltage, unless some additional process can occur at a higher voltage.

B. Equations of Polarographic Waves (14)

The results of polarographic analysis with respect to current-voltage curves, depending on the systems analysed, do differ.

For reversible reactions with soluble products, as in aqueous solutions, the Heyrovsky - Ilkovic equation (Eq. 1) applies.

$$E = E_{\frac{1}{2}} + \frac{RT}{nF} \ln \frac{i_d - i}{i} \quad (1)$$

Where, the surface concentration of oxidant is proportional to $(i_d - i)$ and the surface concentration of reductant is proportional to i .

When the metal ions are reduced directly to the metal, then the equation

$$E = \text{Constant} + \frac{RT}{nF} \ln (i_d - i) \quad (2)$$

would be applicable.

In some cases, however, equation (1), eg. (2, 12), or in others equation (2), eg. (7), provides a better relationship.

For many instances of linear relationship the slopes do not conform to the theoretical value of $2.3 \frac{RT}{nF}$ (2, 12). It has been found that, similar to an irreversible process, the following equation is valid.

$$E = E_{\frac{1}{2}} + \frac{RT}{\alpha nF} \ln \frac{i_d - i}{i} \quad (3)$$

Generally these three equations are used for current-voltage relationships.

C. Activation energy of limiting diffusion current

On a relative basis, the determination of activation energies for the diffusion process in high temperature borate melts can be useful by indicating the kind of ions present in the system. For slow-moving, complex ions the activation energies are high eg. 20-30 Kcal.(2).

The work by Black (7) and Delimarskii (2) established the validity of the equation.

$$\ln i_d = A - \frac{B}{T}$$

$$\text{Letting } A = \ln K \text{ and } B = \frac{U}{R}$$

$$\text{Then } \ln i_d = K e^{-\frac{U}{R}}$$

where, U = activation energy

$$R = 1.978 \text{ cal. deg}^{-1} \text{ mole}^{-1}$$

Thus from the slope of $\log i_d$ vs. $\frac{1}{T}$, the activation energy of the diffusion can be determined.

IV. EXPERIMENTAL PROCEDURE

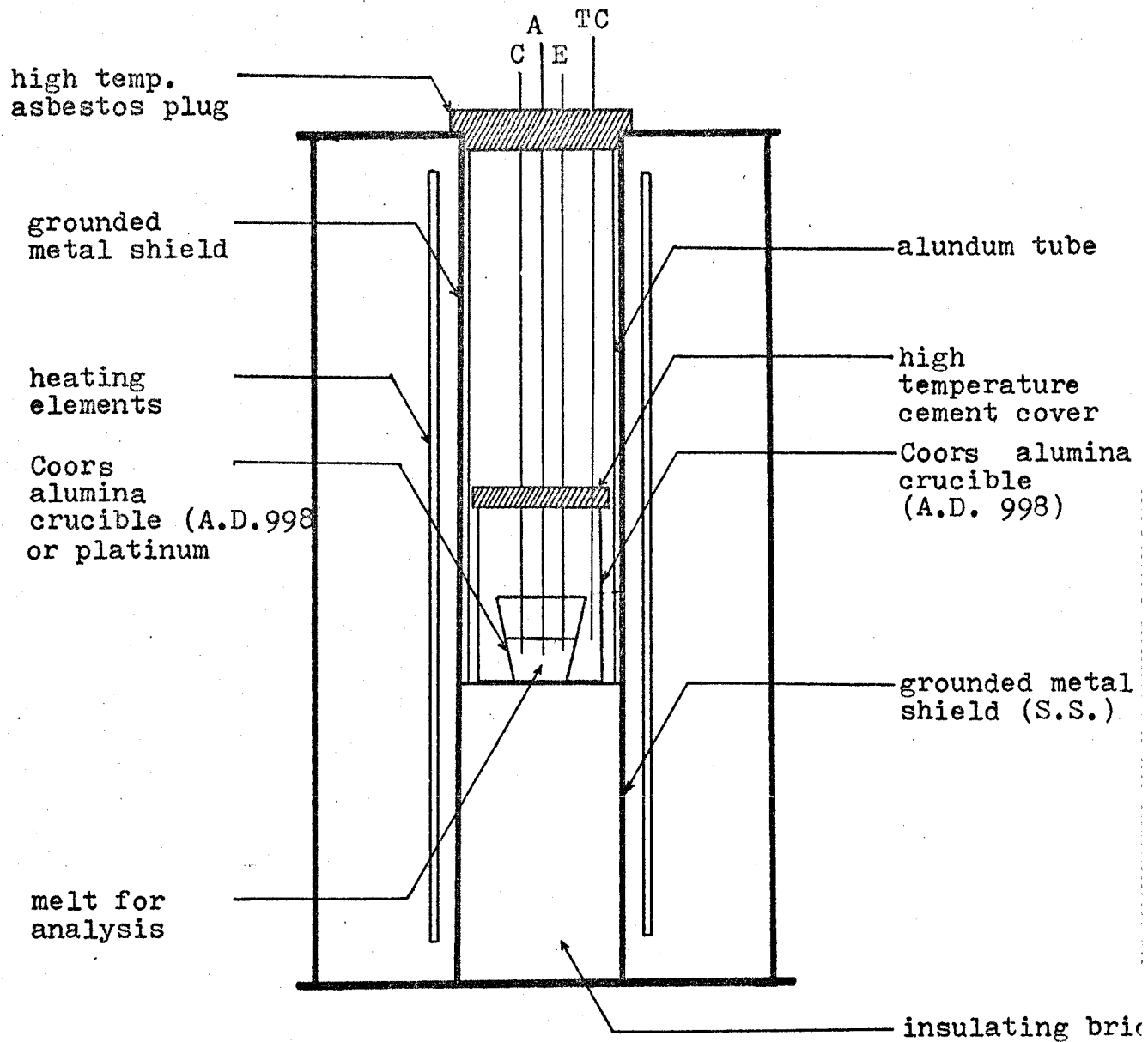
A. Development of Polarographic Method

1. Cell and electrode construction

The Coors porcelain sleeves for the three electrodes were embedded in and cast together with a high temperature porcelain cement in the desired geometrical arrangement. The resulting cylindrical block dried in the moulding apparatus at room temperature until it could be handled safely. Further drying was carried out in a laboratory oven at 120°C., followed by firing at $\geq 1500^{\circ}\text{C}$. for approximately 48 hours.

The incorporation of the porcelain sleeves in this manner provided a rigid construction for protection from undesirable temperature gradients. The small distance (1/16") between the disk, incorporating the electrodes, and tube wall surrounding the cell, insured a reproducible technique for lowering and positioning of the electrodes in the particular melt under study (Figure 4-1).

For the micro cathode a B&S gauge No.24 platinum wire was inserted into the corresponding porcelain sleeve. The regenerating electrode was B&S gauge No.18 platinum wire similarly positioned as the micro cathode.



C: Platinum micro cathode
 A: Platinum anode (reference electrode)
 E: Platinum regenerating electrode
 TC: Chromel-alumel thermocouple

FIGURE 4-1.

EXPERIMENTAL APPARATUS

The reference electrode consisted of a 3/4" square platinum foil positioned over a three sided platinum frame open at the bottom to allow easy immersion in the melt, and drainage upon raising the electrode. The frame of the anode sheet and the lead wire was fabricated from B&S gauge No.18 platinum wire. The anode plate was secured to the holding frame by a "continuous", uniform spot weld.

2. Crucibles

Preliminary investigations showed that even the highest purity of porcelain available was attacked by sodium tetraborate ($\text{Na}_2\text{B}_4\text{O}_7$) and boric oxide (B_2O_3) at 800-900°C. A porcelain crucible should be used for a very short period of time if the interference from the dissolving container is to be avoided. Thus metal oxides may be investigated, using porcelain crucibles with $\text{Na}_2\text{B}_4\text{O}_7$ as the solvent. $\text{Na}_2\text{B}_4\text{O}_7$, being a good solvent, readily dissolves the metal oxides which are added at a temperature of 800°C. or higher. Consequently the polarograms can be quickly run.

Homogeneous dissolution of metal oxides in B_2O_3 may take up to twenty-four hours. However, by this time the level of impurities will be objectionable, and it is recommended that the use of porcelain crucibles be avoided.

Platinum crucibles are not attacked by B_2O_3 or $\text{Na}_2\text{B}_4\text{O}_7$ media and, therefore, can be used. The ideal procedure would have been to homogenize a sample in a platinum crucible and then transfer over to a porcelain crucible just

to carry out the polarographic runs. This high temperature transferring was not feasible with our existing apparatus; therefore, when B_2O_3 was the solvent, the dissolution of oxides, as well as the polarographic runs, were made by using a platinum crucible. As far as reference checks are concerned, runs were made in porcelain as well as platinum crucibles for identical systems, but no difference was noted between the polarograms.

3. Assembly of Apparatus

Heating was provided by a 3" x 18" tube furnace equipped with the usual controlling thermocouple, Barber-Coleman temperature controller, and adjustable autotransformer. After the furnace had reached a steady temperature the variation in the cell temperature did not exceed $\pm 1^\circ C$. A stainless steel pipe was placed adjacent to the furnace heating element and grounded to prevent the buildup of any static charges. A closely fitting fire-brick plug was inserted into the bottom of the stainless steel pipe so that when the cell was placed on the top of it the cell was located in the middle region of the heating elements. The temperature of the cell was measured with a chromel-alumel thermocouple.

4. Cleaning and regeneration of electrode surfaces

After polarographic examinations the electrodes were raised from the melt in the furnace to provide adequate drainage. In case of molten $Na_2B_4O_7$ the temperature was in-

creased to a higher than operational value to obtain better cleaning of the electrodes. The residues remaining on the electrodes were removed by boiling water, in case of B_2O_3 , and by warm HCl for $Na_2B_4O_7$.

The regeneration of the micro electrode surface was carried out by the application of reverse potentials between the micro cathode and the regenerating electrode. The required power was supplied by a small laboratory type rectifier. The basis for regeneration was established by initial polarographic investigations using clean electrodes. For each run, the regeneration was made to the original values of current and voltage. Slow regenerations were carried out in order to prevent roughening of the electrode surface.

B. General Experimental Procedure

All chemicals used were of analytical grades, as supplied by Fisher, B.D.H., and Koch Light Laboratories.

The required amount of solvent was weighed in a 50 ml. platinum crucible, and placed in a muffle furnace for drying purposes. In the case of B_2O_3 , the solvent was held at $450^\circ C$. until no more foaming took place, then it was kept at $900^\circ C$. for at least twelve hours. After the addition of the metal oxide (V_2O_5) the melt was kept at $850^\circ C$. for at least twenty-four hours before the polarographic examination was carried out. The complete dissolution of the oxide was observed visually. The polarographic instrument used was a Sargent

Model XV Polarograph. Polarograms were run at various sensitivities and in different voltage ranges in order to obtain optimum results.

V. RESULTS AND DISCUSSION

A. Aqueous Systems

The range of potentials applicable to platinum electrodes in aqueous solutions is bounded by the limits $E_+ = 1.2 - 0.06$ pH, $E_- = -0.06$ pH wrt. S.C.E. (23). Due to these limits, only two metal oxides were chosen for preliminary examination. The forward polarographic investigation of MoO_3 , as the first oxide selected, was not successful. The occasional waves obtained were inconsistent in nature. The literature indicates that Mo does not give a wave in alkaline media because of extensive hydrolysis (24, p.457). The reductions in such cases are so slow, according to Maites (23, p.335), that appreciable currents are not obtained at any potential up to the beginning of the final current rise.

A half cell, $\text{Hg}/\text{HgSO}_4(\text{s})/17\text{MH}_2\text{SO}_4$ was constructed, but its use did not give the hoped-for results.

The second oxide selected, CrO_3 , gave three waves (table I-1). It is interesting to note that Black and DeVries (5) analysed CrO_3 in molten LiCl-KCl system and their half-wave potential for the first wave was -0.25 volts and the second half-wave potential was -0.82 volts. Based upon the wave heights, three electron transfer in the first instance and

one electron transfer for the second wave was suggested.

The use of a rotating micro electrode did not alter the wave heights to any appreciable degree.

The bubbling flow of nitrogen during analysis created a pulsating effect and as a result the waves formed were very similar to the wave formation with a Dropping Mercury Electrode.

The use of D.M.E. vs. S.C.E. produced reproducible waves. The low solubility of borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) in water, however, limited the investigation to a qualitative study. Consequently, the relationship of i_d vs. solute concentration could not be checked.

The current-voltage relationship for $2.5 \times 10^{-3}\text{M}$ V_2O_5 was analysed (Table I-2, Figures I-1, I-2) and it was found that the Kolthoff and Lingane equation was applicable (24).

$$E_{de} = E_{\frac{1}{2}} + \frac{.0591}{n} \log \frac{i_d - i}{i}$$

where, E_{de} = potential of D.M.E.

$E_{\frac{1}{2}}$ = half-wave potential

i = current at E_{de}

i_d = diffusion current

n = number of electrons involved in reduction

The above equation is a relationship between applied voltage, half-wave potential, and current for the case where the metal ion is reversibly reduced to the metallic state, this metal being soluble in the mercury so that an amalgam is formed.

Calculation of n value for the number of electrons in the reduction of V_2O_5 gave a value of 0.5 to 0.6 for the first wave and 0.3 to 0.9 for the second wave. Laitinen and Rhodes (1962) calculated n values for reduction of V_2O_5 in molten KCl-LiCl between 0.5 to 0.7. Their result was in good agreement with an n value obtained from coulometry of V_2O_5 solutions (6, p.261).

B. High Temperature Work

1. $V_2O_5 - B_2O_3$ system (850°C.)

The solubility of V_2O_5 in B_2O_3 was found to be adequate ($\geq 10^{-2}M$) for polarographic investigation of the oxide. The current-voltage curves were analysed with respect to peak values. Skobets (25) has shown that the use of surge current is fully justified in work with solid electrodes. This has made it possible to use an automatic recording polarograph in the study of fused salts involving solid electrodes.

In each case, except for the lowest concentration, the peak current increased linearly with concentration so that the polarograms could be used for the quantitative determination of V_2O_5 in B_2O_3 (Figure 5-1). The activation energies for the diffusion processes were of the order of 25 - 35 Kcal. mole⁻¹ indicating the presence of complex and relatively slow-moving ions in the melts, (Table 5-1, Figure 5-2). The analysis of the polarographic waves was not satisfactory, however, since no straight line relationship could be obtained for the equations (eqn.1 and eqn. 2) tested (Table 5-2,

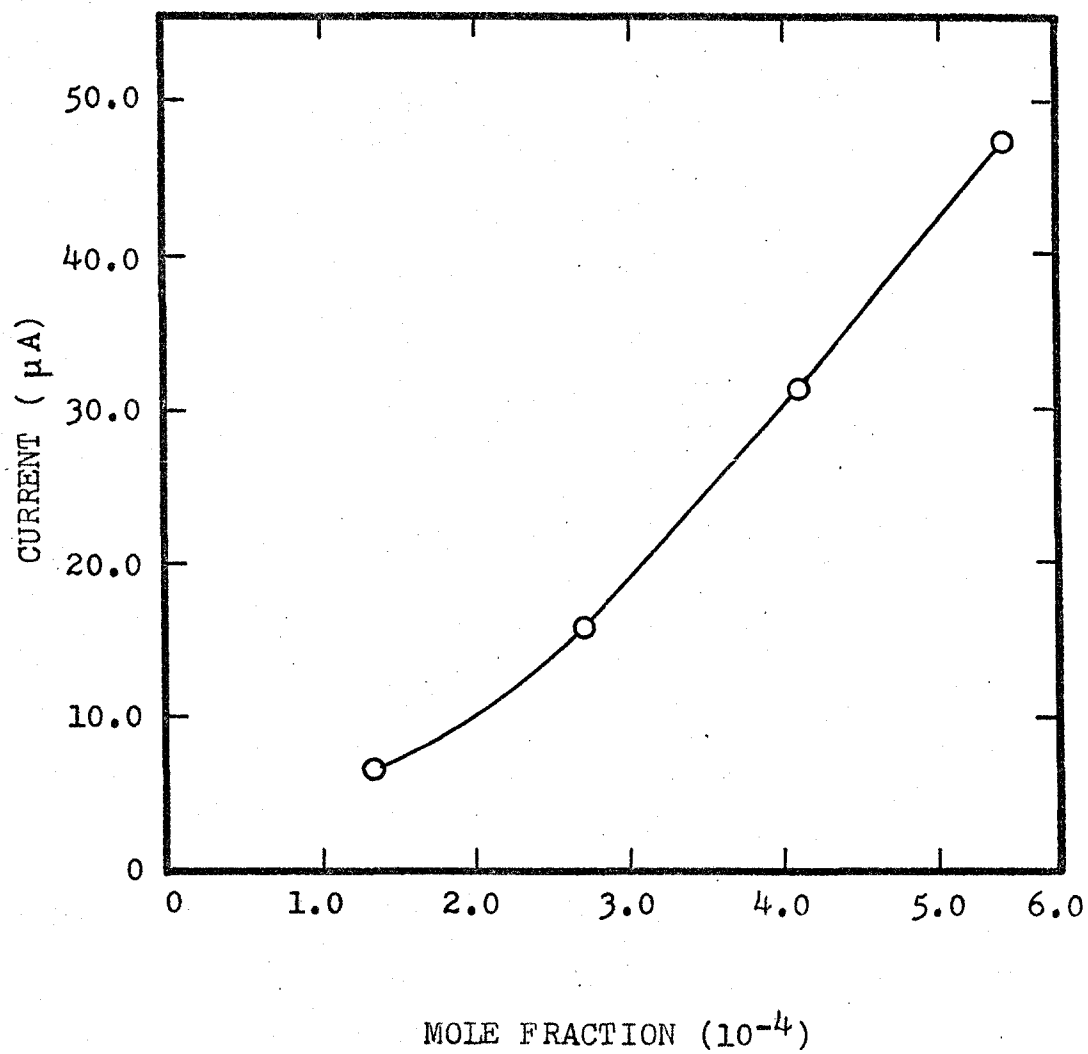


FIGURE 5-1. Plot of Current vs. Mole Fraction of Solute.
 $\text{V}_2\text{O}_5 - \text{B}_2\text{O}_3$ melt at 850°C .

TABLE 5-1

Activation Energy of Diffusion Current
for $V_2O_5-B_2O_3$ Melt

Temp. (°C.)	$\frac{1}{T}$	i_p (μA)	U (Kcal.mole ⁻¹)
800	9.03×10^{-4}	16.2	25.2
850	8.90×10^{-4}	21.0	
800	9.03×10^{-4}	23.4	35.7
850	8.90×10^{-4}	35.4	

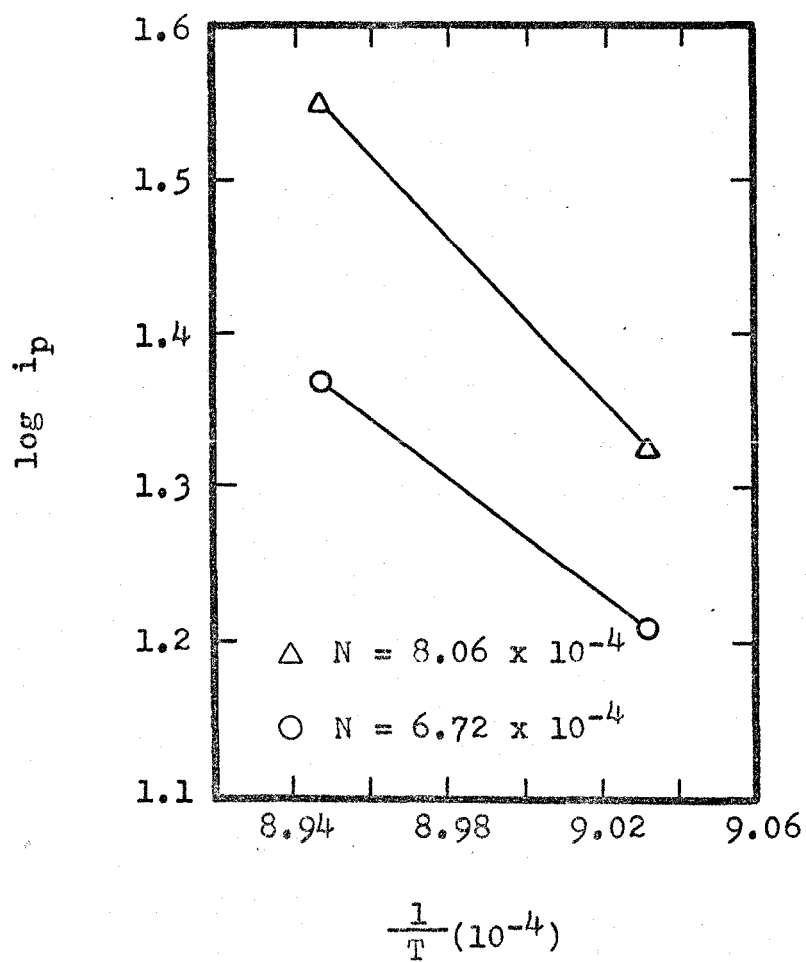


FIGURE 5-2. Plot of $\log i_p$ vs. $\frac{1}{T}$
 $V_2O_5-B_2O_3$ melt

TABLE 5-2

Data to Analyze Current-voltage Relationship

V₂O₅-B₂O₃ System at 850°C.

Mole Fraction of V ₂ O ₅	E _p (-volts)	i _p (μA)	i (μA)	i _{p-i} (μA)	$\frac{i_{p-i}}{i}$	ln(i _{p-i})	$\ln \frac{i_{p-i}}{i}$	Remarks
1.32 x 10 ⁻⁴	0.00	9.78	0.00	9.78		2.28		E _{p₁} = -1.0v
	0.30		2.28	7.50	3.29	2.02	1.19	i _{pr} = 3.3μA
	0.60		3.78	6.00	1.59	1.79	0.46	
	0.90		5.70	4.08	0.72	1.41	-0.33	
	1.20		8.40	1.38	0.16	0.32	-1.83	
	1.30		9.06	0.72	0.08	-0.33	-4.53	
	1.35		9.72	0.06	0.006	-2.81	-5.12	
2.68 x 10 ⁻⁴	0.00	21.00	0.00	21.00		3.05		E _{p₁} = -1.05v
	0.20		4.80	16.20	3.50	2.79	1.28	i _{pr} = 5.4μA
	0.40		5.40	15.60	2.88	2.75	1.06	
	0.60		6.90	14.10	2.04	2.65	0.71	
	0.80		8.40	12.60	1.50	2.53	0.41	
	1.00		12.00	9.00	0.75	2.20	-0.29	
	1.20		16.80	4.40	0.26	1.48	-1.35	
1.38		20.40	0.60	0.06	-0.51	-3.51		

TABLE 5-2 -continued

Mole Fraction of V2O5	(-volts)	i_p (μA)	i (μA)	i_{p-1} (μA)	$\frac{i_{p-1}}{i}$	$\ln(i_{p-1})$	$\ln \frac{i_{p-1}}{i}$	Remarks
4.09×10^{-4}	0.00	38.4	0.00	38.40		3.65		$E_{p\frac{1}{2}} = -0.99v$
	0.20		5.10	33.30	6.53	3.51	1.88	
	0.40		7.80	30.60	3.92	3.42	1.37	$i_{pr} = 7.2\mu A$
	0.60		11.40	27.00	2.37	3.30	0.86	
	0.80		16.20	22.20	1.37	3.10	0.31	
	1.00		23.40	15.00	0.64	2.71	-0.44	
	1.20		31.20	7.20	0.23	1.97	-1.47	
	1.40		37.20	1.20	0.03	0.18	-3.43	
	1.43		37.80	.60	0.16	-0.51	-4.14	
	5.41×10^{-4}	0.00	57.6	0.00	57.60		4.05	
0.30			9.60	48.00	5.00	3.87	1.61	
0.60			16.80	40.80	2.43	3.71	0.89	$i_{pr} = 10.8\mu A$
0.90			40.80	16.80	0.41	2.82	-0.89	
1.20			50.40	7.20	0.14	1.97	-1.95	
1.30			55.20	2.40	0.04	0.88	-3.15	
1.40			56.40	1.20	0.02	0.18	-3.86	

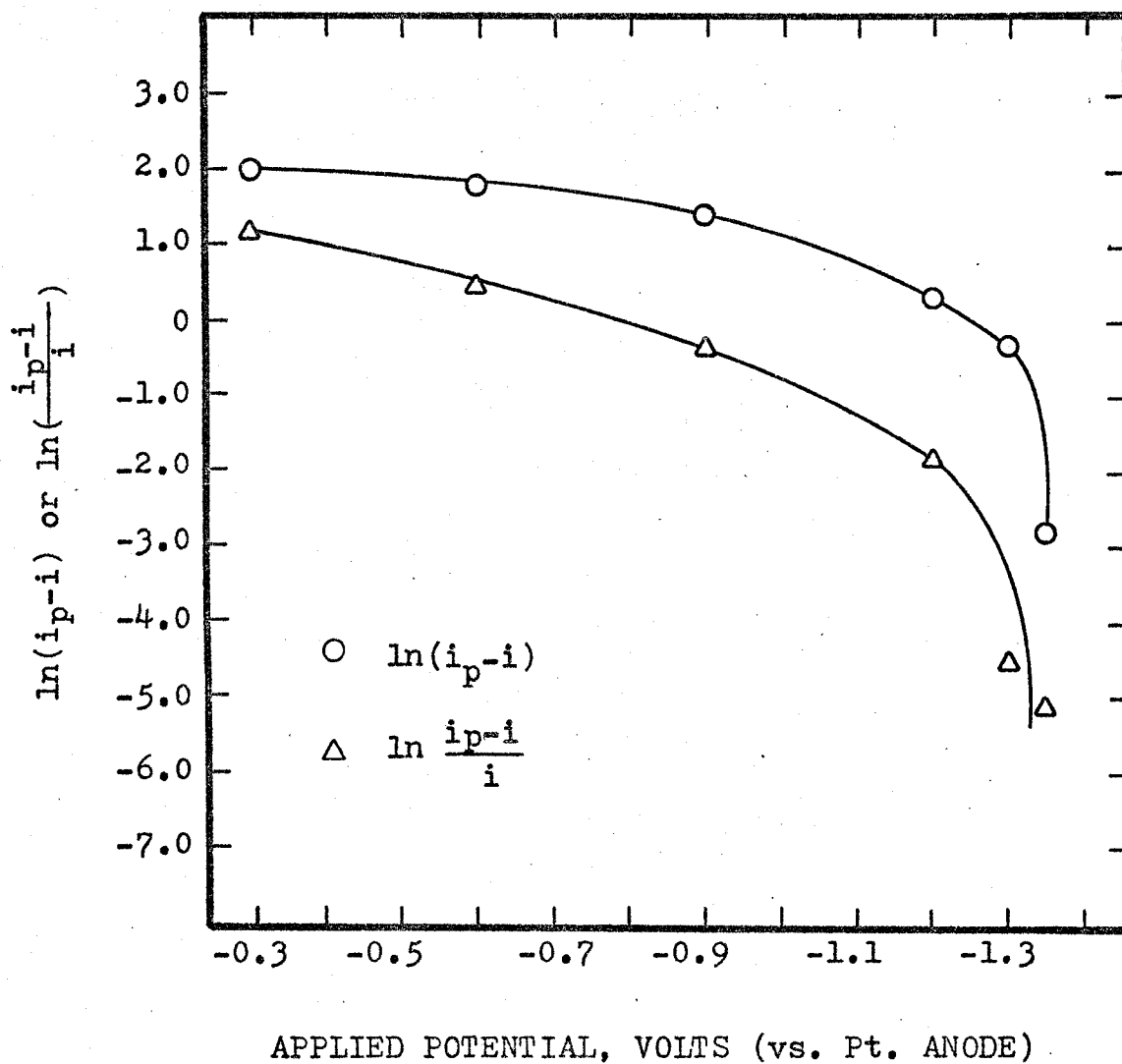


FIGURE 5-3. $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Potential
 $V_2O_5 - B_2O_3$ melt at $850^\circ C$.
 $N = 1.32 \times 10^{-4}$

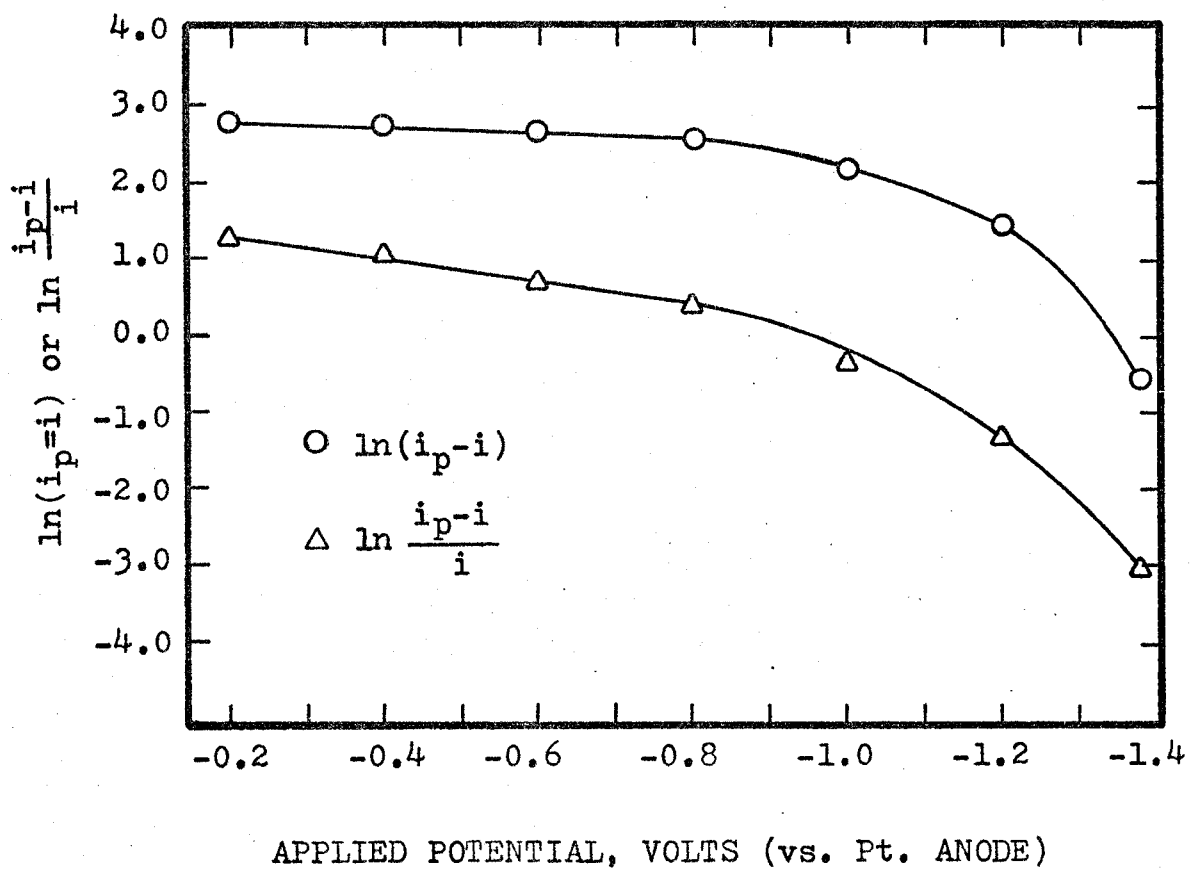


FIGURE 5-4. Plot of $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Potential.

V_2O_5 B_2O_3 melt at $850^\circ C$.

$N = 2.68 \times 10^{-4}$

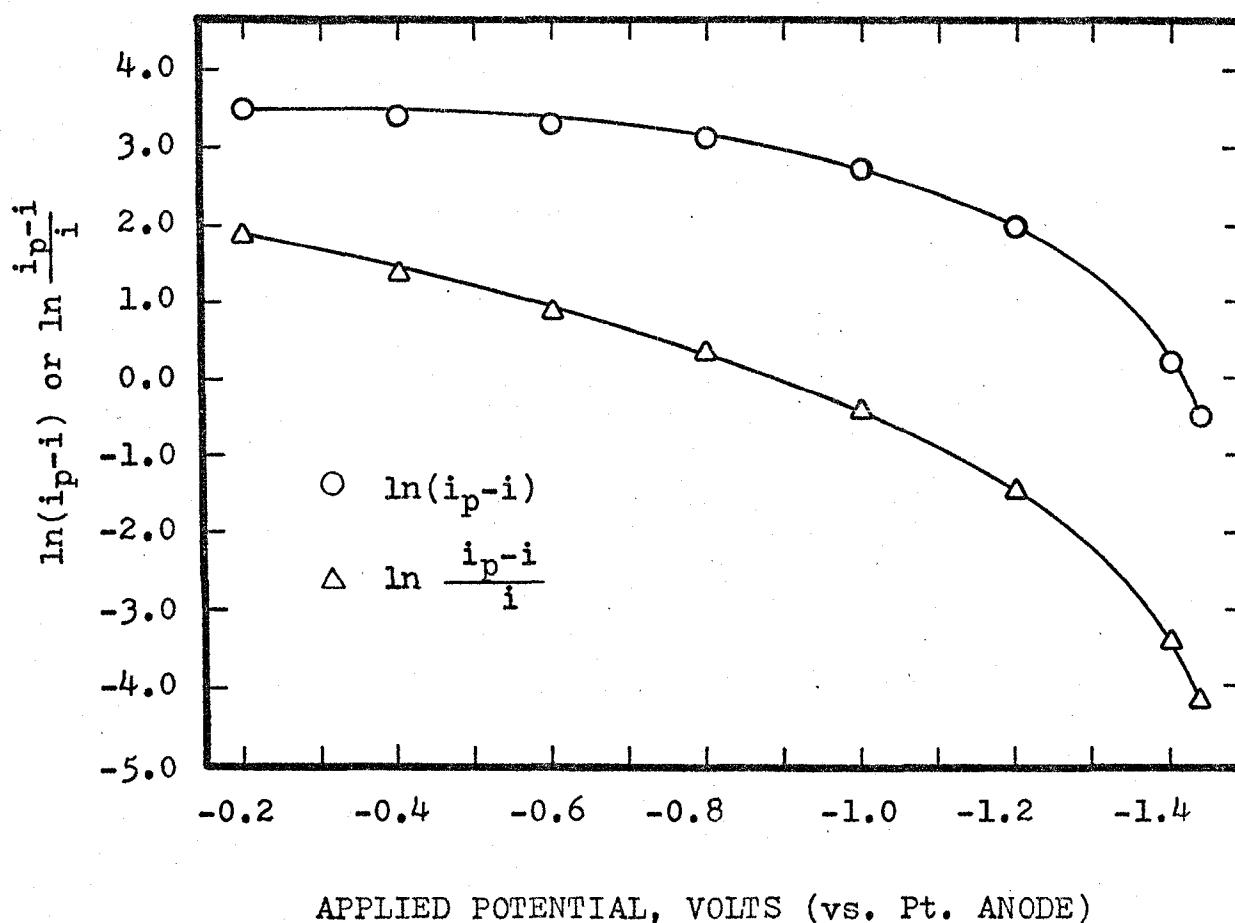


FIGURE 5-5. Plot of $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Voltage. $V_2O_5 - B_2O_3$ melt at $850^\circ C$.
 $N = 4.09 \times 10^{-4}$

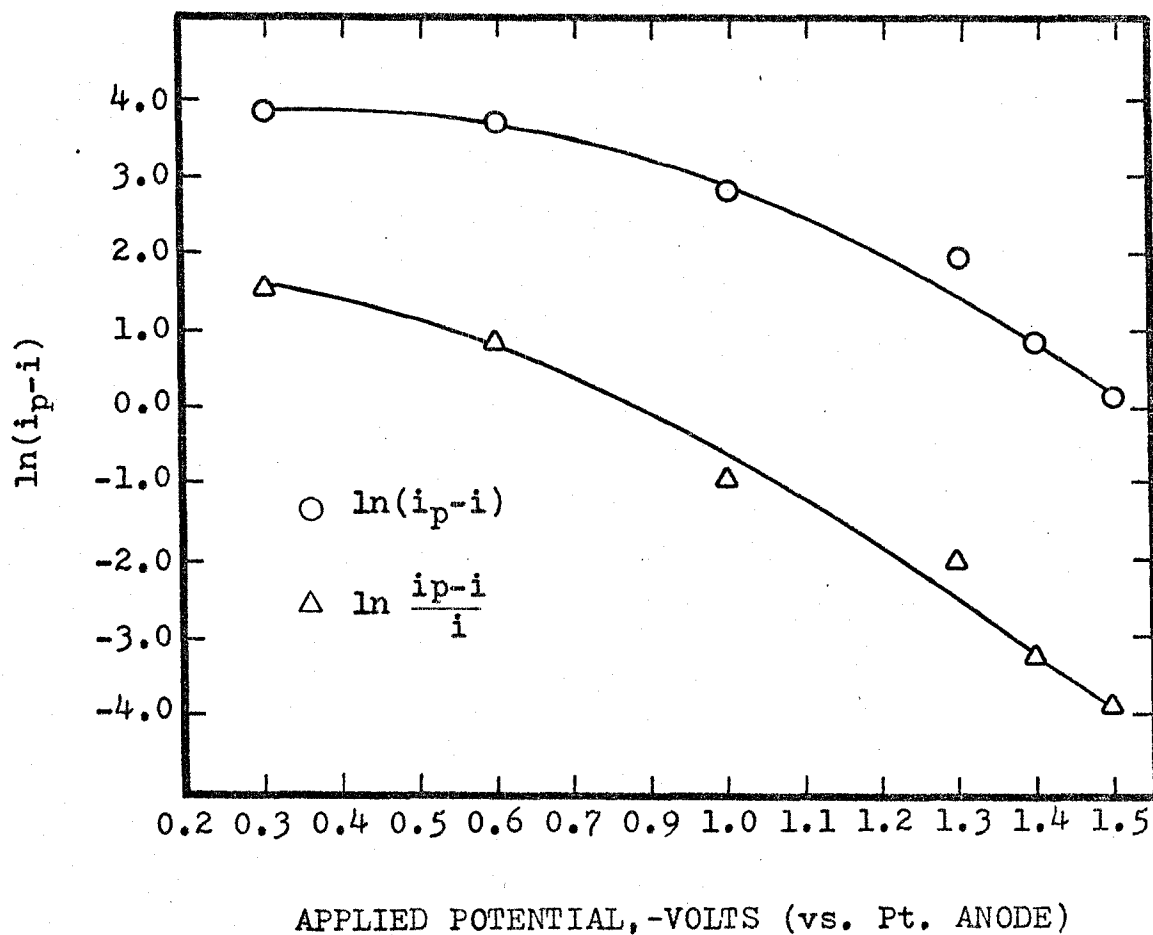


FIGURE 5-6. Plot of $\ln(i_p-i)$ or $\ln \frac{i_p-i}{i}$ vs. Applied Voltage. $V_2O_5 - B_2O_3$ melt at $850^\circ C$.
 $N = 5.41 \times 10^{-4}$

Figure 5-3, 5-4, 5-5, 5-6).

The polarographic wave shown by Johnson and Laitinen (21) for V_2O_5 in $Li_2SO_4 - Na_2SO_4 - K_2SO_4$ at $550^\circ C$. is very similar in shape to that obtained for V_2O_5 in B_2O_3 in this project.

2. $CuO - Na_2B_4O_7$ system

The attempt, to verify the results of Delimarskii and Kalabalina (2) for CuO at $820^\circ C$, was only partially successful. Figure II-1, Table II-1, shows a direct relationship between peak currents and mole fraction of solute. The half-wave potential value of -0.458 volts obtained is comparable with -0.417 volts reported by Delimarskii and Kalabalina.

The analysis of the polarographic waves, as in case of $V_2O_5 - B_2O_3$ system, was not satisfactory (Figures II-2, II-3, II-4).

VI. CONCLUSIONS AND RECOMMENDATIONS

The high temperature polarographic technique developed and used for the investigation of V_2O_5 in B_2O_3 was also successfully applied to the $CuO-Na_2B_4O_7$ system. This is a definite indication that rare earth oxides, when dissolved in molten $Na_2B_4O_7$, also can be investigated, if a more versatile polarograph is used instead of one of a routine nature, (eg. Sargent Polarograph Model XV). For instance, one such instrument on the market, appears to be the ORNL-Model Q-1988A polarograph. The corresponding design specifications and performance of the instrument are described in detail by Kelly, Jones and Fisher (26, 27, 28).

This instrument is capable of recording polarograms in the milliampere range. The limit for Sargent Model XV Polarograph is 250 microamperes. For an investigation in molten $Na_2B_4O_7$, the milliampere range is required as Kimure (13) has indicated.

During the earlier experimental work in this project, it was discovered that it is impossible to maintain a perfect seal for the micro electrode in molten borates. The porcelain-ware and the high temperature cement were severely attacked by the corrosive media. The small diameter platinum electrode

wire, with adjustable immersion, did overcome this difficulty. For future work a similar type of construction or arrangement is recommended. The point of contact with the melt was determined with a conductivity meter and the desired depth of immersion was attained with the aid of a linear scale graduated in 0.5 mm. divisions. For a more accurate method, the micro electrode should be lowered or raised with the aid of a vernier scale type of attachment.

The polarographic method may be further improved by flushing the micro cathode with an inert gas periodically. For this purpose a platinum tube would have to surround the tip of the micro electrode when dipped in the melt. The advantage would be that, with the bubbling of an inert gas around the indicator electrode, the diffusion current would be increased and the maxima would be removed which are related to the application of a continuously changing voltage to the stationary electrodes (24, p.404). The current maxima are the result of the voltage changing at a more rapid rate than that at which a steady state diffusion equilibrium is reached at the electrode.

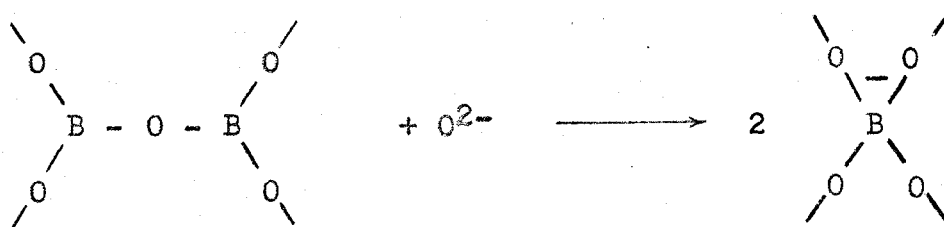
The kinetics of reaction for V_2O_5 in molten B_2O_3 could not be defined as the current-voltage relationship did not show a linear correlation by the application of the derived equations 1 and 2 (Theoretical Considerations) to the data. It is to be noted, however, that the "linearity" is better with the application of equation 1 than equation 2. This fact is most evident in Figure 5-6.

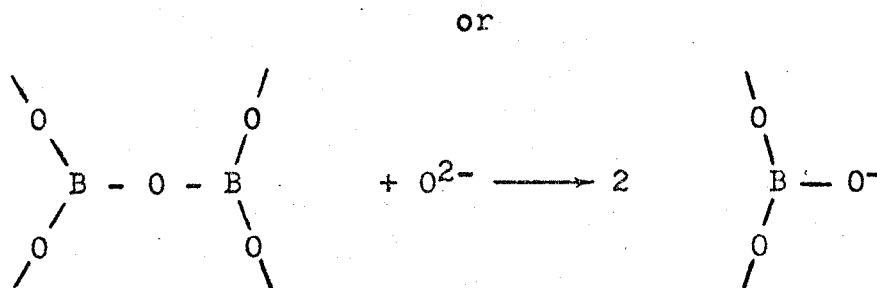
The current vs. mole fraction relationship is essentially linear, with only the lowest concentration deviating from the straight line. This fact would appear to make the technique of interest in analytical procedures.

The high values of activation energies for the diffusion current is typical of borate systems indicating their complex nature. The 25-35 Kcal.mole⁻¹ values for V₂O₅ are at least twenty per cent greater than the values determined by Delimarskii (2) for metal oxides in Na₂B₄O₇. The high values also indicate the "poor" conductivity of B₂O₃ melts.

Laitinen (21) investigated V₂O₅ in a good conducting medium and proposed that a reduction of V(V) to V(IV) took place. It is believed that a similar postulation could be made for vanadium in boric oxide. There was substantiation for this proposition by the fact that the yellowish-brown melt of V₂O₅, in the cooled state, appeared as a pale blue glass, characteristic of VO₂ (20).

With respect to the structural aspects of the melt, (V₂O₅-B₂O₃), the discussion of Rowell (29) can be of assistance. The melt was ionic since a polarographic wave was obtained. Therefore, with V₂O₅ added to B₂O₃, as in the case of alkali oxides, it is theorized that the oxygen adds to the structure in the following manner (29):





The positively charged groups then locate themselves near the negatively charged groups by ionic bonding.

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NOMENCLATURE

μA	microampere
i_d	diffusion current
i_p	peak diffusion current
i_{pr}	peak residual current
V	Volt
E_D	Decomposition Potential
$E_{\frac{1}{2}}$	Half-wave Potential
E_l	Limiting Potential
D.M.E.	Dropping Mercury Electrode
$^{\circ}\text{C}$.	Degrees Centigrade
T	Absolute Temperature ($^{\circ}\text{K}$)
M	Molar
N	Mole Fraction of Solute
n	number of electrons involved in reduction

APPENDIX I
DATA FOR AQUEOUS SYSTEMS

TABLE I-1

Polarographic Examination of Metal Oxides in Aqueous Solutions at 25°C

(Solvent: $5.24 \times 10^{-2}M$ Borax Solution)

Solute & Conc.	Reference Electrode	Voltage Range	S.	1st wave			2nd wave			3rd wave					
				E_D	$E_{\frac{1}{2}}$	E_1	i_d	E_D	$E_{\frac{1}{2}}$	E_1	i_d	E_D	$E_{\frac{1}{2}}$	E_1	i_d
$CrO_3, 10^{-2}M$	Pt	0-3	0.10	0.100	0.250	0.390	2.1	0.570	0.690	0.820	2.8	1.05	1.25	1.36	3.4
	S.C.E.	0-1	0.20	0.245	0.295	0.340	13.8	0.525	0.590	0.655	6.8				
	"	0-1	0.20	0.230	0.290	0.345	13.4	0.505	0.525	0.640	6.2				
	"	0-3	0.003	0.235	0.293	0.352	13.6	0.510	0.575	0.640	6.4				
$BaO, 10^{-4}M$	"	0-3	0.003	0.828	1.056	1.287	0.069								
$MgO, 10^{-4}M$	"	0-3	0.003	0.819	1.05	1.29	0.249								
$V_2O_5, 2.5 \times 10^{-3}M$	"	0-2	0.20	1.28	1.42	1.56	4.8	1.80	1.83	1.86	1.2				
	"	0-3	0.10	1.21	1.37	1.52	5.1	1.79	1.82	1.85	1.4				
	"	0-3	0.15	0.25	1.38	1.68	5.7	1.80	1.84	1.86	1.2				
$CeO_2, 10^{-4}M$	"	0-3	0.006	0.81	1.04	1.26	0.34								
$La_2O_3, 10^{-5}M$	"	0-3	0.003	0.675	1.014	1.35	0.045								
$Nb_2O_5, 10^{-4}M$	"	0-3	0.003	0.126	0.195	0.246	0.039	0.645	1.065	1.47	0.057				
	"	0-3	0.003	0.15	0.213	0.279	0.036	0.705	1.010	1.50	0.063				
$Pr_6O_{11}, 10^{-6}M$	"	0-3	0.003	0.725	1.089	1.35	0.042								
$Yb_2O_3, 10^{-5}M$	"	0-3	0.003	0.09	0.18	0.264	0.219	0.96	1.20	1.38	0.153				
	"	0-3	0.006	0.09	0.18	0.267	0.210	0.93	1.134	1.305	0.12				
"	"	0-3	0.003	0.87	0.975	1.08	0.282								

S. = Sensitivity

E = -volts

TABLE I-2

Data for Plot of $\log \frac{i_d - i}{i}$ vs. Applied Potential

$2.5 \times 10^{-3} \text{M V}_2\text{O}_5$ in $5.243 \times 10^{-2} \text{M Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$

E (-volts)	i_d μA	i μA	$i_d - i$ μA	$\frac{i_d - i}{i}$	$\log \frac{i_d - i}{i}$	COMMENTS
1.28	4.80	0.00				1st wave
1.30		0.40	4.40	11.00	1.04	D.M.E. vs.
1.35		1.20	3.60	3.00	0.47	S.C.E.
1.40		2.20	2.60	1.18	0.07	
1.45		3.00	1.80	0.60	-0.22	
1.50		4.20	0.60	0.14	-0.85	
1.52		4.50	0.30	0.07	-1.15	
1.81	1.20	0.40	0.80	2.00	0.30	2nd wave
1.82		0.70	0.50	0.71	-0.15	
1.83		0.80	0.40	0.50	-0.30	
1.84		1.00	0.20	0.20	-0.70	
1.85		1.10	0.10	0.09	-1.04	

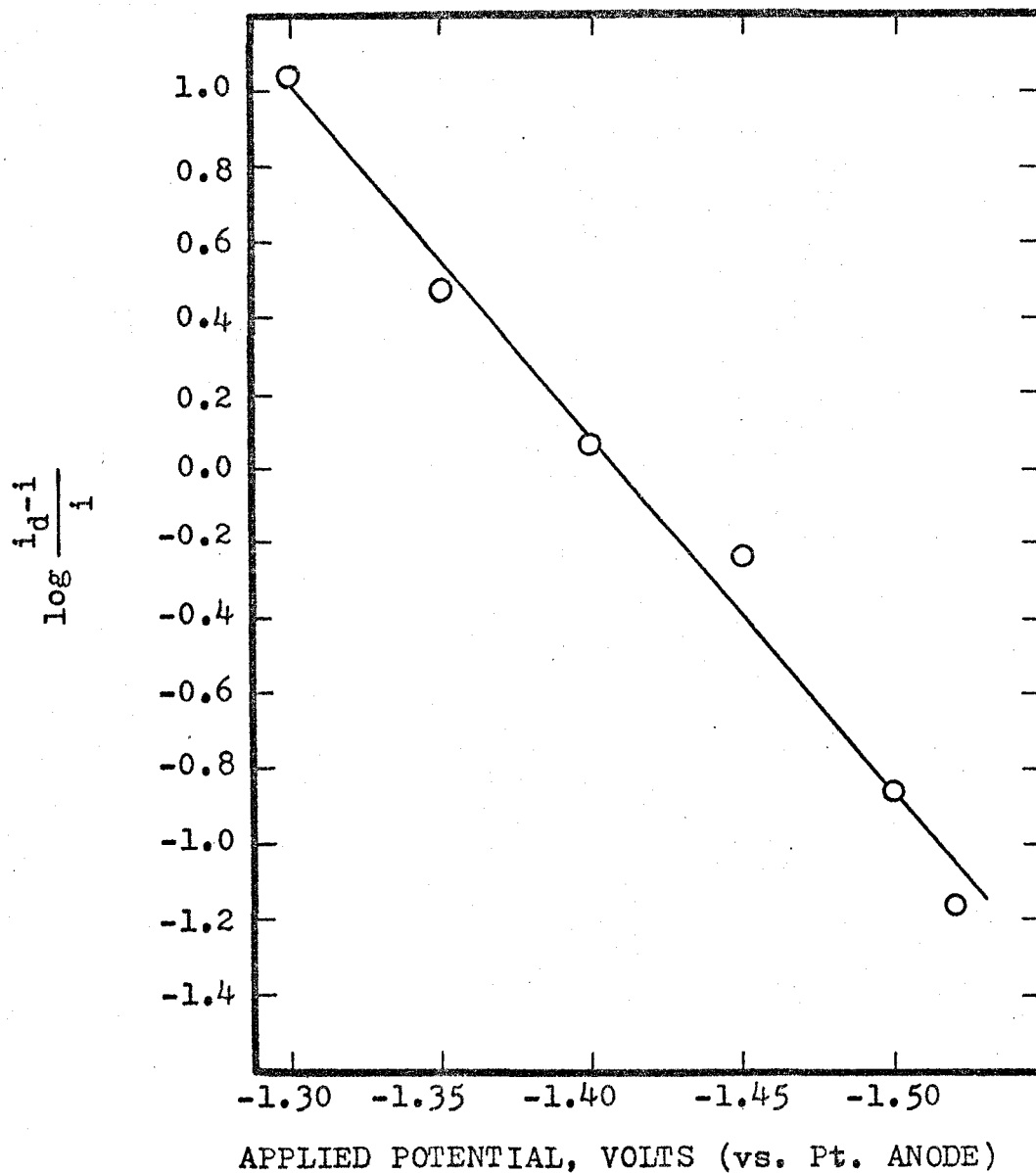
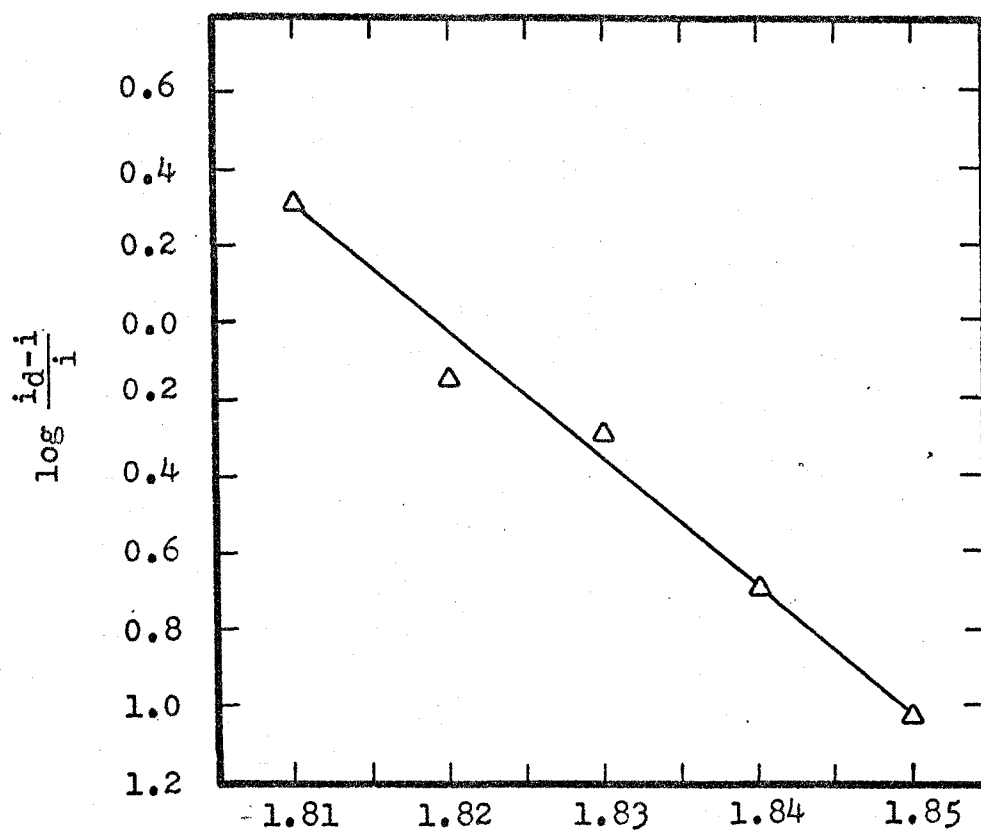


FIGURE I-1. Plot of $\log \frac{i_d - i}{i}$ vs. Applied Potential. D.M.E. vs. S.C.E., 25°C, $2.5 \times 10^{-2}M$ V_2O_5 in $5.24 \times 10^{-2}M$ Borax Solution FIRST WAVE.



APPLIED POTENTIAL, VOLTS (vs. Pt. ANODE)

FIGURE I-2. Plot of $\log \frac{i_d-i}{i}$ vs. Applied Potential. D.M.E. vs. S.C.E., 25°C, $2.5 \times 10^{-2}M$ V_2O_5 in $5.24 \times 10^{-2}M$ Borax Solution SECOND WAVE.

TABLE II-1

Data to Analyse Current-voltage Relationship

CuO - Na₂B₄O₇ System at 820°C.

Mole Fraction of CuO	(-volts)	i _p (μA)	i (μA)	i _{p-i} (μA)	$\frac{i_{p-i}}{i}$	ln(i _{p-i})	$\ln \frac{i_{p-i}}{i}$	Remarks
2.82 x 10 ⁻²	0.36	68.00	35.00	33.00	0.94	3.50	-0.06	E _{p₂} = -0.443V i _{pr} = 34.0 μA
	0.39		40.00	28.00	0.70	3.33	-0.36	
	0.42		44.00	24.00	0.54	3.18	-0.61	
	0.44		51.00	17.00	0.33	2.83	-1.10	
	0.46		64.00	4.00	0.06	1.39	-2.77	
3.70 x 10 ⁻⁴	0.36	105.00	64.00	41.00	0.64	3.71	-0.44	E _{p₂} = -0.474V i _{pr} = 59.0 μA
	0.39		69.00	36.00	0.52	3.58	-0.65	
	0.42		73.00	32.00	0.44	3.47	-0.83	
	0.45		78.00	27.00	0.35	3.29	-1.06	
	0.47		82.00	23.00	0.28	3.14	-1.27	
	0.49		102.00	3.00	0.03	1.10	-3.54	
6.05 x 10 ⁻⁴	0.34	126.00	67.00	59.00	0.88	4.08	-0.13	E _{p₂} = -0.457V i _{pr} = 63.0 μA
	0.37		71.00	55.00	0.77	4.01	-0.25	
	0.40		75.00	51.00	0.68	3.93	-0.39	
	0.43		81.00	45.00	0.56	3.81	-0.59	
	0.457		94.50	31.50	0.33	3.45	-1.10	
	0.46		116.00	10.00	0.09	2.30	-2.45	
	0.47		122.00	4.00	-0.033	1.39	-3.41	

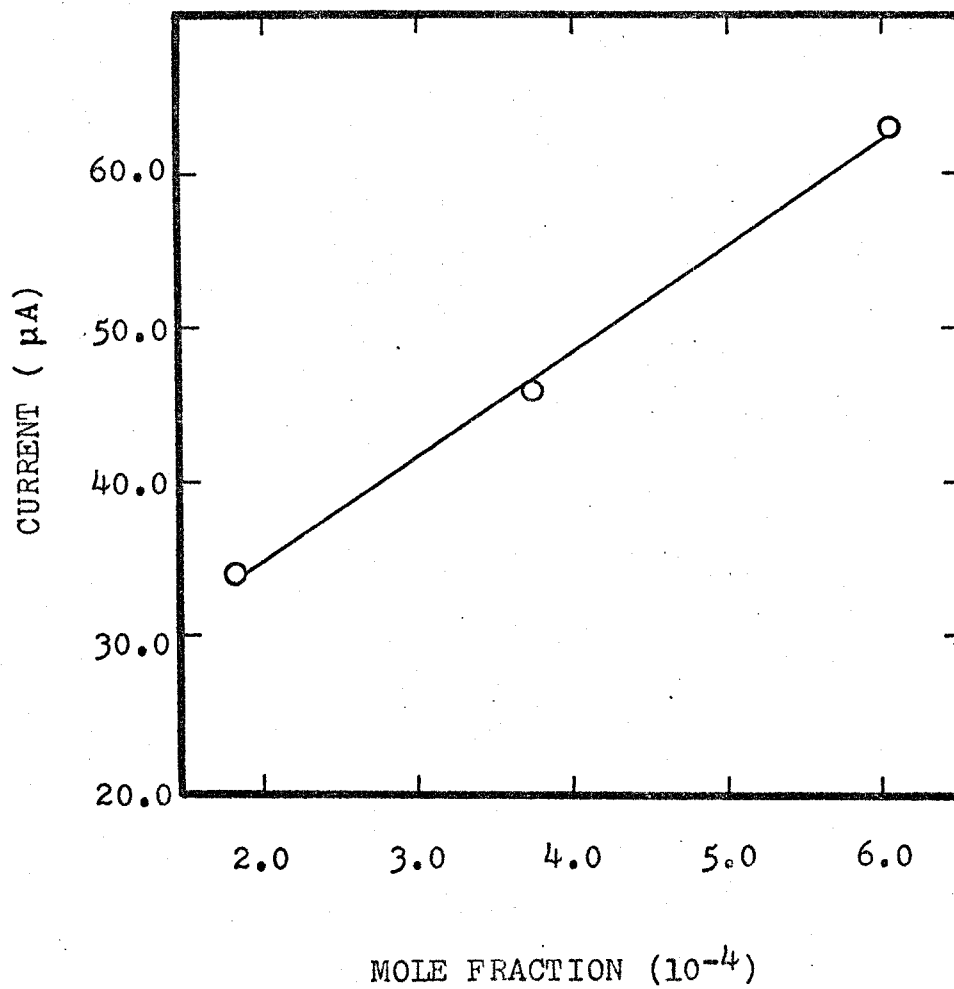
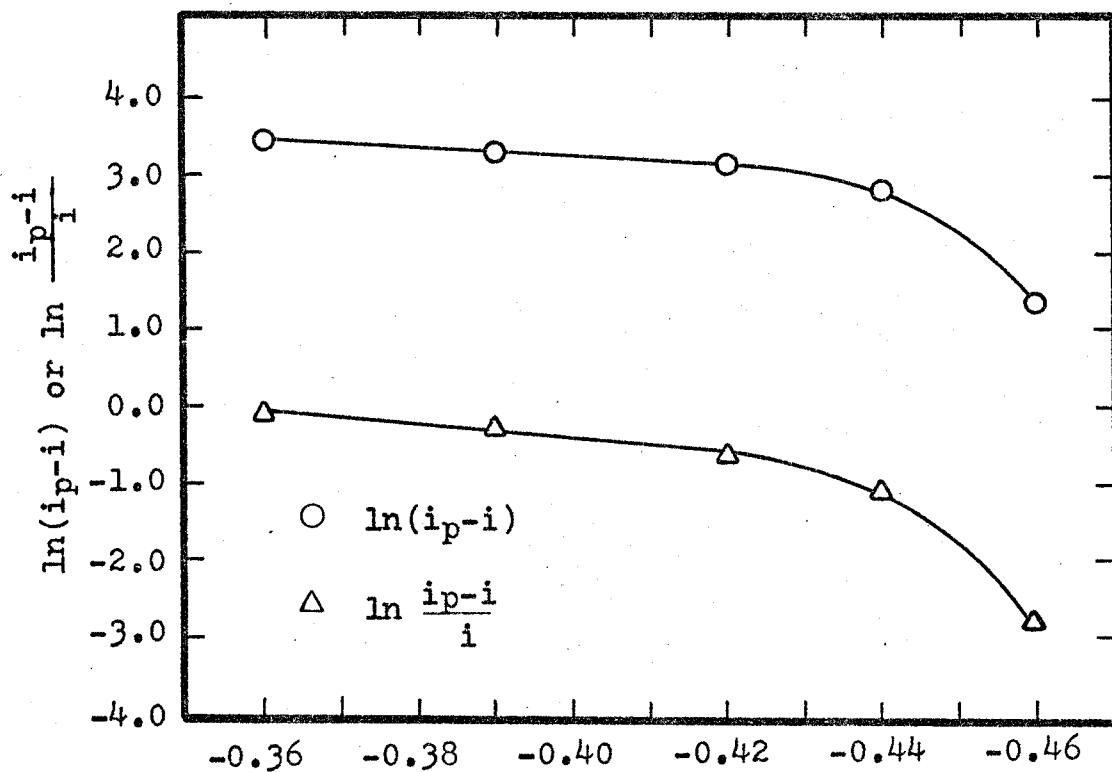


FIGURE II-1. Plot of Current vs. Mole Fraction
CuO in Na₂B₄O₇ melt at 820°C.
N = 2.81 x 10⁻⁴, 3.7 x 10⁻⁴,
6.05 x 10⁻⁴

APPENDIX II

DATA FOR $\text{CuO-Na}_2\text{B}_4\text{O}_7$ SYSTEM



APPLIED POTENTIAL, VOLTS (vs. Pt. ANODE)

FIGURE II-2. Plot of $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Potential
 CuO in $\text{Na}_2\text{B}_4\text{O}_7$ melt at 820°C .
 $N = 2.81 \times 10^{-4}$

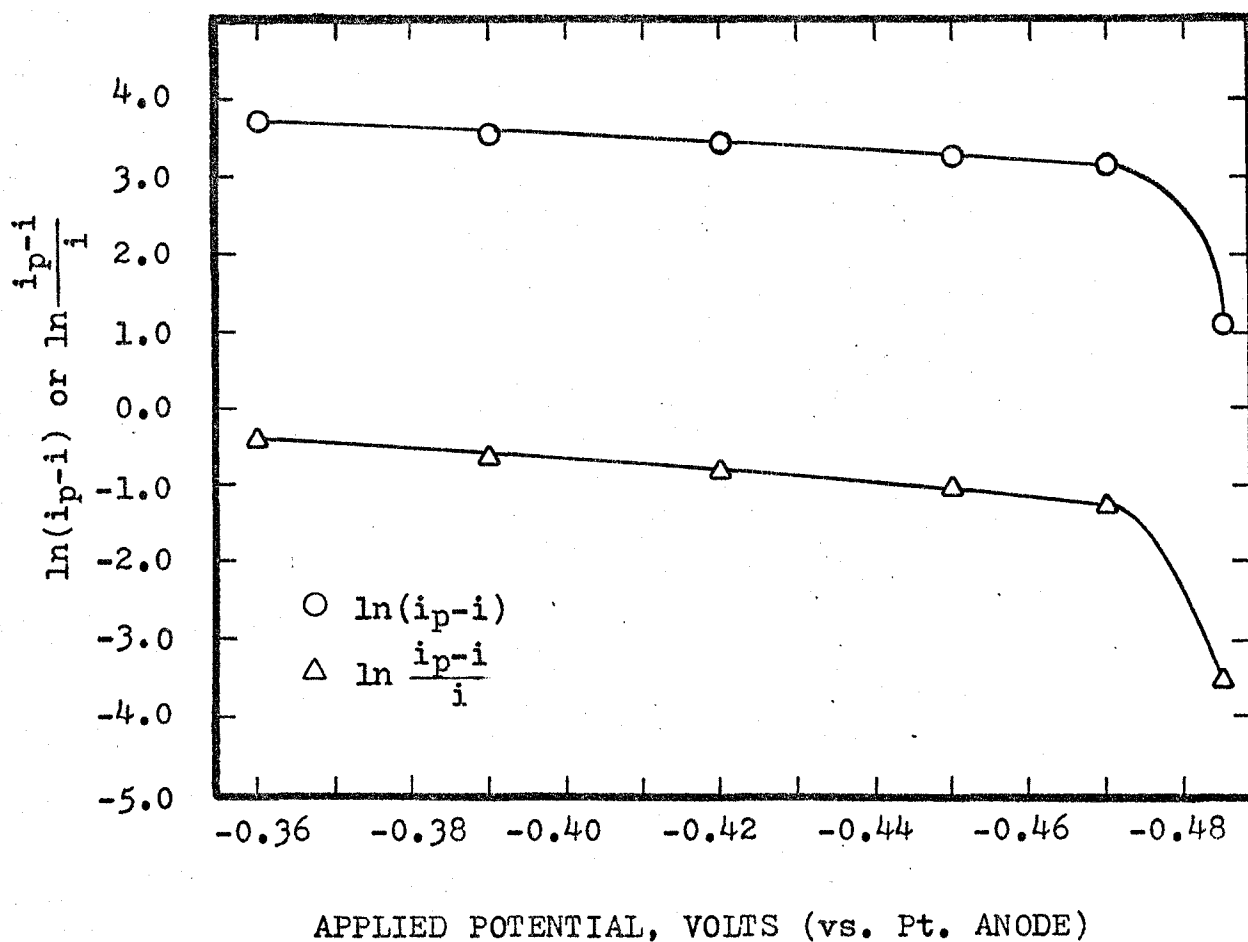


FIGURE II-3. Plot of $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Potential. CuO in $\text{Na}_2\text{B}_4\text{O}_7$ melt at 820°C .
 $N = 3.70 \times 10^{-4}$

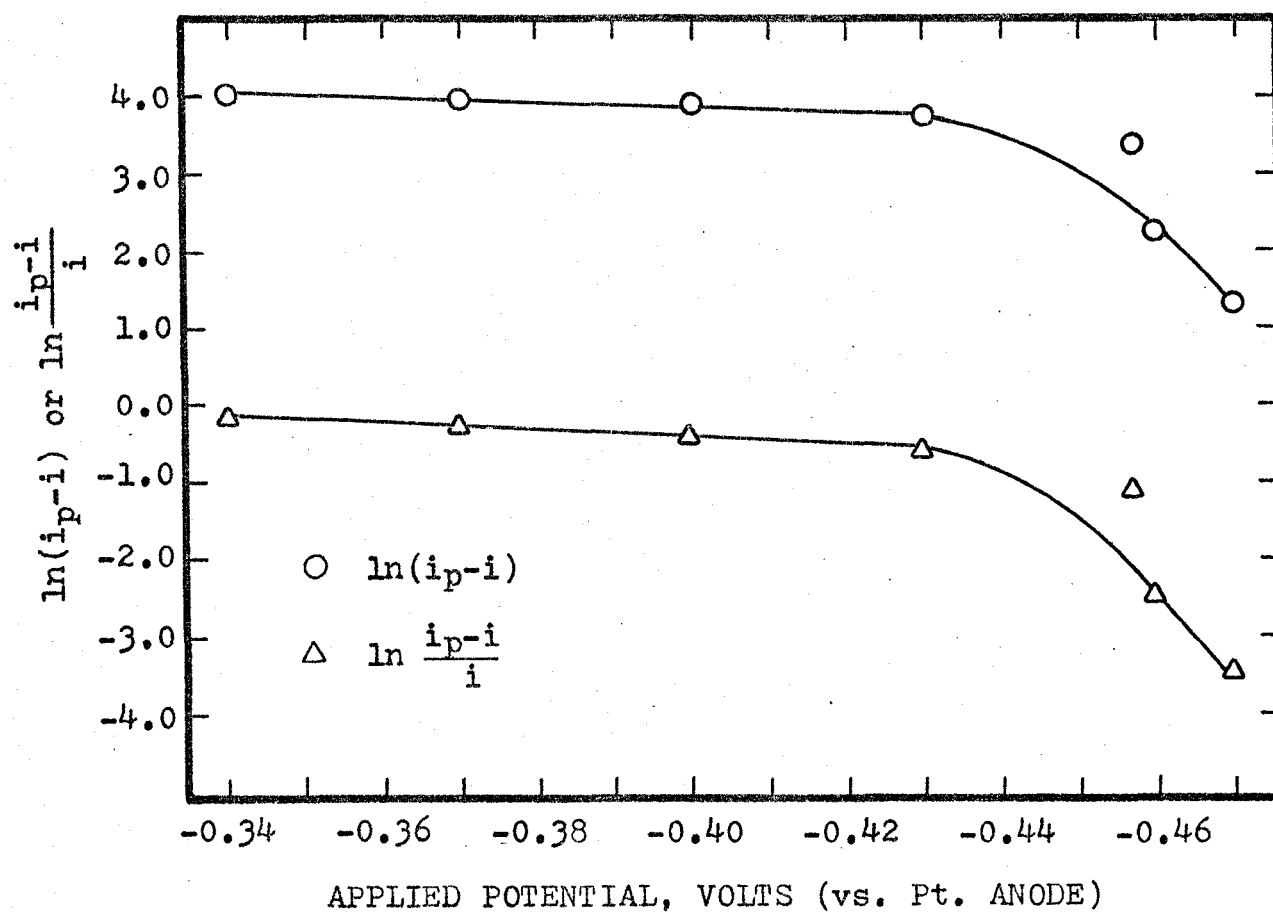


FIGURE II-4. Plot of $\ln(i_p - i)$ or $\ln \frac{i_p - i}{i}$ vs. Applied Potential. CuO in $\text{Na}_2\text{B}_4\text{O}_7$ melt at 820°C
 $N = 6.05 \times 10^{-4}$

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