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THE ANODIC DISSOLUTION OF CADMIUM IN AQUEOUS SOLUTIONS

BY

SAN-CHENG LAI - 1940 -

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THESIS

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ABSTRACT

The purpose of this investigation was to study the effect of cadmium ions on the anodic dissolution of cadmium in salt solutions of constant ionic strength. The concentration of the cadmium ions was varied from 0.001 to 1 N and the current density ranged from 0.001 to 0.1 amp·cm^{-2}. The temperature was controlled at 25°C. The results lead to the following conclusions:

(1) In $Cd(NO_3)_2$-KNO_3 solutions, the apparent valence of cadmium is not appreciably affected by the presence of cadmium ions. An empirical equation was obtained relating the apparent valence to the nitrate and cadmium ion concentrations (gmole/liter) and the current density (ma/cm^2):

$$V_i = 2 - 0.107(C_{NO_3^-})^{0.41}(C_{Cd^{+2}})^{0.005}(i)^{0.383}$$

(2) In $CdCl_2$-KCl, $CdBr_2$-KBr, CdI_2-KI, $CdSO_4$-K_2SO_4, and $Cd(Ac)_2$-KAc solutions, the valence of cadmium was normal.

A mathematical model was postulated expressing the anodic dissolution rate as the sum of electrochemical, local corrosion, and disintegration rates.

A mechanism for the dissolution was proposed as follows:

$$Cd(s) + H_2O(aq) \rightarrow Cd(OH)(s) + H^+(aq) + e \qquad (1)$$

$$Cd(OH)(s) \rightarrow CdO(s) + H^+ + e \qquad (2)$$

$$CdO(s) + 4x^-(aq) + H_2O \rightarrow Cdx_4^{=}(aq) + 2OH^- \qquad (3a)$$

$$CdO(s) + 2H_2O(aq) \rightarrow Cd^{+2}(aq) + 2OH^- \qquad (3b)$$

In solutions with high concentrations of complexing ions, reaction (2) is rate determining. In other solutions, (3b) controls.

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NOTATION

A = Atomic weight of cadmium = 112.40 gm
C = Concentration, gmole/liter
E = Dissolution potential, volts
F = Faraday constant = 96,500 coulombs/gm-equiv.
I = Current, amps
i = Current Density, $\text{amp}\cdot\text{cm}^{-2}$
k, k_1, k_2, k_3, k_4, a, p, q, s = Constants
n = Normal cationic charge of cadmium = 2
R = Gas constant = 8.314 joules/gmole $^{\circ}$K
r = Rate of anodic dissolution, $\text{gm/cm}^2\cdot\text{sec}$
r_D = Rate of anodic dissolution by disintegration, $\text{gm/cm}^2\cdot\text{sec}$
r_E = Rate of electrochemical anodic dissolution, $\text{gm/cm}^2\cdot\text{sec}$
r_L = Rate of anodic dissolution by local corrosion, $\text{gm/cm}^2\cdot\text{sec}$
r_T = Total rate of anodic dissolution (experimental), $\text{gm/cm}^2\cdot\text{sec}$
T = Absolute temperature, $^{\circ}$K
t = Time of run, sec
V_i = Apparent valence
V_n = Normal valence = 2
W_a = Apparent weight of cadmium dissolved, gm
W_e = Experimental weight of cadmium dissolved, gm
η = Overpotential, volts

I. INTRODUCTION

The world's resources of metals are decreasing. Due to this and the cost of replacing corroded materials, it has come to be realized that prevention is better than cure. The increased demand for protective metals as coatings and non-corrosive alloys has stimulated extensive research on the fundamental behavior of metals in corrosive media.

The basic mechanism of the anodic dissolution of metals such as cadmium, zinc, magnesium, beryllium, and aluminum in aqueous salt solutions is still vague. Several investigators have proposed different and opposing theories to explain the discrepancies which arise between coulometric data and the weight loss of metal electrodes in certain salt solutions.

The purpose of this investigation was to study the anodic dissolution of cadmium in neutral salt solutions containing Cd^{+2} ions and to establish a mechanism consistant with the results. To do this, experiments were performed to determine the relationship between the current density, the overpotential, and the faradaic efficiency of the dissolution of cadmium in various solutions.

II. LITERATURE REVIEW

The literature review for this investigation is divided into two parts: (1) anodic dissolution of cadmium in aqueous solutions, and (2) the study of the kinetics and polarization of cadmium during the dissolution in aqueous solutions.

A. Anodic Dissolution of Cadmium in Aqueous Solutions

When metals such as cadmium and zinc dissolve anodically in aqueous salt solution in the absence of oxidizing agents, a normal oxidation state is usually obtained. However, in the presence of oxidizing agents, such as nitrate and perchlorate ions, the amount of coulombs required to dissolve one equivalent weight of metal is sometimes less than that calculated from Faraday's law. This abnormality has been investigated and several mechanisms have been proposed. Among them are: (1) chunk effect, (2) uncommon valence, (3) film control, and (4) disintegration.

As early as 1900, Bredig (1) found that by means of an E.M.F. of 30 to 40 volts and a current of 5 to 10 amperes, an arc could be obtained between cadmium electrodes immersed in pure, air-free water. During this process, the cadmium was dispersed with formation of a deep-brown colloidal solution.

Burton (2) reported that during electrolysis, colloidal solutions from metals such as platinum, gold, silver, bismuth, lead, and iron could be produced. The mechanism of the process was described as involving vaporization of the electrodes and condensation of the metal vapor in the solution. Occasionally large, coarse particles or "chunks" were found in the solution.

In 1933, Del Boca (3) studied electrolysis of certain salts of metals in liquid ammonia and proposed a mechanism for zinc and cadmium undergoing anodic dissolution. He suggested that a portion of the anode is dissolved as atoms in the form of $Cd \cdot Cd^{+2}$ or $Zn \cdot Zn^{+2}$.

More recently, Marsh and Schaschl (4) proposed that when steel was dissolved anodically at high rates, the corrosion proceeded by removal of "chunks of iron" containing several atoms. This expulsion of metallic particles would account for more iron dissolving than that predicted by Faraday's law. This mechanism was termed the "chunk effect".

Later, Straumanis and Mathis (5) confirmed a similiar effect termed "disintegration" using optical methods with high magnification. Working with beryllium metal, the authors observed a large number of deformation twins in the metallic residue collected during anodic dissolution. Deformation twins arise in the casting of a metal as a consequence of stresses from temperature gradients and do not occur in nucleation. Therefore, their studies provided conclusive proof that the origin of the particles was the electrode.

Straumanis and Bhatia (6) showed that Mg disintegrated partially into small metallic particles under certain conditions of dissolution or corrosion. The dark color of the flakes separating from the anode was caused by the presence of minute Mg particles held in a matrix of $Mg(OH)_2$ as confirmed under high magnification employing both reflected and transmitted light.

A phenomenon which can sometimes be related to the apparent valence of metals undergoing anodic dissolution is called the "difference effect". Straumanis (9,10) explained the positive difference effect in terms of anodic polarization. According to his view, this effect is pronounced if there is interference with the delivery of electrons to the local cathode, or if there is interference with dissipation of ions into the corrosive media. Thus, with increasing anodic current, whether originating in local cells or externally applied, there is increasing anodic polarization which decreases the driving force for local action and gives rise to the observed positive effect.

Kroenig and Uspensakaja (11) found a negative difference effect for some metal-corrodent combinations. They explained this as the result of disruption of a surface film. According to their theory, application of current to a specimen gradually breaks down its shielding film, exposing more metal to attack by the corrodent, and thus increases local action. In some cases, these investigators observed flaking of films in systems in which the negative difference effect was found.

Straumanis and Wang (10) also suggested that the negative difference effect which sometimes changes to positive at low current densities can be explained by the assumption that every difference effect appears as the result of an overlapping of both positive and negative effects.

A report of positive and negative difference effects occuring in the same metal-acid system (Mg-acid) was made by James, et al. (7). They suggested that for magnesium dissolving in acids, the difference effect resulted from: (a) the change in electrochemical conditions at the interface (polarization of local elements) while an anodic current is flowing, (b) the ease with which a protective surface film is formed or disrupted, and (c) the rate at which metallic particles separate from the anode surface. The deviation from linearity of the plots of difference effect versus current was attributed to the increased effect of anodic disintegration.

March and Schaschl (4) suggested that the chunk effect and anodic polarization occur on the same piece of corroding metal. Thus, either the positive or negative difference effect may be observed, depending on the corrodent.

The second mechanism to explain deviations from Faraday's law which has received much support is the concept of the "uncommon valence" ion. Davidson, et al., (12-15) reasoned that the metal enters solution as the univalent ion. They evaluated the initial valence number of magnesium ions going into solution in various electrolytes. The valence numbers were found to lie between one and two. These values were dependent on temperature and to a slight extent on concentration. The lower values were obtained at higher concentrations and temperatures. The results were explained using the hypothesis that the primary reaction at the metal anode consisted of a stepwise oxidation, the first step being the oxidation of the metal to the unipositive ion:

$$M \longrightarrow M^{+} + e \quad \text{(at the electrode)} \qquad (1)$$

The unipositive ion would be expected to be very reactive and would readily form the normal bipositive ion. There are two ways in which this second step could occur: (1) further electrolytic oxidation at the anode, and (2) chemical oxidation by an oxidizing agent in the electrolyte, i.e.,

$$M^{+} \longrightarrow M^{+2} + e \quad \text{(at the electrode)} \qquad (2)$$

$$M^{+} + \text{oxidant} \longrightarrow M^{+2} + \text{reductant} \quad \text{(in the electrolyte)} \qquad (3)$$

With non-reducible electrolytes, reaction (3) could not occur and consequently an initial valence number of two is observed. With reducible electrolytes, however, the two steps would be competitive and the one which predominates depends on the nature of the oxidizing electrolyte and the conditions of the experiment. The initial mean valence might then range from 1 to 2, depending on the relative extents of the reactions (2) and (3). The fact that the apparent valence, especially of cadmium, tends to decrease with increasing concentration of the oxidant is expected, since reaction (3) should occur more rapidly as the concentration of oxidant is increased.

Another mechanism suggested by Greenblatt (16) for the anodic dissolution of magnesium was that as ions leave the metal lattice, a finite time is required for them to diffuse through the oxide film, thus creating an excess of positive ions. The film containing excess positive ions must also have an equal number of anion vacancies. To obtain electrical neutrality, electrons flow across the film, filling the anion vacancies and do not pass through the external circuit. Thus, the amount of current measured through the external circuit is deficient due to this flow of electrons. This results in a greater amount of metal being dissolved than the number of coulombs passing through the external circuit would indicate.

In 1958, Lake and Casey (17) studied the anodic oxidation of cadmium in KOH, K_2CO_3, and mixed electrolytes. A general mechanism at the anode was hypothesized in which the primary reaction was the formation of cadmium monoxide. The monoxide is converted to either the hydroxide or carbonate (depending on the electrolyte) through a soluble intermediate. The rate of conversion is governed by the solubility of the monoxide and the rate of transport of the dissolving species. Cadmium monoxide is also the passivating species when the resistance of the film becomes high enough to raise the potential of the CdO surface above the oxygen evolution potential.

A film-control mechamism has been supported by Hoey and Cohen (18). Using X-ray diffraction analysis, they identified a film of $Mg(OH)_2$ which formed on the surface of the Mg anode during electrolysis. They further observed, using a microscope, a dispersion of very small magnesium particles in the film. Accordingly, they proposed the corrosion rate as film controlled, that is, with the passage of an anodic current, the hydroxide film was partially spalled off the surface carrying the metallic particles with it. The small particles would be oxidized by either water or by the oxidizing electrolyte:

$$Mg \cdot Mg(OH)_2 + 2H_2O \longrightarrow 2Mg(OH)_2 + H_2 \tag{4}$$

$$Mg \cdot Mg(OH)_2 + \text{oxidant} \longrightarrow Mg(OH)_2 + Mg^{+2} + \text{reductant} \tag{5}$$

In 1963, Stoner (19) reported that during electrolysis in potassium nitrate, a grey film was formed on the surface of a zinc electrode. This film was not present in either potassium chloride or potassium chlorate solutions. The interesting fact was that this film was present only when it was also found that the apparent valence was less than two. A similar phenomenon was observed with cadmium in nitrate solutions (20). It was suspected that these films on the metal anodes were in some manner responsible for the abnormal behavior during dissolution. Hoar (21) suggested that the mechanism of anodic dissolution be studied by the use of an amalgamated electrode to possibly prevent formation of films such as are observed on the pure zinc and cadmium electrodes. As the diffusion of cadmium ions of any valence would not be prevented by the amalgamation, one would expect the behavior of cadmium amalgam to correspond to that of cadmium in the same electrolyte as regards the initial mean valence. No valences less than normal were found using amalgamated surfaces.

A mechanism by Sun (20) suggested that the reaction of cadmium in nitrate solutions is film controlled. The film which is continuously expelled from the electrode surface contains many metallic particles originating from disintegration of the anode. These particles, possibly due to their tiny size, are very reactive and are oxidized immediately by nitrate ion or by water to form insoluble $Cd(OH)_2$.

$$Cd + NO_3^- + H_2O \longrightarrow Cd(OH)_2 + NO_2^- \qquad (6)$$

$$Cd + 2H_2O \longrightarrow Cd(OH)_2 + H_2 \qquad (7)$$

B. <u>The Study of the Kinetics and Polarization of Cadmium during the Dissolution in Aqueous Solutions</u>

Polarization measurements are important research tools in investigations of a variety of electrochemical phenomena. Such measurements permit studies of the reaction mechanism of corrosion processes and metal deposition.

Kolotyrkin (22) studied the effect of anions such as Cl^-, Br^-, and I^- ions, on the dissolution kinetics of metals. He pointed out that the dissolution in electrolytic solutions is an electrochemical process. Thus the rate depends not only on the usual variables of chemical kinetics, concentration and temperature, but also on electrochemical parameters of the system. First and foremost among these are the electrode potential and the structure of the double layer at the metal-solution interface. In acidic solutions, Cl^-, Br^-, and I^- ions increased the true anodic dissolution rates of cadmium and of indium amalgams. This was accounted for by the direct participation of these ions in the elementary process of ionizing the metal atoms. The chemisorptive interaction of halide ions with surface atoms of a metal takes place at potential much more negative than the dissolution potential of the metal. The extent of "filling" the surface with the adsorbed anions increases considerably with shifts of potential to more positive values. The dissolution of metals occurs with the direct participation of halide ions and, consequently, the kinetics of these reactions at a constant pH may be expressed as follows:

$$r = k\ c^{a} \exp\ (FE/RT)$$

Uhlig (23) explained that chloride ions, and to a lesser extent other halide ions, break down passivity or prevent it on Fe, Cr, and the stainless steels. From the point of view of the oxide film theory, chloride ions penetrate the protective oxide film through pores or defects easier than do other ions such as $SO_4^{=}$. This may colloidally disperse the oxide film and increase its permeability. On the other hand, according to the adsorption theory, chloride ions favor hydration of metal ions and increase the ease with which metal ions enter into solution. This is just opposite to the effect of adsorbed oxygen which decreases the rate of metal dissolution. In other words, adsorbed chloride ions increase the exchange current (decrease overvoltage) for anodic dissolution of the above metals over the value prevailing when oxygen covers the surface. Breakdown of passivity by chloride ion occurs locally rather than generally over the passive surface. The preferred sites are determined perhaps by small variations in the passive film structure and thickness.

Halogen ions have less effect on the anodic behavior of titanium, tantalum, tungsten, and zirconium. Their passivity may continue in media of high chloride concentration in contrast to Fe, Cr, and Fe-Cr alloys which lose passivity. This is sometimes explained by formation of insoluble protective Ti-, Ta-, Zr-, etc., basic chloride films.

Evans (24) considered that in a very dilute solution, the potential gradient at an electrode will cause the water molecules near the anode surface to orient themselves with the oxygen portion nearest the metal, providing an easy mechanism for film formation. Cations from the metal, instead of passing out into the liquid, take up places between the oxygen ions, and in their stead hydrogen ions from the water molecules move out into the liquid. If, however, the liquid contains an appreciable concentration of anions carrying a negative charge, the same potential gradient will cause them to displace the water molecules which carry no net charge, from the metal surface. Chloride ions, thus, will displace water molecules and break up the water phalanx without providing any new mechanism for passivation. Hence, their presence is unfavorable to passivity.

Krochmal, et al., (25) reported that the potential of the zinc anode before electrolysis depended on the kind of cations involved, the effect decreased in the order Zn→Mg →Na→NH_4. Recently Yoshino (26) measured the anodic potential of a zinc electrode in water at 80°C. He reported that the anions HCO_3^-, NO_3^-, and PO_4^{-3} increased the potential, whereas Cl^- and SO_4^{-2} decreased the potential. The degree of increase of anodic potential at higher temperatures was similiar to that at room temperature.

Stern and Geary (27) have stated that deviations from Tafel behavior may be caused by local action, concentration polarization, IR effects, or changes in the predominant electrode reaction.

III. EXPERIMENTAL

The purpose of this investigation was to study the anodic dissolution of cadmium in constant ionic strength (1.5) solution containing cadmium ions and to obtain electrochemical information in order to propose a mechanism of dissolution. The solutions were of $CdCl_2$ with KCl, $CdBr_2$ with KBr, CdI_2 with KI, $CdSO_4$ with K_2SO_4, $Cd(Ac)_2$ with KAc, and $Cd(NO_3)_2$ with KNO_3.

The experimental plan consisted of the following major phases: (1) the effect of various electrolytes and current densities on the apparent valence of cadmium undergoing anodic dissolution, and (2) the effect of concentration of cadmium ions and current densities on the dissolution potential of cadmium. Studies were made at 25°C.

A. Materials

The list of materials is given in Appendix A.

B. Equipment

The list of equipment is presented in Appendix B.

C. The Apparent Valence of Cadmium Undergoing Anodic Dissolution in Various Electrolytes at 25°C

1. Apparatus. The apparatus consisted of an electrolytic cell with separated compartments of 400 milliliter capacity, a cadmium anode, a platinized-platinum cathode, a milliammeter, a constant current power supply, a decade power resistor, and a knife-blade switch, all connected in series. A diagram of the apparatus is shown in Figure 1. A timer with one-second divisions was used for

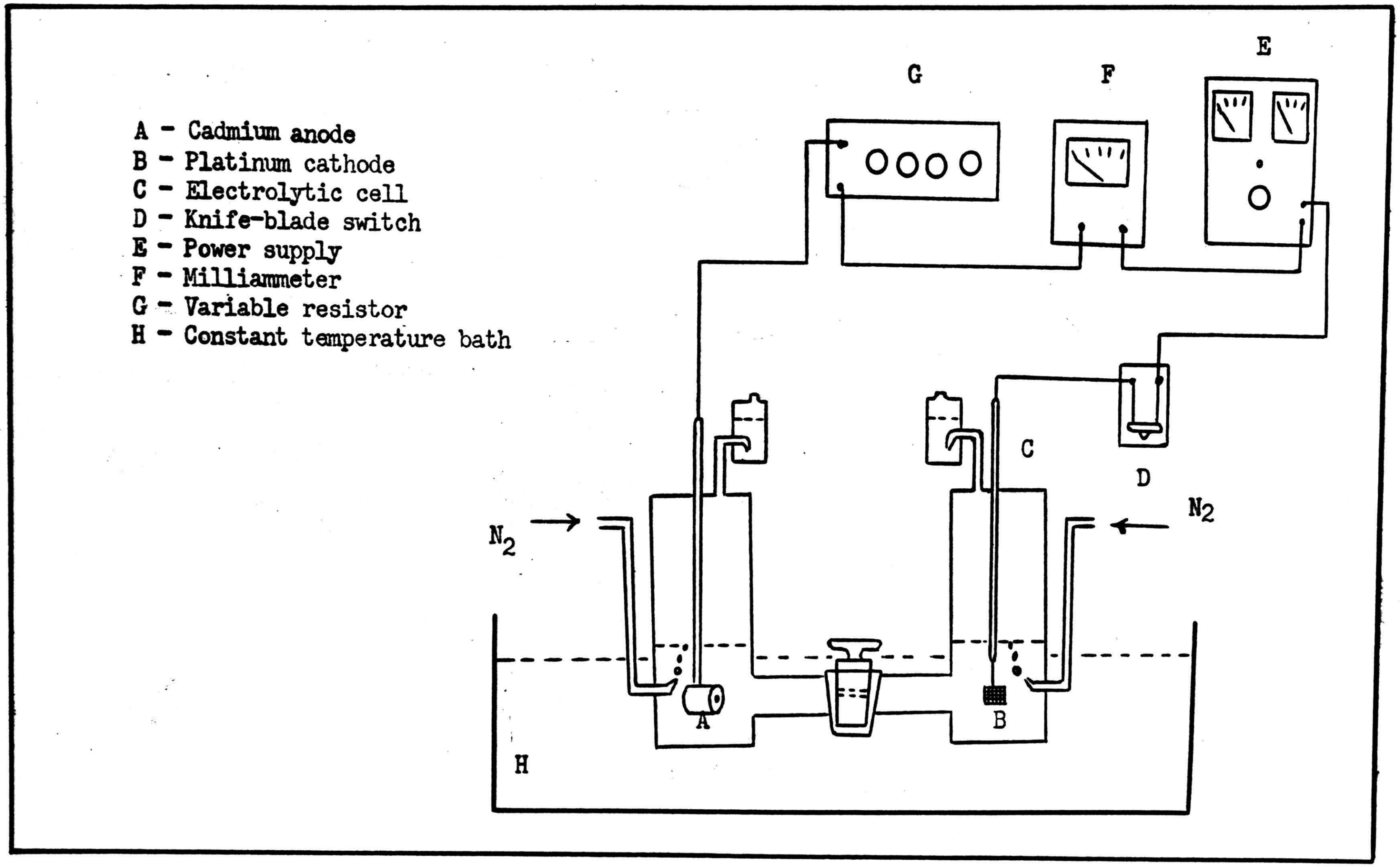


Figure 1. Apparatus used for measurement of the apparent valence of cadmium undergoing anodic dissolution.

measuring the elapsed time. The cell was immersed in a water bath controlled at 25±0.1°C.

2. Procedure. A specimen was cut from a bar of cadmium metal of 99.999 percent purity. It was turned on a lathe to smooth the surface and the diameter determined with a micrometer. The specimen was then mounted in teflon by press fitting and the electrode prepared as previously described (29). It was polished immediately before each run according to the procedure listed in Appendix C. Approximately 250 milliliters of electrolyte were transfered to the electrolysis cell. The cell was placed into the constant temperature water bath in such a position as to insure complete submergence of the electrolyte. The electrolyte was allowed to remain in the water bath for about an hour to bring the system to constant temperature before starting a run. The mounted metal anode was dried with a hot-air blower to constant weight. It and the platinized-platinum cathode were then immersed into the anodic and cathodic compartments respectively, and were connected into the external circuit (see Figure 1). Nitrogen was bubbled through both the anodic and cathodic compartments. To begin a run, the knife-blade switch was closed and the current was adjusted to a desired value with the variable resistor. The timer and milliammeter were used for measuring the number of coulombs passed. At the end of a test run, the cadmium electrode was taken out, dried, and reweighed. Thus, the weight of cadmium dissolved was determined. A grey film was formed on the cadmium

electrode during electrolysis in nitrate solutions. Its treatment is described in Appendix C. The same procedure was employed for all electrolysis experiments.

3. Data and Results. The data from this part of the experimentation are given in Appendix D. A brief summary of the results for each follows separately.

a. Cadmium halide-potassium halide. The anodic dissolution of cadmium was observed in solutions of constant ionic strength containing $CdCl_2$-KCl, $CdBr_2$-KBr, and CdI_2-KI. The Cd^{+2} concentration varied from 0.001 to 1 N in each system. The current densities varied from 0.001 to 0.1 $amp \cdot cm^{-2}$. The data are shown in Tables III to XVIII, Appendix D. The valence at all current densities was approximately two, the normal valence. During the electrolysis, a dark film was formed on the cadmium electrode. It disappeared when the electrode was placed in water. The metal surface beneath the film was pitted.

b. Cadmium sulfate-potassium sulfate. The anodic dissolution of cadmium in $CdSO_4$-K_2SO_4 was carried out at current densities ranging from 0.001 to 0.1 $amp \cdot cm^{-2}$. The concentration of cadmium ions was varied from 0.001 to 1 N. Data from these runs are shown in Tables XVIII to XXI, Appendix D. The current density had no influence on the valence. The normal valence was again found. A black film formed on the cadmium electrode surface as the electrolysis proceeded.

c. Cadmium acetate-potassium acetate. The anodic dissolution of cadmium in $Cd(Ac)_2$-KAc was carried out at current densities varying from 0.001 to 0.1 $amp \cdot cm^{-2}$. The Cd^{+2} concentration varied from 0.001 to 1 N. The valence of cadmium was normal. A black film formed on the cadmium electrode surface during the electrolysis. The data are shown in Tables XXII to XXVI, Appendix D.

d. Cadmium nitrate-potassium nitrate. The anodic dissolution of cadmium in $Cd(NO_3)_2$-KNO_3 mixtures was observed at current densities varying from 0.001 to 0.1 $amp \cdot cm^{-2}$. The data are shown in Tables XXVII to XXXI, Appendix D, and presented graphically in Figure 2. It can be seen that the apparent valence decreased with increasing current density with considerable deviations from the normal value. During the electrolysis, a grey film formed on the surface of the cadmium electrode which gradually turned white. At higher current densities, the deposit was continually spalled off the surface in small portions. X-ray analyses have reported this white deposit to be $Cd(OH)_2$ (20).

4. Sample Calculations. The same method was used to calculate the apparent valence in all the above solutions. The data from the experiment in 0.001 N $CdCl_2$-1.499 N KCl solution (Table III) have been used to illustrate these calculations.

a. Calculation of the apparent weight of cadmium dissolved from coulombic data. The apparent weight of cadmium dissolved according to Faraday's law, assuming a normal valence of two, was calculated as follows:

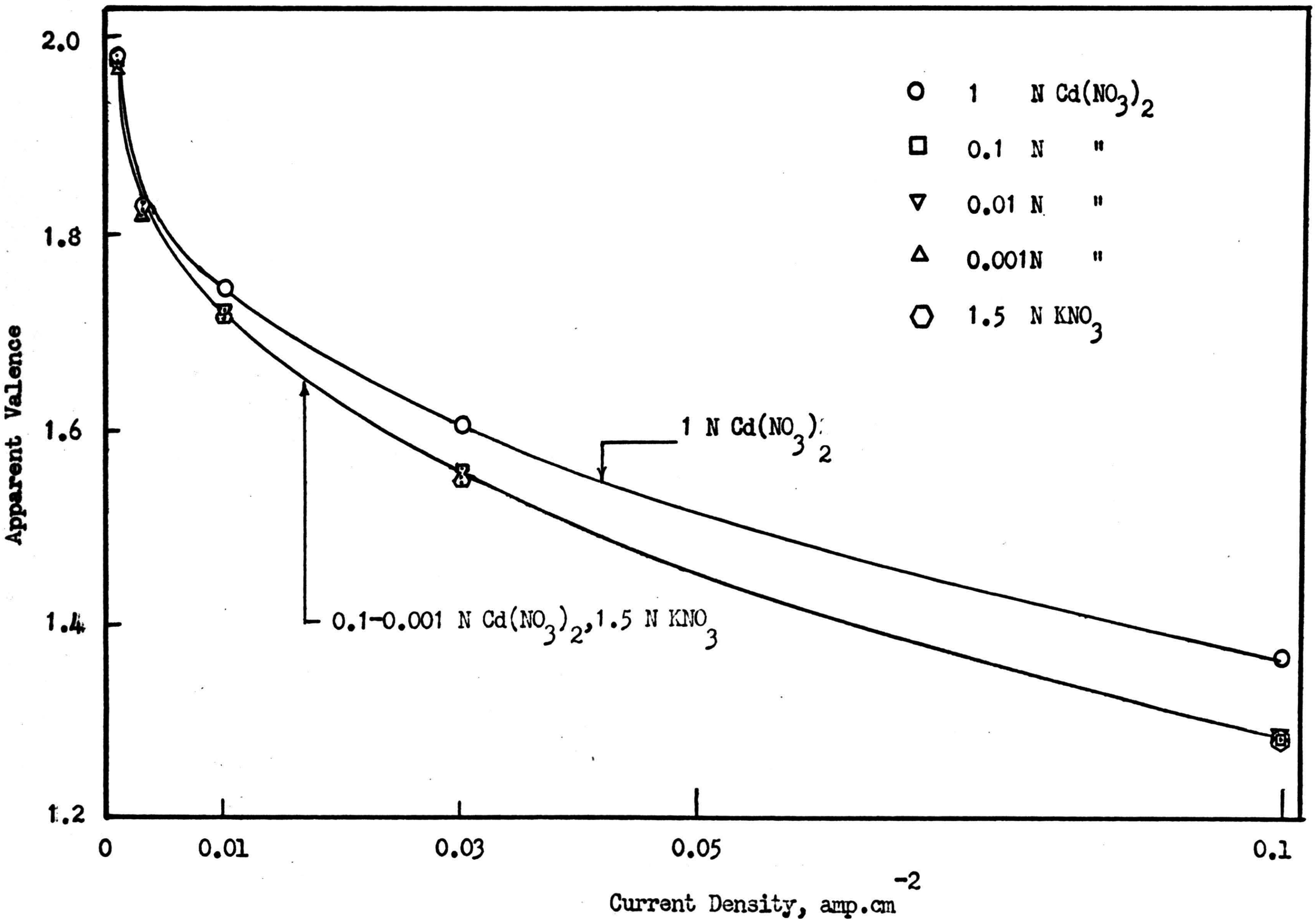


Figure 2. The apparent valence of cadmium undergoing anodic dissolution in $Cd(NO_3)_2$-KNO_3 solutions (ionic strength=1.5) at 25°C.

$$W_a = \frac{ItA}{nF} \tag{8}$$

$$= \frac{(0.0062)(9,000)(112.40)}{(2)(96,500)}$$

$$= 0.0325 \text{ gm}$$

b. Calculation of the apparent valence. The apparent valence was calculated by the equation.

$$V_i = \frac{(W_a)(V_n)}{(W_e)} \tag{9}$$

$$= \frac{(0.0325)(2)}{(0.0327)} = 1.99$$

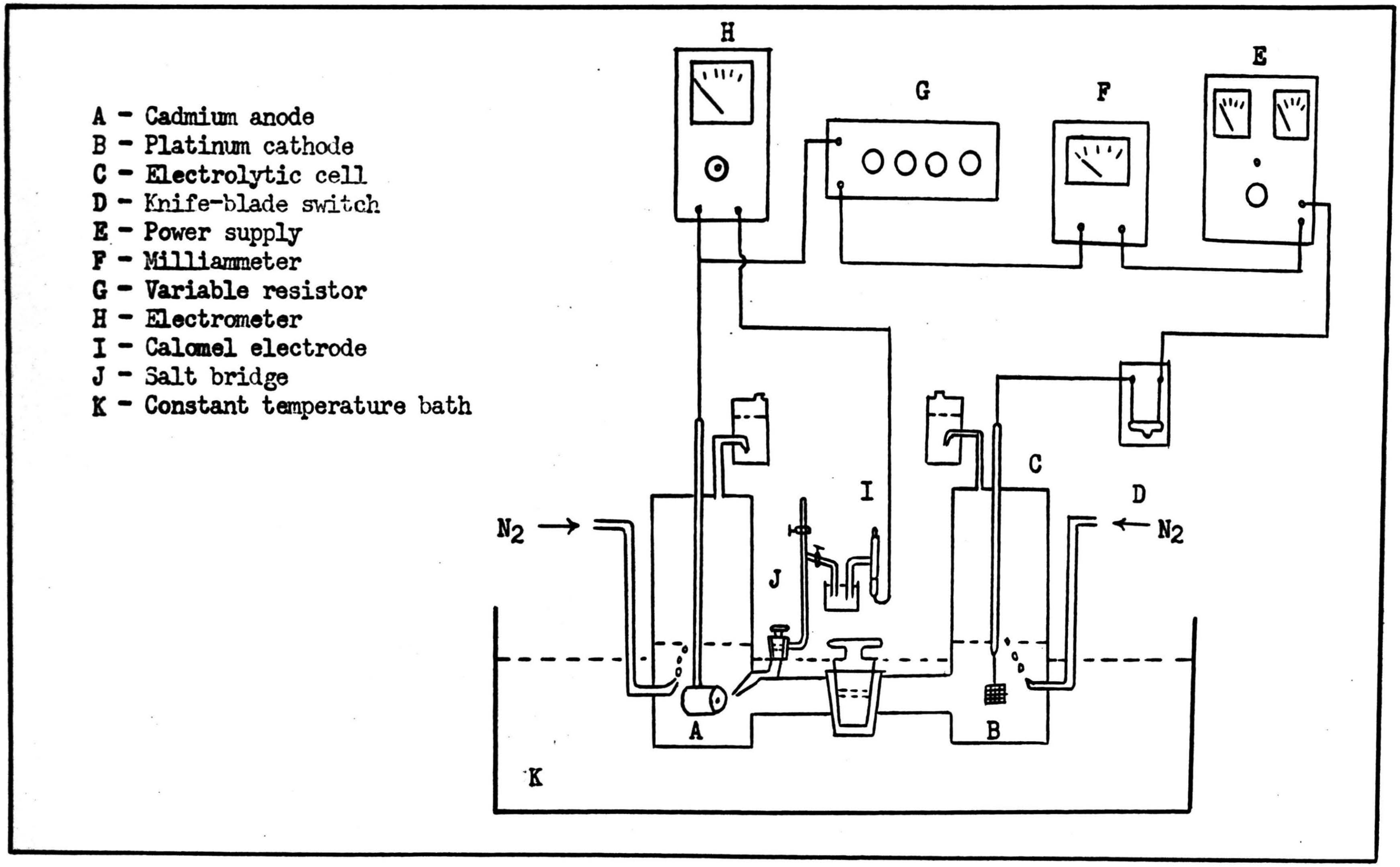
D. The Polarization Study of Cadmium Undergoing Anodic Dissolution in Various Electrolytes at 25°C

1. Apparatus. The apparatus was the same as described previously except a 1 N calomel reference electrode was connected to the cadmium anode through a salt bridge. A high impedance electrometer was used to measure the dissolution potential. A diagram of the apparatus is shown in Figure 3.

2. Procedure. The procedure was similiar to that described previously. Initially in the absence of applied current, the potential of the cadmium anode was measured at intervals of 15 minutes until it reached a constant value. Similiar measurements were then made at different constant current densities.

3. Data and Results. The data from these measurements are presented in Appendix D. All the potentials are referred to the normal hydrogen scale. A brief summary of the results for each follows.

a. Cadmium halide-potassium halide. Dissolution



A - Cadmium anode
B - Platinum cathode
C - Electrolytic cell
D - Knife-blade switch
E - Power supply
F - Milliammeter
G - Variable resistor
H - Electrometer
I - Calomel electrode
J - Salt bridge
K - Constant temperature bath

Figure 3. Apparatus used for measurement of the dissolution potential of cadmium.

potentials were obtained at current densities ranging from zero to 0.1 amp•cm^{-2} in the same solutions as the apparent valences. The data are shown in Tables XXXII to XLIII. Appendix D. Plots of overpotential as a function of current density are also shown in Figures 4 to 6. The overpotential has been taken as the difference between the steady potential at a constant current density and the steady potential at zero current density. As some anions used in this study complexed with cadmium, it was not possible to calculate reversible potentials for overpotential calculations. For these solutions, the dissolution potential was very stable with time.

b. Cadmium sulfate-potassium sulfate. The potentials of the cadmium electrode undergoing anodic dissolution in sulfate solutions are shown in Tables XLIV to XLVI. The current densities ranged from zero to 0.1 amp•cm^{-2}. Plots of overpotential versus current density are shown in Figure 7.

c. Cadmium acetate-potassium acetate. The potentials of the cadmium electrode in acetate solutions are shown in Tables XLVII to L. Figure 8 shows graphically the relationship between the overpotential and current density. The range of current densities was from zero to 0.1 amp•cm^{-2}.

d. Cadmium nitrate-potassium nitrate. The potentials of the cadmium electrode were relatively unstable in these solutions. At higher current densities, the potential fluctuated widely. This was probably due to the grey film which formed on the surface of the anode and continuously spalled off. The data are shown in Tables LI to LIV. Overpotentials as a function of current density are shown in Figure 9.

4. Sample Calculations. The method for calculating the overpotentials is illustrated below. Data from Table XXXII have been used for the illustration.

$$\eta = E_i - E_{i=0} \tag{10}$$

$$\eta = -0.550 - (-0.599) = 0.049 \text{ volts}$$

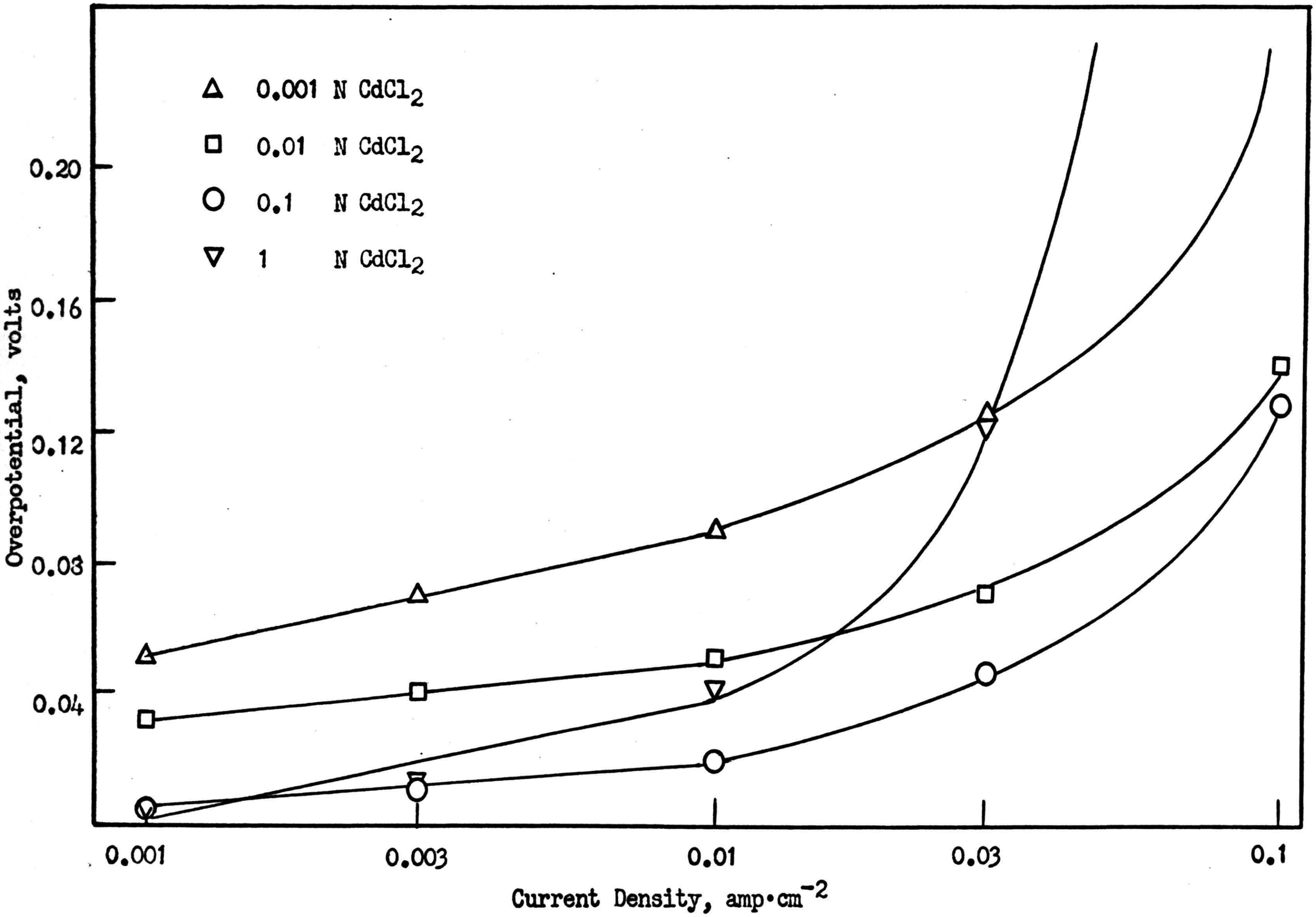


Figure 4. Tafel curves for the anodic dissolution of cadmium $CdCl_2$-KCl solutions (ionic strength=1.5) at 25°C.

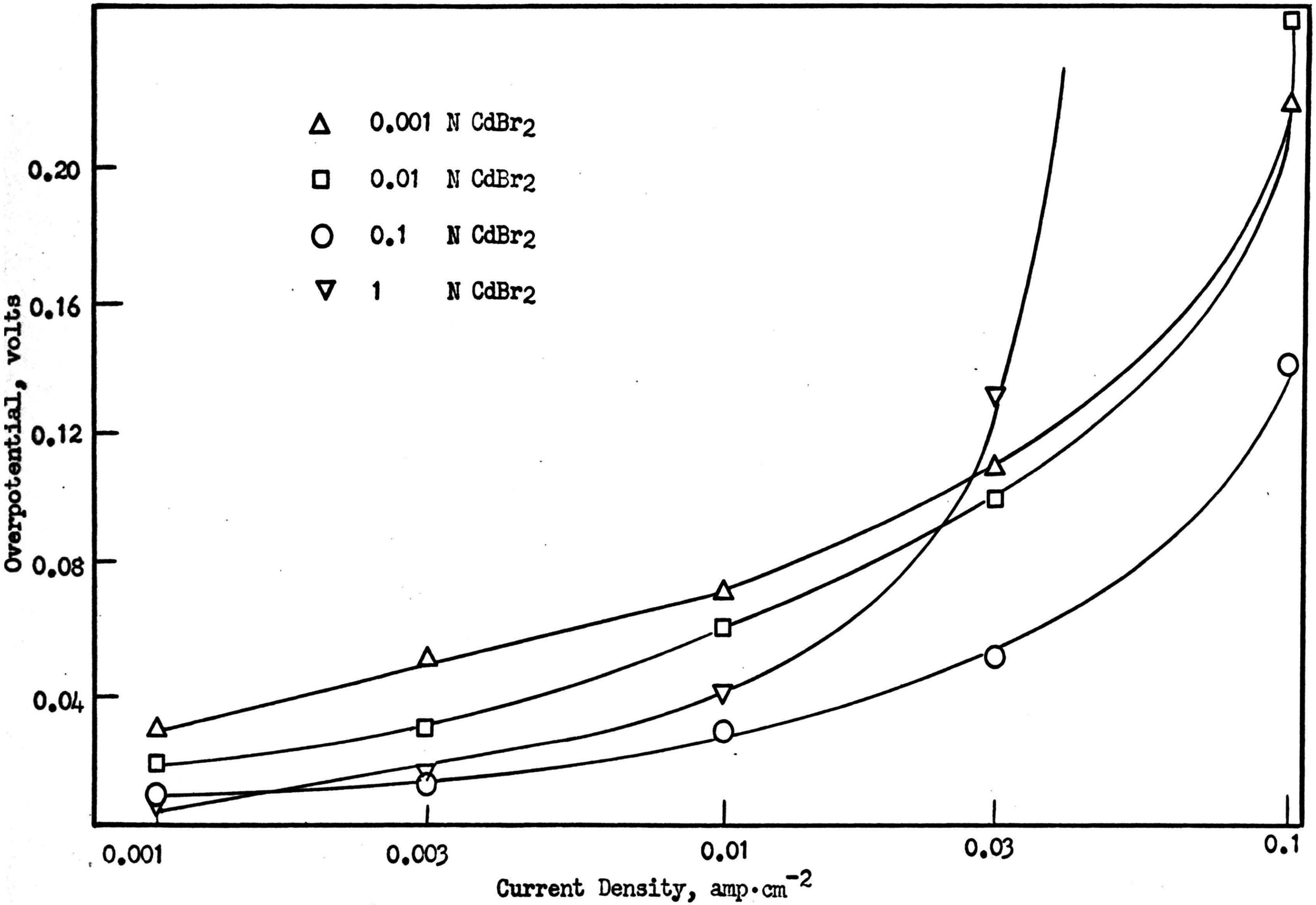


Figure 5. Tafel curves for the anodic dissolution of cadmium $CdBr_2$-KBr solutions (ionic strength=1.5) at 25°C.

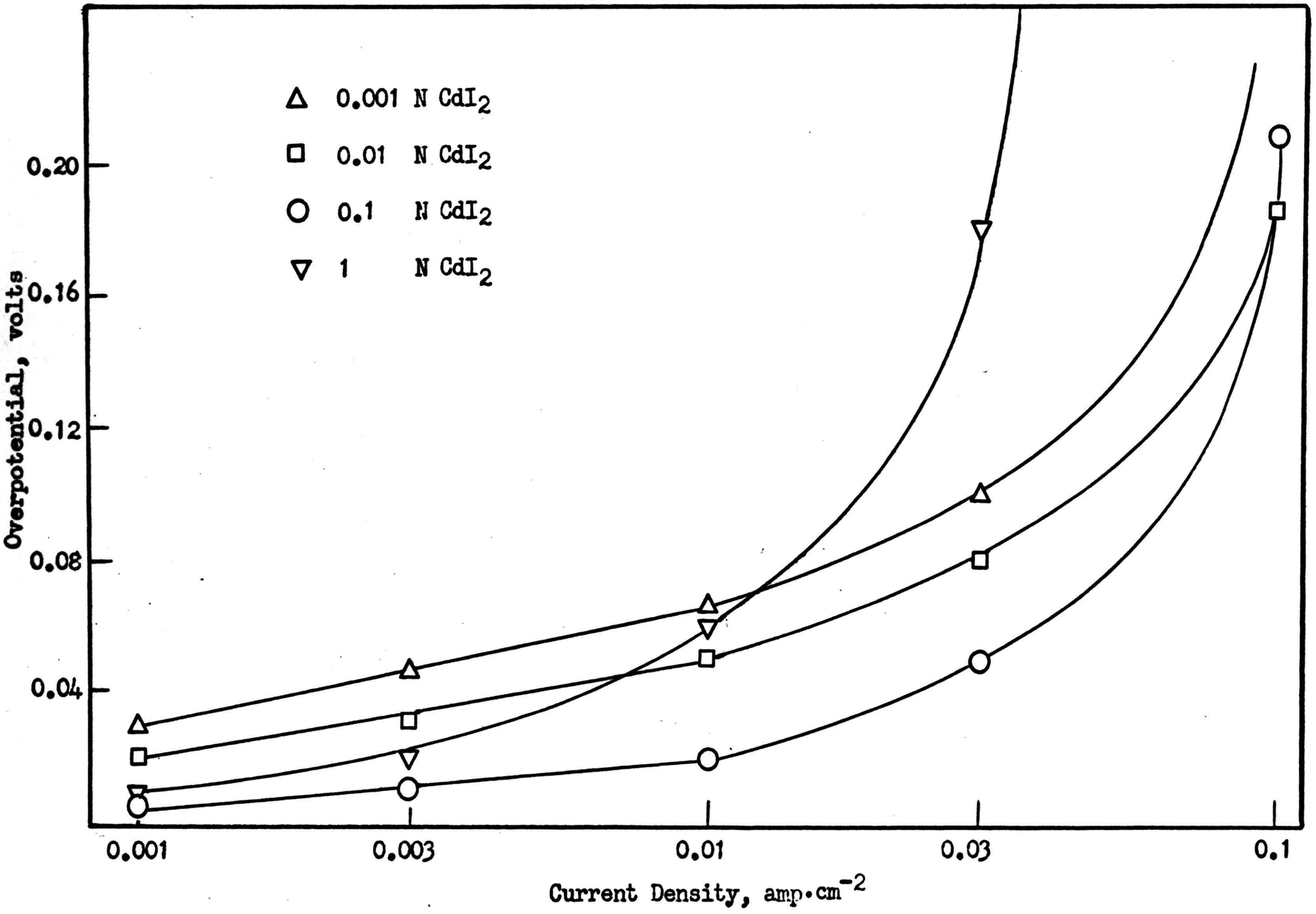


Figure 6. Tafel curves for the anodic dissolution of cadmium in CdI_2-KI solutions (ionic strength=1.5) at 25°C.

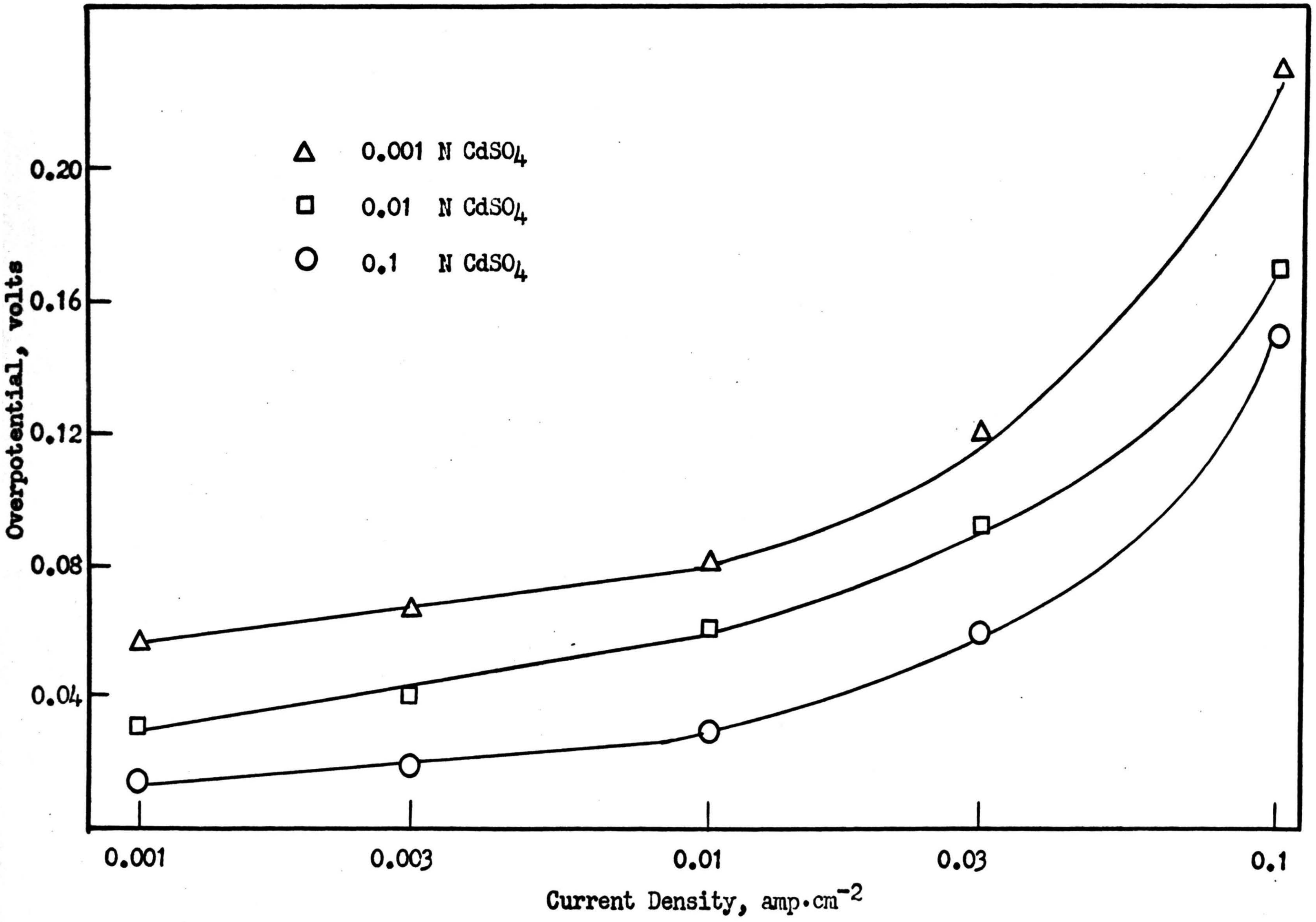


Figure 7. Tafel curves for the anodic dissolution of cadmium in $CdSO_4$-K_2SO_4 solutions (ionic strength=1.5) at 25°C.

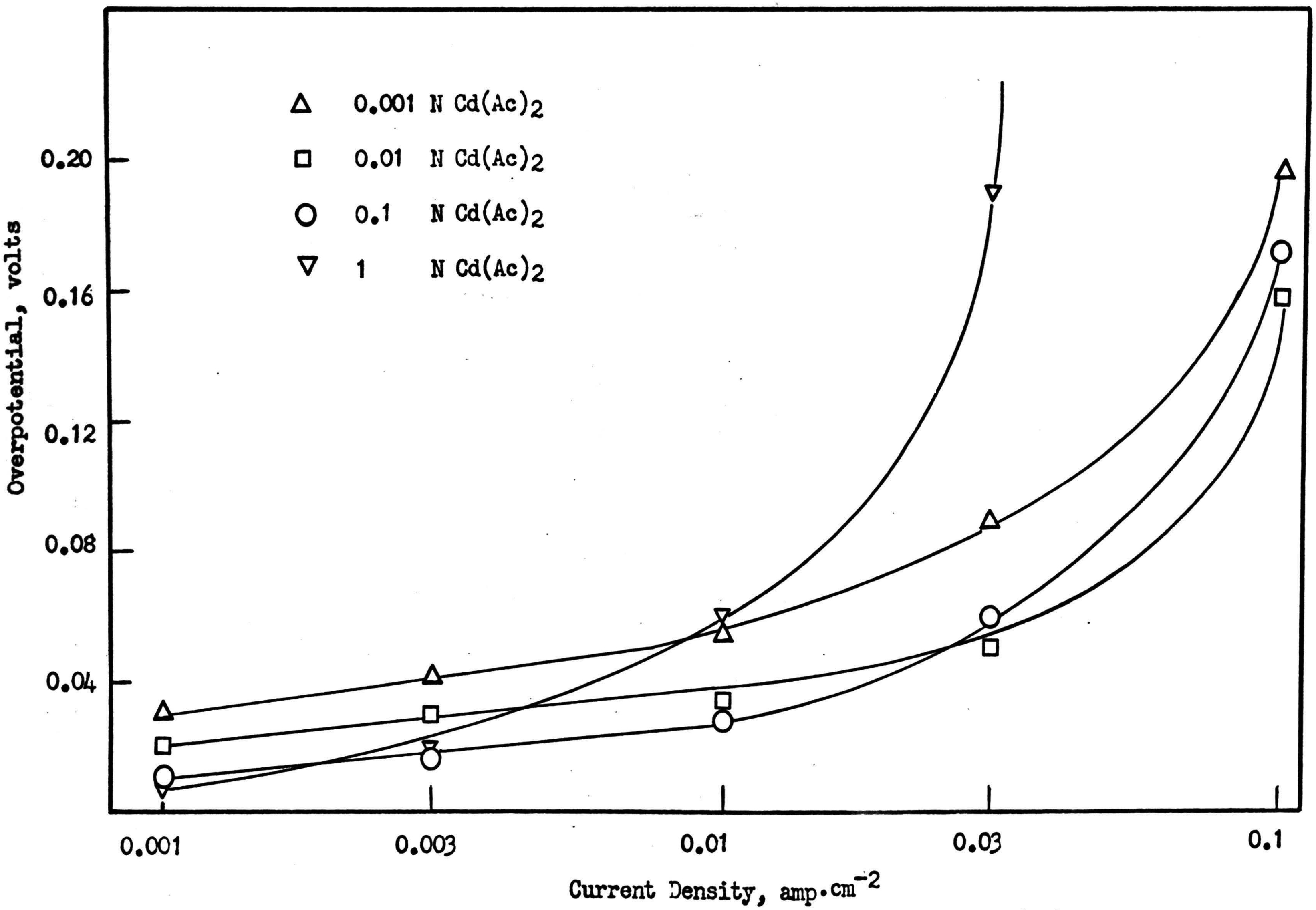


Figure 8. Tafel curves for the anodic dissolution of cadmium in $Cd(Ac)_2$-KAc solutions (ionic strength=1.5) at 25°C.

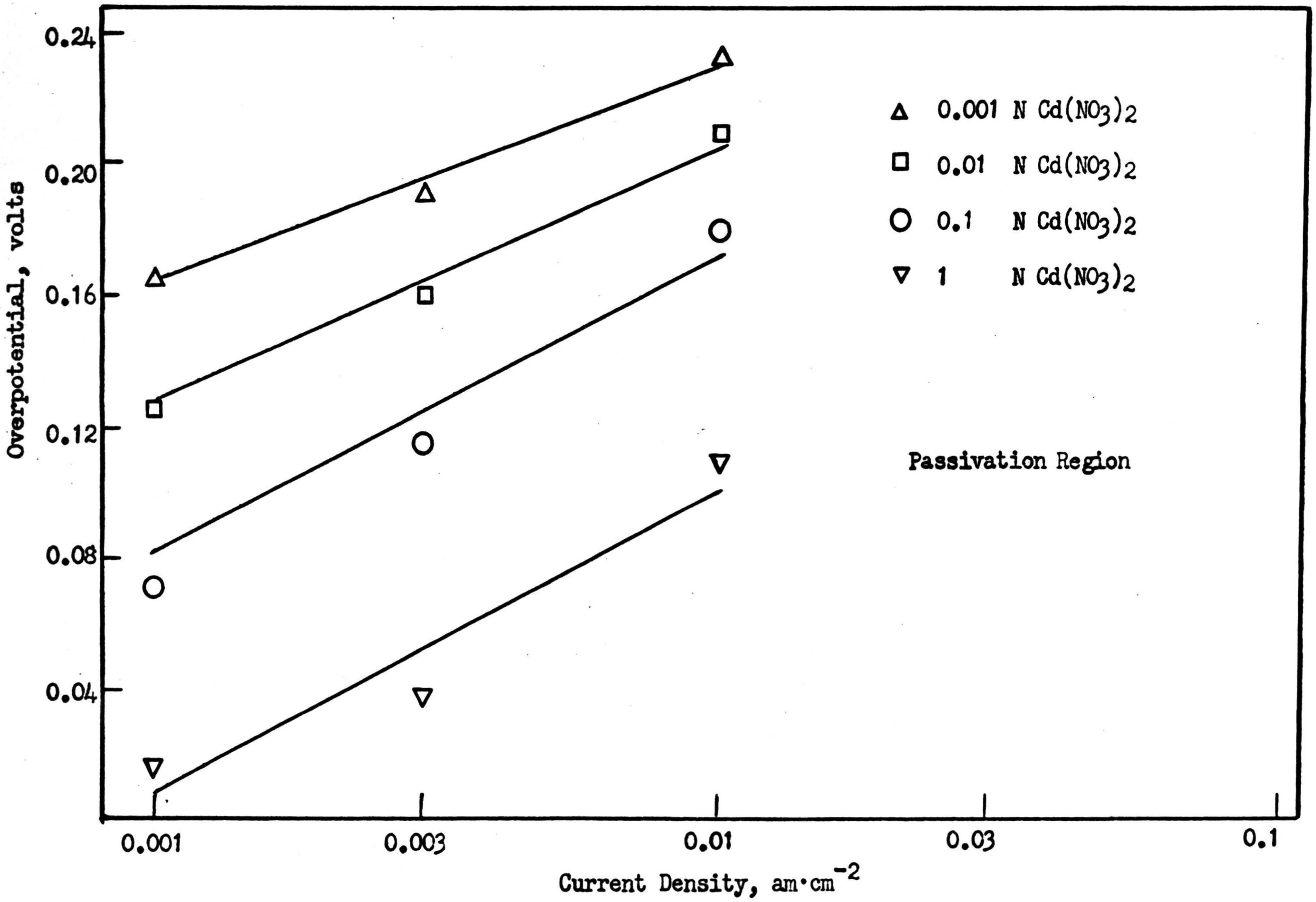


Figure 9. Tafel curves for the anodic dissolution of cadmium in $Cd(NO_3)_2$-KNO_3 solutions (ionic strength=1.5) at 25°C.

IV. DISCUSSION

Sorensen, Davidson, and Kleinberg (12) have proposed that the apparent valence of cadmium dissolving anodically in nitrate solutions is due to the formation of "uncommon" valence ions. James, et al., (20, 30) have studied the same process but have attributed the apparent valence to the corrosion and disintegration of cadmium. During electrolysis, a grey film was formed on the surface of the cadmium anode, but was not formed in either potassium chloride or potassium chlorate solution. This film was present only in certain oxidizing salt solutions where the apparent valence was less than two. It was suspected that this film was associated with the abnormal behavior of the anodic dissolution. It was shown rather conclusively that local corrosion and disintegration are responsible for the uncommon valence of cadmium.

With the view of extending some of these previous studies, this work was undertaken to obtain information pertaining to the anodic dissolution of cadmium in aqueous solutions of various anions which also contained appreciable concentrations of cadmium ions. This might lead to a better understanding of the corrosion and disintegration phenomena and check some existing theories of their occurrence.

In $Cd(NO_3)_2$-KNO_3 solutions, the apparent valence dropped continuously and rapidly from near the normal valence of 2 to 1.28 as current densities increased from

0.001 to 0.1 amp·cm^{-2}. The dissolution in solutions containing Cl^-, Br^-, I^-, $SO_4^=$, and $C_2H_3O_2^-$ ions showed valences that did not depart significantly from the normal value. The evolution of hydrogen at the cadmium anode was not observed at any time during this investigation. This observation has also been reported by other investigators (12).

It is proposed that the anodic dissolution of cadmium in neutral salt solutions consists of two reactions; (1) a normal electrochemical reaction involving cadmium as the anode and platinized-platinum as the cathode, and (2) a local cell action producing corrosion or self-dissolution of cadmium as well as disintegration. The cadmium anode is normally covered with a protective film (oxide or hydroxide) prior to electrolysis. As an external current is applied, the protective film is disrupted and corrosion develops at local areas on an otherwise unattacked surface. The flow of electrons from the local anodes through the metal to the local cathodes is a function of differences in potential between the areas. The potential difference may arise because of inhomogeneity of the surface with respect to the films on the metal, inclusions in the form of impurities, nonuniform stress distribution, temperature gradients, and differences in concentration in portions of the surrounding solution. Due to the high hydrogen overpotential (1.0-1.5 volts) on cadmium, if corrosion is to proceed, the H^0 formed on the local cathodes must be removed by oxidizing agents, e.g. NO_3^-, in the electrolyte serving as a depolarizer. The hydrogen forming on the local cathodes protects these areas from corrosion, but allows metal in the surrounding area to be dissolved until the local cathodes are detached. This gives rise to the metal particles in solution or the "disintegration" of the anode. The metallic particles from the anode are very active and react rapidly with the electrolyte due to their tiny size.

Several quantitative studies have been made to determine the amount of nitrite ion formed during electrolysis in potassium nitrate (20). The results showed that the amount formed accounts for the difference between the amount of cadmium dissolved based on a valence of plus two and the actual weight loss of the cadmium electrode. Thus, the metal particles were most probably consumed by corrosion made possible by the nitrate depolarizer.

Accordingly, the reactions involved in the dissolution process may be written:

<u>Electrochemical reaction</u> (reaction responsible for current in the external circuit)

$$Cd(s) = Cd^{+2}(aq) + 2e$$

<u>Local corrosion reaction</u>

a. anodic

$$Cd(s) = Cd^{+2}(aq) + 2e \qquad (11)$$

b. cathodic

$$2H_2O + 2e = 2H^o(ads) + 2OH^- \qquad (12a)$$

$$\text{or } 2H^+ + 2e = 2H^o(ads) \qquad (12b)$$

$$2H^o(ads) + NO_3^-(aq) = NO_2^-(aq) + H_2O \qquad (13)$$

Disintegration reaction (particles removed by corrosion)

$$\text{Cd(electrode)} = \text{Cd(particles)} \qquad (14)$$

$$\text{Cd(particles)} + NO_3^- + H_2O = Cd^{+2} + 2OH^- + NO_2^- \qquad (15)$$

On the basis of these reactions, a mathematical model for the anodic dissolution of cadmium in nitrate solution can be derived in the manner given by Sun (31):

Expressing the total dissolution rate as the sum of electrochemical, local corrosion, and disintegration rates,

$$r_T = r_C + r_L + r_D \qquad (16)$$

The electrochemical dissolution rate is proportional to the current, therefore,

$$r_E = k\cdot(i) \qquad (17)$$

The rate of corrosion would be dependent on several variables, among these are the electro-negativity of the metal, the number of local cathodes (purity and metallic structure) and the rate at which they are uncovered (external current), the concentration of hydrogen ions, and the concentration of the depolarizer (NO_3^-). Any additional effect of the Cd^{+2} should be associated with its influence on the corrosion potential. If reaction (12) should be the slow step in the local corrosion sequence, then the Cd^{+2} concentration would affect the local corrosion rate and thus the apparent valence through its effect on the corrosion potential. If reaction (13) is slow, then a very small, if any, effect of Cd^{+2} concentration should be noticed as the depolarizer concentration is the important variable. For a given metal and electrolyte of constant pH, the local corrosion rate may be expressed as:

$$r_L = k_2(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'} \qquad (18)$$

Since disintegration results directly from corrosion, a first approximation would be to assume that the disintegration rate is directly proportional to it, i.e.,

$$r_D = k_3'(r_L) = k_3(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'} \qquad (19)$$

Thus,

$$\begin{aligned} r_T &= k_1(i) + k_2(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'} \\ &\quad + k_3(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'} \\ &= k_1(i) + k_4(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'} \qquad (20) \end{aligned}$$

But,

$$\begin{aligned} V_i &= \frac{2r_E}{r_T} \\ &= \frac{2k_1(i)}{k_1(i) + k_4(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^{s'}} \\ &= \frac{2}{1 + k'(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^s} \\ &= 2[1 - k'(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^s + \cdots] \qquad (21) \end{aligned}$$

Omitting the higher ordered terms, equation (21) may be expressed as:

$$V_i = 2 - k(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^s$$

or

$$2 - V_i = k(C_{NO_3^-})^p(C_{Cd^{+2}})^q(i)^s \qquad (22)$$

The data in this investigation shows the apparent valence as a function of the nitrate ion concentration, cadmium ion concentration, and current density. A previous work (31) studied the anodic dissolution of cadmium in KNO_3-K_2SO_4 solutions and an empirical equation was obtained:

$$V_i = 2 - (C_{NO_3^-})^{0.41}(i)^{0.55}(2.2\cdot10^{-4}T - 3.96\cdot10^{-3}) \qquad (23)$$

Since $SO_4^=$ had no effect on the apparent valence, the order for the $C_{NO_3^-}$ should be the same in (22) and (23). Therefore, the effect of cadmium ions on the apparent valence can be observed and a linear relationship should be obtained for a plot of log $2-V_i/(C_{NO_3^-})^{0.41}$ versus log $C_{Cd^{+2}}$. These were prepared at various current densities and are shown in Figure 10. The slopes of the straight lines were 0.005. Thus, the effect of the Cd^{+2} is very small, indicating the depolarization reaction controls the local corrosion rate. This is also apparent from Figure 11 which shows V_i as a function of current density for 1 N $Cd(NO_3)_2$ (this work) and 1 N KNO_3(Deng's work). These were the only solutions that had common nitrate concentrations that would lend themselves to a direct comparison.

Similiar plots were prepared for various current densities at constant nitrate and cadmium ion concentration. Straight lines were obtained as shown on Figure 12. These slopes were 0.383 ± 0.004. Therefore, the empirical equation of the apparent valence as a function of the concentration of nitrate ion, cadmium ion, and current density is,

$$V_i = 2 - k(C_{NO_3^-})^{0.41}(C_{Cd^{+2}})^{0.005}(i)^{0.383} \qquad (24)$$

where k is constant for a given temperature. Its value at

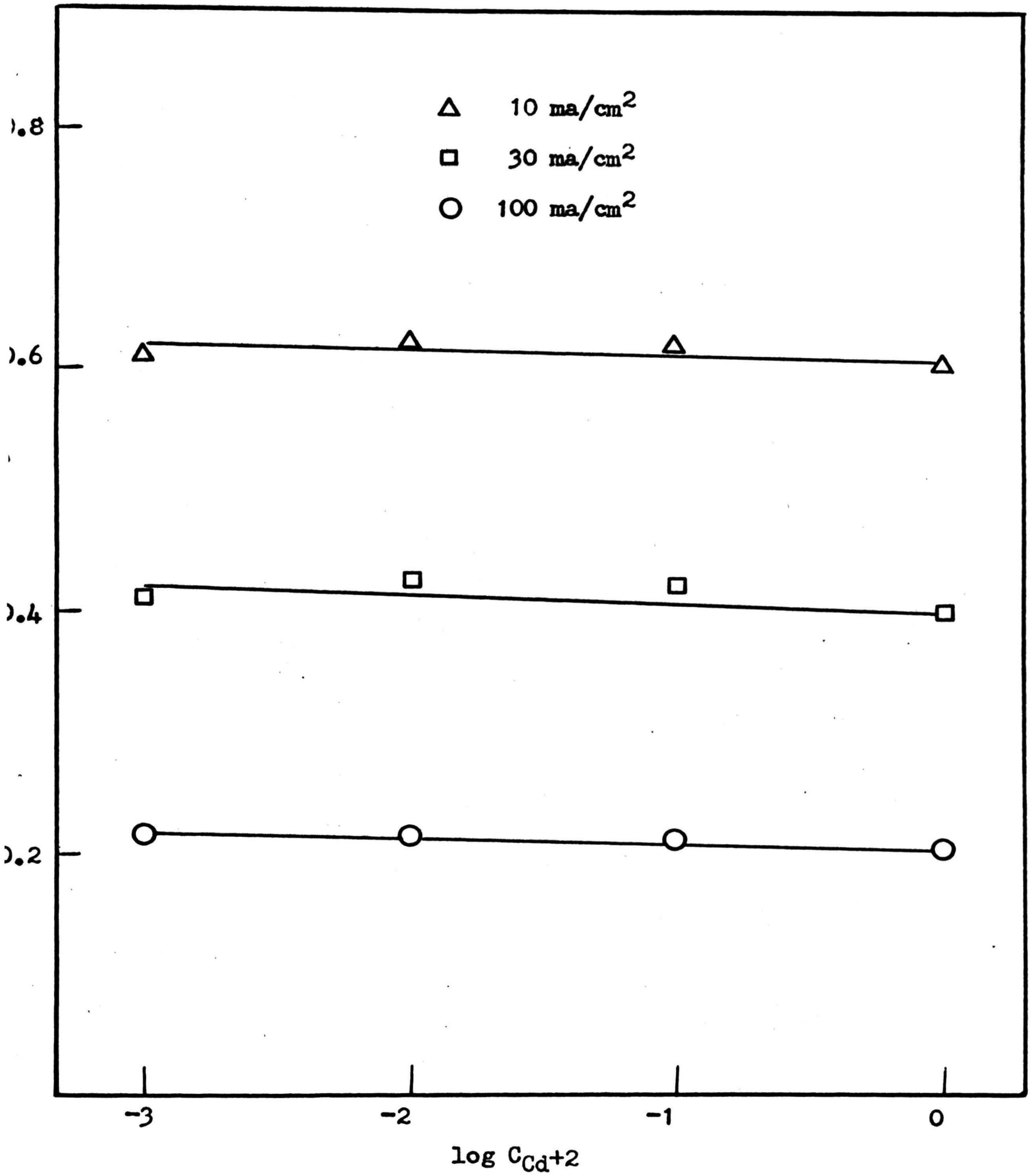


Figure 10. The effect of cadmium ion concentration on the apparent valence of cadmium undergoing anodic dissolution in $Cd(NO_3)_2$-KNO_3 solutions at 25°C.

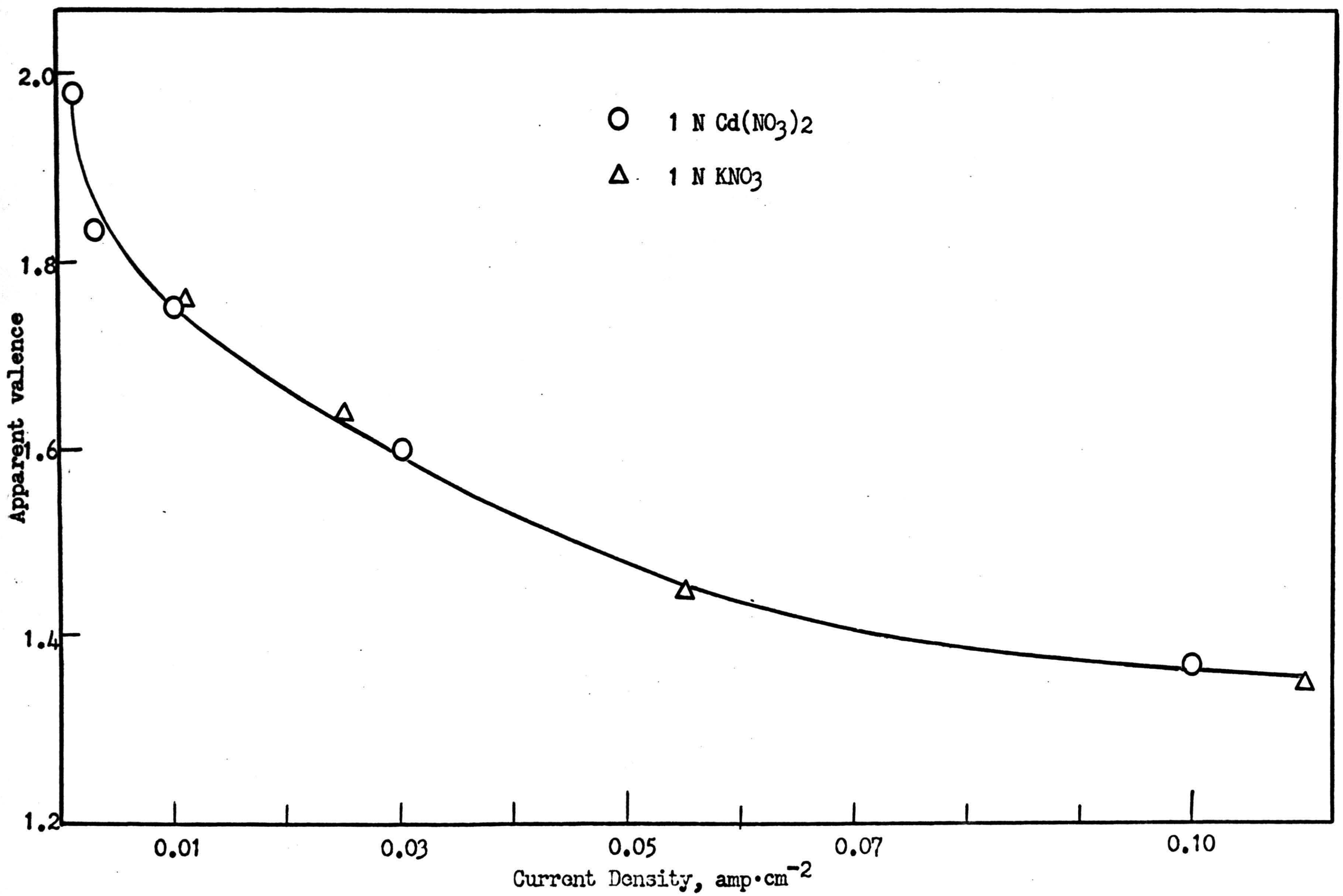


Figure 11. The effect of current density on the apparent valence of cadmium undergoing anodic dissolution at 25°C.

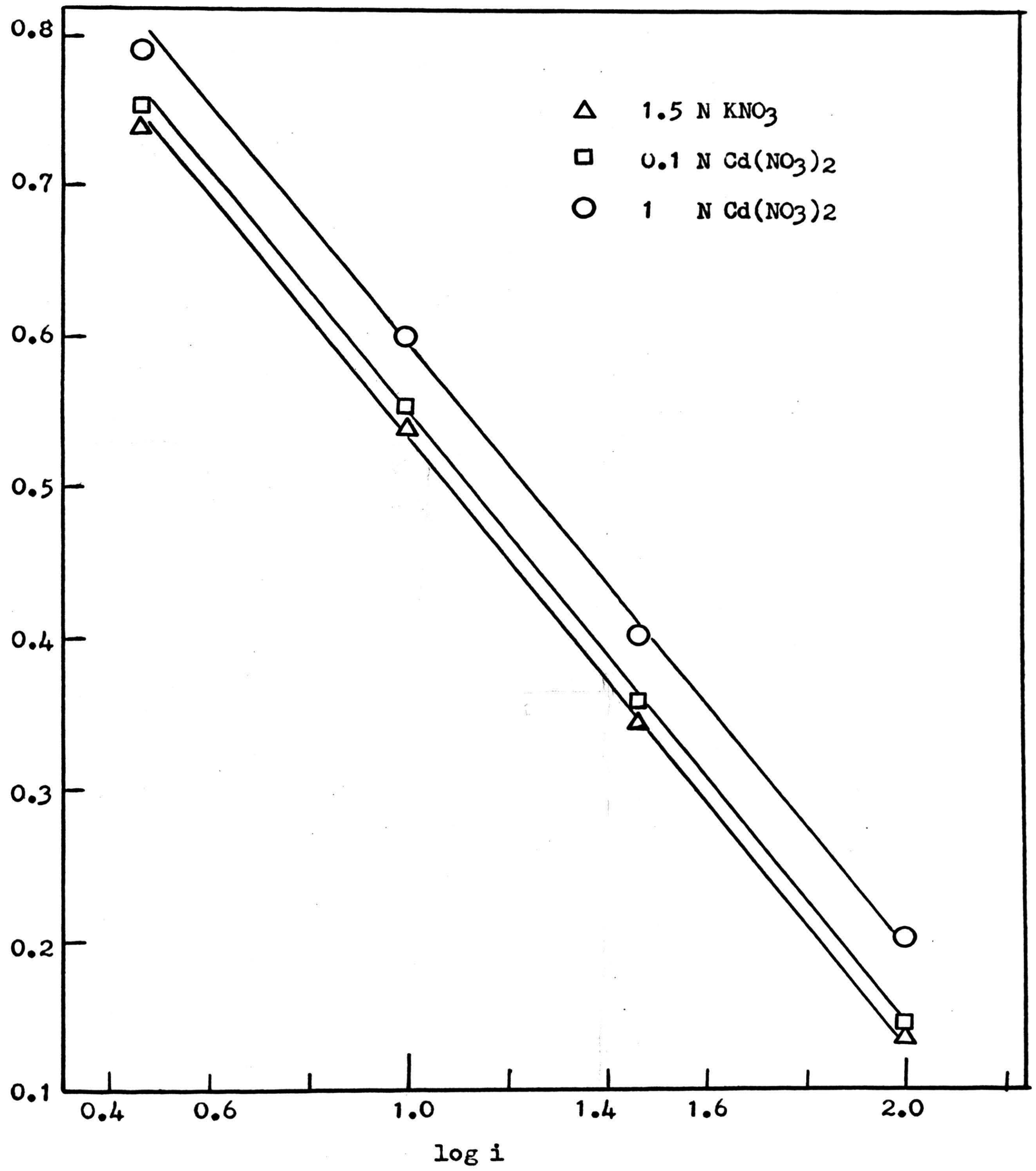


Figure 12. The effect of current density on the apparent valence of cadmium undergoing anodic dissolution in $Cd(NO_3)_2$-KNO_3 solutions (ionic strength=1.5) at 25°C.

$25^{\circ}C$ from these experiments is 0.107.

It might be noted that the exponent on the current density term, equation (24), of 0.383 compares to a value of 0.56 from Deng's work. Figure 13 shows log-log plots of (2-Vi) versus i for the data given in Figure 11. The solid triangles are the data used by Deng in determing his constant. From this more extensive data, it can be seen that the points used by Deng would give an abnormally high slope. It is felt the value from this study is more nearly correct.

Overpotential measurements of the cadmium anode as a function of current density were made in various electrolytes. Such measurements indicate the extent of film formation and sometimes assist in studying the reaction mechanism and kinetics of a dissolution process.

From the overpotential-current density (Tafel) plots, a linear region was observed at current densities below 0.01 $amp \cdot cm^{-2}$. A summary of these slopes is given in Table I. It can be seen that the slopes in nitrate solutions range from 0.074 to 0.098 volts, in halide solutions from 0.014 to 0.042 volts, and in $SO_4^{=}$ and Ac^{-} solutions from 0.016 to 0.032 volts. This is an indication that there may be a difference in the dissolution mechanism in these salt solutions. Calculated exchange currents were on the order of 10^{-5} $amp \cdot cm^{-2}$ indicating an activation controlled reaction.

A dark film was initially formed on the anode during the electrolysis. It's composition has been reported as

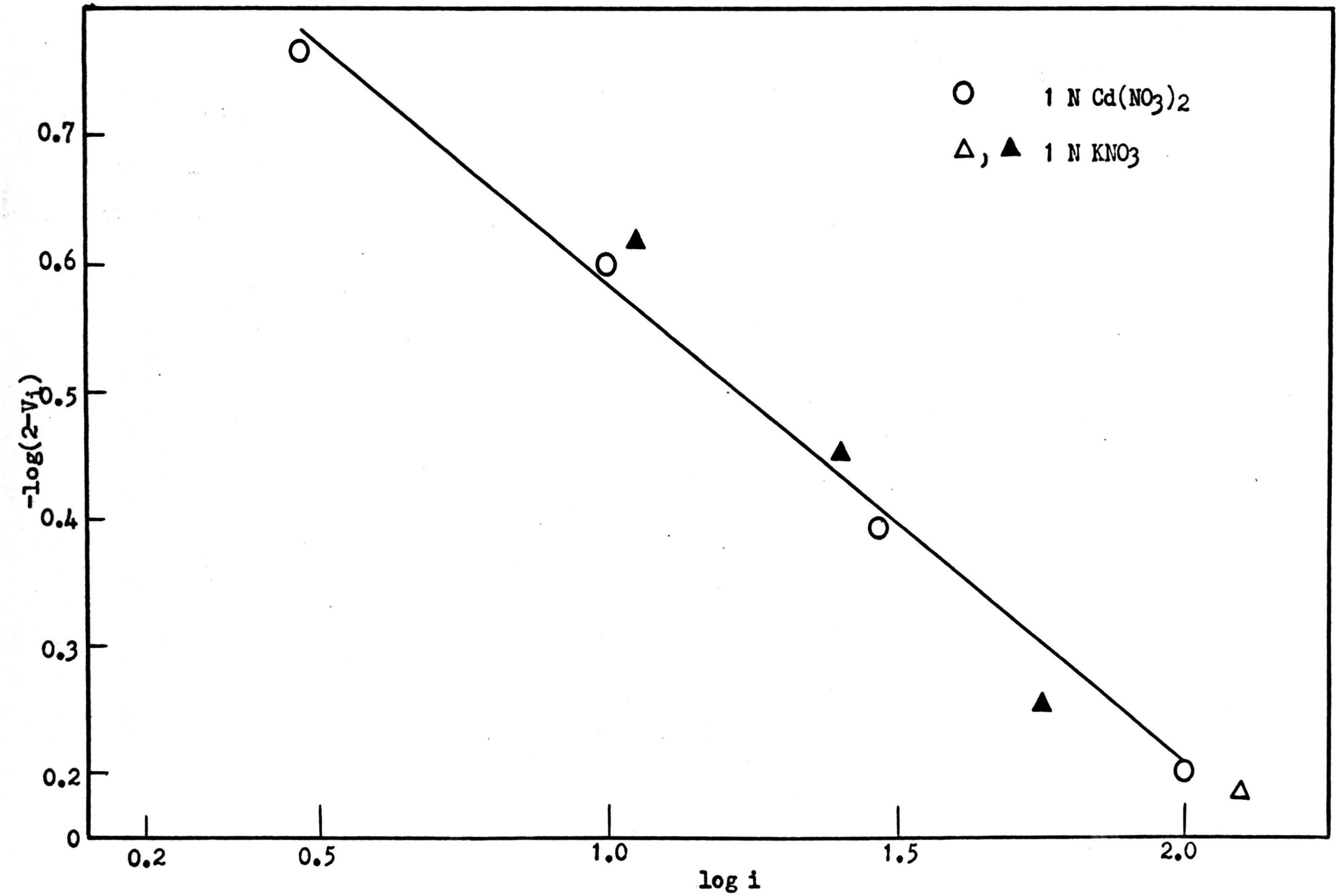


Figure 13. The effect of current density on the apparent valence of cadmium undergoing anodic dissolution at 25°C.

TABLE I

Electrolytes	Tafel curve slopes (volts)
0.001 N $CdCl_2$-1.499 N KCl	0.038
0.01 N $CdCl_2$-1.485 N KCl	0.020
0.1 N $CdCl_2$-1.35 N KCl	0.014
1 N $CdCl_2$	0.024
0.001 N $CdBr_2$-1.499 N KBr	0.042
0.01 N $CdBr_2$-1.485 N KBr	0.038
0.1 N $CdBr_2$-1.35 N KBr	0.018
1 N $CdBr_2$	0.032
0.001 N CdI_2-1.499 N KI	0.034
0.01 N CdI_2-1.485 N KI	0.026
0.1 N CdI_2-1.35 N KI	0.018
1 N CdI_2	0.026
0.001 N $CdSO_4$-0.999 N K_2SO_4	0.026
0.01 N $CdSO_4$-0.987 N K_2SO_4	0.022
0.1 N $CdSO_4$-0.867 N K_2SO_4	0.016
0.001 N $Cd(Ac)_2$-1.499 N KAc	0.024
0.01 N $Cd(Ac)_2$-1.485 N KAc	0.018
0.1 N $Cd(Ac)_2$-1.35 N KAc	0.018
1 N $Cd(Ac)_2$	0.032
0.001 N $Cd(NO_3)_2$-1.499 N KNO_3	0.074
0.01 N $Cd(NO_3)_2$-1.485 N KNO_3	0.082
0.1 N $Cd(NO_3)_2$-1.35 N KNO_3	0.098
1 N $Cd(NO_3)_2$	0.080

CdO (17). Since normal valences were obtained in all except the nitrate solutions, it is obvious that the color was not due to small metallic particles caused by disintegration.

During the anodic dissolution, the cadmium oxide was believed to dissolve, either as the oxide or as a complex (17). Cadmium hydroxide was precipitated when solubility limits were reached. Thus, a mechanism for dissolution can be postulated as follows:

$$Cd(s) + H_2O(aq) \longrightarrow Cd(OH)(s) + H^+(aq) + e \qquad (25)$$

$$Cd(OH)(s) \longrightarrow CdO(s) + H^+(aq) + e \qquad (26) \quad 40$$

$$CdO(s) + 4x^-(aq) + H_2O \longrightarrow Cdx_4^{=}(aq) + 2OH^- \qquad (27a) \quad 30$$

or

$$CdO(s) + \cancel{2}H_2O(aq) \longrightarrow Cd^{+2}(aq) + 2OH^- \qquad (27b) \quad 30$$

If reaction (26) is rate controlling, the theoretical Tafel slope would be 40 mv. For either (27a) or (27b) controlling, the slope would be 30 mv. If the specific rates of (26) and (27) were approximately equal, then control could be changed from one to the other, depending on the presence of an appreciable concentration of a complexing agent. As cadmium is known to complex readily with halide ions (32), it might be expected that reaction (27a) would occur faster than (27b). At high concentration of halides, the Tafel slopes would be 40 mv, at low halide concentrations, as well as in non-complexing solutions, the slope would be 30 mv. Table II shows the slopes segregated in this manner. The fit is seen to be reasonably well, especially at upper and lower limits of the concentrations. The low slopes, especially at 0.1 N

Cd^{+2}, are not understood.

In nitrate solutions, film thickening of the electrode was obvious and lead to periodic passivation at higher current densities. It is believed the higher Tafel slopes here are due to film resistance rather than kinetic effects.

TABLE II

Cd^{+2} concentration	Tafel slopes (mv)				
	Cl^-	Br^-	I^-	$SO_4^=$	Ac^-
0.001 N	38	42	34	26	24
0.01 N	20	38	26	22	18
0.1 N	14	18	18	16	18
1 N	24	32	26	—	32

V. RECOMMENDATIONS

In this study, the dissolution rates of cadmium are postulated to vary with the concentration of hydrogen ion. As this is changing during the course of reaction, a suitable pH meter might be used to measure the pH of the solutions and record it simultaneously. It would be helpful in establishing or confirming the dissolution mechanism.

Studies at various cadmium ion concentrations, keeping the other ion concentrations constant, might clarify the influence of the cadmium ion on the anodic dissolution.

Anodic dissolution of cadmium in acids, such as HCl, HBr, HI, H_2SO_4, etc., and in bases, such as NaOH, KOH, $Ca(OH)_2$, etc., to determine the dissolution behavior might be of interest.

VI. APPENDICES

A. Materials

The following is a list of the major materials used in this investigation.

1. Cadmium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

2. Cadmium Bromide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

3. Cadmium Iodide. Reagent grade, meets ACS specifications. Allied Chemical, Morristown, N.J.

4. Cadmium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

5. Cadmium Acetate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

6. Cadmium Nitrate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

7. Potassium Chloride. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

8. Potassium Bromide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

9. Potassium Iodide. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

10. Potassium Sulfate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

11. Potassium Acetate. Reagent grade, meets ACS specifications. Fisher Scientific Co., Fair Lawn, N.J.

12. Potassium Nitrate. Reagent grade, meets ACS

specifications. Fisher Scientific Co., Fair Lawn, N.J.

13. Nitrogen. Prepurified grade. Matheson Co., Joliet, Ill.

14. Cadmium. 99.999 + percent purity. American Smelting and Refining Co., South Plain-field, N.J.

B. Equipment

1. Surface Preparation of Cadmium Specimens.

a. Belt surfacer. Buehler No. 1250. Buehler Ltd., Evanston, Ill.

b. Hand grinder. Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Ill.

2. Electrolysis Apparatus.

a. Power supply. Sorensen, QRB(40 V, 0.75 amp) D.C. power supplies. A unit of Raytheon Co., South Norwalk, Conn.

b. Electrometer. Multi-range type, Model 610 B, Keithley Instruments Inc., Cleveland, Ohio.

c. Ammeter. Ultra high sensitivity volt-ohm-microammeter, Simpson 269, Simpson Electric Co., Chicago, Ill.

C. Miscellaneous Experimental Procedures

1. Surface Preparation of Cadmium Specimens. The following procedures were used for the cadmium metal surface preparation:

a. All pits and irregularities were removed from the metal surface with a belt surfacer equipped with a No. 150 grit abrasive cloth belt.

b. The sample surface was finished on a water-flushed four-stage hand grinder equipped with Nos. 240, 320, 400, and 600 abrasive strips, proceeding from the coarsest to the finest.

c. The sample was rinsed with distilled water.

d. The surface was etched in dilute nitric acid and again rinsed with distilled water.

2. Treatment of Grey Films Formed on the Cadmium Electrode. The following procedures were used for treating the grey film formed during the anodic dissolution of cadmium in nitrate solutions.

a. Three drops of 1:10 diluted HCl were put on grey film of the metal electrode.

b. The surface was massaged with a rubber policeman until the film was removed.

c. The electrode was rinsed with distilled water.

D. Appendix D (Tables III to LIV)

TABLE III

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N $CdCl_2$-1.499 N KCl at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0252	0.0252	2.0
28,800	0.003	0.0302	0.0297	2.03
9,000	0.010	0.0325	0.0327	1.99
3,600	0.030	0.0390	0.0394	1.98
1,200	0.100	0.0433	0.0437	1.98

TABLE IV

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N $CdCl_2$-1.485 N KCl at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0252	0.0253	1.99
28,800	0.003	0.0302	0.0305	1.98
9,000	0.010	0.0325	0.0327	1.99
3,600	0.030	0.0390	0.0395	1.98
1,200	0.100	0.0433	0.0440	1,97

TABLE V

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N $CdCl_2$-1.35 N KCl at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
86,400	0.001	0.0302	0.0301	2.0
28,800	0.003	0.0302	0.0304	1.99
9,000	0.010	0.0325	0.0330	1.97
3,600	0.030	0.0390	0.0400	1.95
1,200	0.100	0.0433	0.0446	1.94

TABLE VI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N $CdCl_2$ at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0252	0.0252	2.0
28,800	0.003	0.0302	0.0303	1.99
9,000	0.010	0.0325	0.0328	1.98
3,600	0.030	0.0390	0.0398	1.96
1,200	0.100	0.0433	0.0444	1.95

TABLE VII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1.5 N KCl at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.0
28,800	0.003	0.0302	0.0302	2.0
9,000	0.010	0.0325	0.0326	1.99
3,600	0.030	0.0390	0.0391	2.00
1,200	0.100	0.0433	0.0435	1.99

TABLE VIII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N $CdBr_2$-1.499 N KBr at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0252	0.0252	2.0
28,800	0.003	0.0302	0.0304	1.99
9,000	0.010	0.0325	0.0330	1.97
3,600	0.030	0.0390	0.0398	1.96
1,200	0.100	0.0433	0.0440	1.97

TABLE IX

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N $CdBr_2$-1.485 N KBr at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0261	1.99
28,800	0.003	0.0302	0.0305	1.98
9,000	0.010	0.0325	0.0330	1.97
3,600	0.030	0.0390	0.0390	2.00
1,200	0.100	0.0433	0.0448	1.93

TABLE X

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N $CdBr_2$-1.35 N KBr at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0126	2.0
28,800	0.003	0.0302	0.0305	1.98
9,000	0.010	0.0325	0.0328	1.98
3,600	0.030	0.0390	0.0394	1.98
1,200	0.100	0.0433	0.0434	2.00

TABLE XI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N $CdBr_2$ at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.0
28,800	0.003	0.0302	0.0304	1.99
7,200	0.010	0.0260	0.0263	1.98
3,600	0.030	0.0390	0.0389	2.0
1,200	0.100	0.0433	0.0442	1.96

TABLE XII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1.5 N KBr at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.0
28,800	0.003	0.0302	0.0304	1.99
7,200	0.010	0.0260	0.0267	1.95
3,600	0.030	0.0390	0.0389	2.0
1,200	0.100	0.0433	0.0444	1.95

TABLE XIII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N CdI_2-1.499 N KI at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.0
28,800	0.003	0.0302	0.0304	1.99
9,000	0.010	0.0325	0.0326	1.99
3,790	0.030	0.0410	0.0415	1.98
1,200	0.100	0.0433	0.0435	1.99

TABLE XIV

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N CdI_2-1.485 N KI at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0258	2.01
32,040	0.003	0.0336	0.0339	1.98
9,000	0.010	0.0325	0.0328	1.98
3,600	0.030	0.0390	0.0394	1.98
1,200	0.100	0.0433	0.0437	1.98

TABLE XV

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N CdI_2-1.35 N KI at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0261	1.99
34,310	0.003	0.0360	0.0366	1.97
9,000	0.010	0.0325	0.0332	1.96
3,600	0.030	0.0390	0.0398	1.96
1,200	0.100	0.0433	0.0440	1.97

TABLE XVI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N CdI_2 at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0258	2.01
29,150	0.003	0.0306	0.0306	2.00
9,000	0.010	0.0325	0.0325	2.00
3,600	0.030	0.0390	0.0390	2.00
1,240	0.100	0.0448	0.0450	1.99

TABLE XVII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1.5 N KI at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.00
28,800	0.003	0.0302	0.0302	2.00
9,000	0.010	0.0325	0.0326	1.99
3,600	0.030	0.0390	0.0396	1.99
1,200	0.100	0.0433	0.0428	2.02

TABLE XVIII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N $CdSO_4$-0.999 K_2SO_4 at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0123	2.05
18,000	0.003	0.0189	0.0190	1.99
7,200	0.010	0.0260	0.0262	1.98
3,600	0.030	0.0390	0.0398	1.96
1,800	0.100	0.0650	0.0670	1.94

TABLE XIX

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N $CdSO_4$-0.987 N K_2SO_4 at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0126	2.00
18,000	0.003	0.0189	0.0191	1.98
7,200	0.010	0.0260	0.0265	1.96
3,600	0.030	0.0390	0.0395	1.98
1,250	0.100	0.0451	0.0458	1.97

TABLE XX

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N $CdSO_4$-0.867 N K_2SO_4 at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0126	2.00
18,000	0.003	0.0189	0.0190	1.99
7,200	0.010	0.0260	0.0261	1.99
3,600	0.030	0.0390	0.0394	1.98
1,200	0.100	0.0433	0.0437	1.98

TABLE XXI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N K_2SO_4 at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.00
28,800	0.003	0.0302	0.0303	1.99
9,000	0.010	0.0325	0.0328	1.98
3,600	0.030	0.0390	0.0396	1.97
1,200	0.100	0.0433	0.0443	1.96

TABLE XXII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N $Cd(Ac)_2$-1.499 N KAc at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
52,340	0.001	0.0189	0.0181	2.04
28,800	0.003	0.0302	0.0303	1.99
9,000	0.010	0.0325	0.0328	1.98
3,600	0.030	0.0390	0.0398	1.96
1,200	0.100	0.0433	0.0442	1.96

TABLE XXIII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N $Cd(Ac)_2$-1.485 N KAc at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.00
28,800	0.003	0.0302	0.0303	1.99
9,000	0.010	0.0325	0.0327	1.99
3,600	0.030	0.0390	0.0390	2.00
1,200	0.100	0.0433	0.0433	2.00

TABLE XXIV

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N $Cd(Ac)_2$-1.35 N KAc at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
32,180	0.001	0.0114	0.0113	2.02
28,800	0.003	0.0302	0.0301	2.0
9,000	0.010	0.0325	0.0329	1.97
3,600	0.030	0.0390	0.0396	1.97
1,200	0.100	0.0433	0.0436	1.99

TABLE XXV

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N $Cd(Ac)_2$ at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0261	1.99
28,800	0.003	0.0302	0.0304	1.97
9,000	0.010	0.0325	0.0332	1.96
3,600	0.030	0.0390	0.0398	1.96
1,200	0.100	0.0433	0.0442	1.96

TABLE XXVI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1.5 N KAc at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0260	2.00
28,905	0.003	0.0303	0.0302	2.0
9,000	0.010	0.0325	0.0326	1.99
3,600	0.030	0.0390	0.0396	1.97
1,200	0.100	0.0433	0.0445	1.95

TABLE XXVII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.001 N $Cd(NO_3)_2$-1.499 N KNO_3 at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0127	1.98
18,000	0.003	0.0189	0.0207	1.82
7,270	0.010	0.0262	0.0306	1.71
3,600	0.030	0.0390	0.0506	1.54
1,200	0.100	0.0433	0.0676	1.28

TABLE XXVIII

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.01 N $Cd(NO_3)_2$-1.485 N KNO_3 at 25°C

t (sec)	i (amp·cm^{-2})	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0128	1.97
14,400	0.003	0.0151	0.0165	1.82
7,200	0.010	0.0260	0.0302	1.72
3,600	0.030	0.0390	0.0500	1.56
1,200	0.100	0.0433	0.0676	1.28

TABLE XXIX

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 0.1 N $Cd(NO_3)_2$-1.35 N KNO_3 at 25°C

t (sec)	i ($amp\cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
36,000	0.001	0.0126	0.0127	1.98
18,000	0.003	0.0189	0.0207	1.824
7,200	0.010	0.0260	0.0302	1.72
3,600	0.030	0.0390	0.0500	1.56
1,200	0.100	0.0433	0.0674	1.284

TABLE XXX

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1 N $Cd(NO_3)_2$ at 25°C

t (sec)	i ($amp\cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
46,800	0.001	0.0134	0.0135	1.98
18,000	0.003	0.0189	0.0206	1.83
7,200	0.010	0.0260	0.0297	1.75
3,600	0.030	0.0390	0.0487	1.60
1,200	0.100	0.0433	0.0632	1.37

TABLE XXXI

APPARENT VALENCE OF CADMIUM DISSOLVING ANODICALLY IN 1.5 N KNO_3 at 25°C

t (sec)	i ($amp \cdot cm^{-2}$)	W_a (gm)	W_e (gm)	V_i
72,000	0.001	0.0260	0.0265	1.96
28,800	0.003	0.0302	0.0331	1.82
9,000	0.010	0.0325	0.0380	1.71
3,600	0.030	0.0390	0.0503	1.55
1,200	0.100	0.0433	0.0676	1.28

TABLE XXXII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N $CdCl_2$-1.499 N KCl at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.599	0.010	0	-0.512
	15	-0.599		15	-0.511
	30	-0.599		30	-0.511
0.001	0	-0.549	0.030	0	-0.476
	15	-0.550		15	-0.477
	30	-0.550		30	-0.477
0.003	0	-0.537	0.100	0	-0.379
	15	-0.537		15	-0.392
	30	-0.537		30	-0.391
				45	-0.391

TABLE XXXIII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N $CdCl_2$-1.485 N KCl at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.560	0.010	30	-0.507
	15	-0.560		45	-0.509
	30	-0.560		60	-0.509
0.001	0	-0.530	0.030	0	-0.477
	15	-0.529		15	-0.486
	30	-0.529		30	-0.488
				45	-0.488
0.003	0	-0.518			
	15	-0.519	0.100	0	-0.416
	30	-0.519		15	-0.421
				30	-0.420
0.010	0	-0.498		45	-0.420
	15	-0.500			

TABLE XXXIV

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.1 N $CdCl_2$-1.35 N KCl at 25°C

i $(amp \cdot cm^{-2})$	t (min)	E (volts)	i $(amp \cdot cm^{-2})$	t (min)	E (volts)
0.000	0	-0.527	0.010	0	-0.494
	15	-0.520		15	-0.501
	30	-0.520		30	-0.500
				45	-0.500
0.001	0	-0.504			
	15	-0.511	0.030	0	-0.471
	30	-0.514		15	-0.474
	45	-0.514		30	-0.474
0.003	0	-0.502	0.100	0	-0.391
	15	-0.509		15	-0.390
	30	-0.510		30	-0.390
	45	-0.510			

TABLE XXXV

THE DISSOLUTION POTENTIAL OF CADMIUM IN 1 N $CdCl_2$ at 25°C

i ($amp{\cdot}cm^{-2}$)	t (min)	E (volts)	i ($amp{\cdot}cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.452	0.030	0	-0.332
	15	-0.453		15	-0.331
	30	-0.453		30	-0.329
				45	-0.329
0.001	0	-0.449			
	15	-0.449	0.100	0	-0.039
	30	-0.449		15	-0.021
				30	0.001
0.003	0	-0.439		45	0.021
	15	-0.439		60	0.035[a]
	30	-0.439			
0.010	0	-0.411			
	15	-0.411			
	30	-0.411			

[a] potential kept increasing

TABLE XXXVI

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N $CdBr_2$-1.499 N KBr at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.608	0.010	30	-0.539
	15	-0.609		45	-0.539
	30	-0.609			
			0.030	0	-0.498
0.001	0	-0.571		15	-0.499
	15	-0.578		30	-0.499
	30	-0.578			
			0.100	0	-0.412
0.003	0	-0.561		15	-0.408
	15	-0.562		30	-0.399
	30	-0.562		45	-0.398
				60	-0.391[a]
0.010	0	-0.540			
	15	-0.540			

[a] potential kept increasing

TABLE XXXVII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N $CdBr_2$-1.485 N KBr at 25°C

i ($amp \cdot cm^{-2}$)	t (min)	E (volts)	i ($amp \cdot cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.589	0.010	30	-0.531
	15	-0.589		45	-0.529
	30	-0.589		60	-0.529
0.001	0	-0.569	0.030	0	-0.480
	15	-0.571		15	-0.488
	30	-0.571		30	-0.488
0.003	0	-0.559	0.100	0	-0.364
	15	-0.560		15	-0.359
	30	-0.559		30	-0.351
	45	-0.559		45	-0.348
				60	-0.344[a]
0.010	0	-0.538			
	15	-0.537			

[a] potential kept increasing

TABLE XXXVIII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.1 N $CdBr_2$-1.35 N KBr at 25°C

i (amp•cm^{-2})	t (min)	E (volts)	i (amp•cm^{-2})	t (min)	E (volts)
0.000	0	-0.554	0.010	0	-0.530
	15	-0.555		15	-0.531
	30	-0.557		30	-0.531
	45	-0.557			
			0.030	0	-0.506
0.001	0	-0.549		15	-0.506
	15	-0.549		30	-0.506
	30	-0.549			
			0.100	0	-0.436
0.003	0	-0.541		15	-0.431
	15	-0.543		30	-0.428
	30	-0.543		45	-0.425
				60	-0.419[a]

[a] potential kept increasing

TABLE XXXIX

THE DISSOLUTION POTENTIAL OF CADMIUM IN 1 N $CdBr_2$ at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.458	0.030	0	-0.334
	15	-0.459		15	-0.330
	30	-0.459		30	-0.329
				45	-0.327
0.001	0	-0.451		60	-0.327
	15	-0.451			
	30	-0.451	0.100	0	-0.009
				15	0.012
0.003	0	-0.443		30	0.038
	15	-0.444		45	0.046
	30	-0.444		60	0.053[a]
0.010	0	-0.417			
	15	-0.418			
	30	-0.418			

[a] potential kept increasing

TABLE XL

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N CdI_2-1.499 N KI at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.687	0.010	0	-0.621
	15	-0.687		15	-0.622
	30	-0.687		30	-0.622
0.001	0	-0.653	0.030	0	-0.589
	15	-0.654		15	-0.584
	30	-0.654		30	-0.587
				45	-0.587
0.003	0	-0.640			
	15	-0.641	0.100	0	-0.459
	30	-0.641		15	-0.471
	45	-0.641		30	-0.422
				45	-0.391
				60	-0.387[a]

[a] potential kept increasing

TABLE XLI

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N CdI_2-1.485 N KI at 25°C

i (amp•cm^{-2})	t (min)	E (volts)	i (amp•cm^{-2})	t (min)	E (volts)
0.000	0	-0.669	0.010	0	-0.621
	15	-0.669		15	-0.621
	30	-0.669		30	-0.621
0.001	0	-0.649	0.030	0	-0.591
	15	-0.649		15	-0.590
	30	-0.649		30	-0.590
0.003	0	-0.639	0.100	0	-0.479
	15	-0.639		15	-0.497
	30	-0.639		30	-0.488
				45	-0.486
				60	-0.484[a]

[a] potential kept increasing

TABLE XLII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.1 N CdI_2-1.35 N KI at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp.cm^{-2})	t (min)	E (volts)
0.000	0	-0.629	0.010	0	-0.609
	15	-0.631		15	-0.609
	30	-0.631		30	-0.609
0.001	0	-0.628	0.030	0	-0.578
	15	-0.628		15	-0.578
	30	-0.628		30	-0.578
0.003	0	-0.620	0.100	0	-0.451
	15	-0.621		15	-0.449
	30	-0.621		30	-0.437
				45	-0.429
				60	-0.419[a]

[a] potential kept increasing

TABLE XLIII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 1 N CdI_2 at 25°C

i ($amp \cdot cm^{-2}$)	t (min)	E (volts)	i ($amp \cdot cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.450	0.030	0	-0.271
	15	-0.450		15	-0.269
	30	-0.450		30	-0.267
				45	-0.264
0.001	0	-0.441		60	-0.262[a]
	15	-0.441			
	30	-0.441	0.100	0	0.141
				15	0.171
0.003	0	-0.430		30	0.191
	15	-0.430		45	0.211
	30	-0.430		60	0.229[a]
0.010	0	-0.389			
	15	-0.389			
	30	-0.389			

[a] potential kept increasing

TABLE XLIV

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N $CdSO_4$-0.999 N K_2SO_4 at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.529	0.010	0	-0.454
	15	-0.532		15	-0.458
	30	-0.539		30	-0.458
	45	-0.539			
			0.030	0	-0.418
0.001	0	-0.459		15	-0.419
	15	-0.476		30	-0.419
	30	-0.479			
			0.100	0	-0.311
	45	-0.482			
				15	-0.310
	60	-0.482			
				30	-0.309
0.003	0	-0.469		45	-0.309
	15	-0.470			
	30	-0.472			
	45	-0.475			
	60	-0.475			

TABLE XLV

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N $CdSO_4$-0.987 N K_2SO_4 at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.491	0.010	0	-0.458
	15	-0.502		15	-0.459
	30	-0.509		30	-0.459
	45	-0.519			
	60	-0.519	0.030	0	-0.429
				15	-0.430
0.001	0	-0.469		30	-0.430
	15	-0.480			
	30	-0.481	0.100	0	-0.347
	45	-0.487		15	-0.343
	60	-0.487		30	-0.347
				45	-0.347
0.003	0	-0.473			
	15	-0.477			
	30	-0.477			

TABLE XLVI

THE DISSOLUTION POTENTIAL OF CADMIUM IN $0.1\ N\ CdSO_4$-$0.867\ N\ K_2SO_4$ at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.469	0.010	0	-0.449
	15	-0.473		15	-0.453
	30	-0.478		30	-0.455
	45	-0.482		45	-0.455
	60	-0.484	0.030	0	-0.421
	75	-0.484		15	-0.424
0.001	0	-0.463		30	-0.426
	15	-0.467		45	-0.426
	30	-0.470	0.100	0	-0.332
	45	-0.470		15	-0.331
0.003	0	-0.461		30	-0.329
	15	-0.465		45	-0.329
	30	-0.467			
	45	-0.467			

TABLE XLVII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N $Cd(Ac)_2$-1.499 N KAc at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.556	0.010	0	-0.489
	15	-0.549		15	-0.494
	30	-0.551		30	-0.497
	45	-0.551		45	-0.497
0.001	0	-0.521	0.030	0	-0.459
	15	-0.521		15	-0.461
	30	-0.521		30	-0.461
0.003	0	-0.500	0.100	0	-0.339
	15	-0.509		15	-0.350
	30	-0.509		30	-0.359
	45	-0.509		45	-0.351
				60	-0.348[a]

[a] potential kept increasing

TABLE XLVIII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N $Cd(Ac)_2$-1.485 N KAc at 25°C

i ($amp \cdot cm^{-2}$)	t (min)	E (volts)	i ($amp \cdot cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.518	0.010	0	-0.465
	15	-0.520		15	-0.469
	30	-0.521		30	-0.487
	45	-0.521		45	-0.487
0.001	0	-0.481	0.030	0	-0.447
	15	-0.449		15	-0.465
	30	-0.500		30	-0.465
	45	-0.500			
			0.100	0	-0.351
0.003	0	-0.481		15	-0.374
	15	-0.489		30	-0.369
	30	-0.490		45	-0.364
	45	-0.490		60	-0.359[a]

[a] potential kept increasing

TABLE XLIX

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.1 N $Cd(Ac)_2$-1.35 N KAc at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.511	0.010	0	-0.492
	15	-0.526		15	-0.498
	30	-0.529		30	-0.499
	45	-0.529		45	-0.499
0.001	0	-0.499	0.030	0	-0.466
	15	-0.509		15	-0.467
	30	-0.511		30	-0.467
	45	-0.517			
	60	-0.517	0.100	0	-0.341
				15	-0.350
0.003	0	-0.507		30	-0.362
	15	-0.509		45	-0.357
	30	-0.511		60	-0.352[a]
	45	-0.511			

[a] potential kept increasing

TABLE L

THE DISSOLUTION POTENTIAL OF CADMIUM IN
1 N $Cd(Ac)_2$ at 25°C

i ($amp \cdot cm^{-2}$)	t (min)	E (volts)	i ($amp \cdot cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.449	0.030	0	-0.270
	15	-0.450		15	-0.269
	30	-0.450		30	-0.267
				45	-0.264
0.001	0	-0.440		60	-0.259[a]
	15	-0.440			
	30	-0.440	0.080	0	0.049
				15	0.066
0.003	0	-0.430		30	0.078
	15	-0.430		45	0.096
	30	-0.430		60	0.118[a]
0.010	0	-0.389			
	15	-0.389			
	30	-0.389			

[a] potential kept increasing

TABLE LI

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.001 N $Cd(NO_3)_2$-1.499 N KNO_3 at 25°C

i (amp•cm^{-2})	t (min)	E (volts)	i (amp•cm^{-2})	t (min)	E (volts)
0.000	0	-0.374	0.003	0	-0.189
	15	-0.414		30	-0.229
	30	-0.418		45	-0.230
	45	-0.418		60	-0.230
0.001	0	-0.339	0.010	0	-0.182
	30	-0.318		15	——[b]
	45	-0.297			
	60	-0.271	0.030		——[c]
	75	-0.256[a]			
			0.100		——[c]

[a] potential kept increasing

[b] potential started to fluctuate

[c] potential couldn't be measured due to wide fluctuations

TABLE LII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.01 N $Cd(NO_3)_2$-1.485 N KNO_3 at 25°C

i (amp.cm^{-2})	t (min)	E (volts)	i (amp.cm^{-2})	t (min)	E (volts)
0.000	0	-0.349	0.003	0	-0.177
	15	-0.414		15	-0.184
	30	-0.408		30	-0.239
	50	-0.401		45	——[b]
	65	-0.400			
	80	-0.399	0.010	0	-0.169
	95	-0.399		15	——[b]
0.001	0	-0.360	0.030		——[c]
	30	-0.334	0.100		——[c]
	45	-0.327			
	60	-0.278			
	75	-0.277[a]			

[a] potential kept increasing

[b] potential started to fluctuate

[c] potential couldn't be measured due to wide fluctuation

TABLE LIII

THE DISSOLUTION POTENTIAL OF CADMIUM IN 0.1 N $Cd(NO_3)_2$-1.35 N KNO_3 at 25°C

i ($amp \cdot cm^{-2}$)	t (min)	E (volts)	i ($amp \cdot cm^{-2}$)	t (min)	E (volts)
0.000	0	-0.291	0.003	0	-0.209
	15	-0.271		15	-0.251
	30	-0.364		30	-0.247
	45	-0.358		45	-0.239
	60	-0.351		60	-0.235[a]
	75	-0.349			
	90	-0.349	0.010	0	-0.167
				15	———[b]
0.001	0	-0.258			
	30	-0.269	0.030		———[c]
	45	-0.281	0.100		———[c]
	60	-0.279			
	75	-0.279			

[a] potential kept increasing

[b] potential started to fluctuate

[c] potential couldn't be measured due to wide fluctuation

TABLE LIV

THE DISSOLUTION POTENTIAL OF CADMIUM IN 1 N $Cd(NO_3)_2$ at 25°C

i (amp·cm^{-2})	t (min)	E (volts)	i (amp·cm^{-2})	t (min)	E (volts)
0.000	0	-0.278	0.003	0	-0.219
	15	-0.279		15	-0.228
	30	-0.274		30	-0.228
	45	-0.269			
	60	-0.264	0.010	0	-0.154
	75	-0.264		15	———[b]
0.001	0	-0.229	0.030		———[c]
	15	-0.248	0.100		———[c]
	30	-0.248			

[b] potential started to fluctuate

[c] potential couldn't be measured due to wide fluctuation

BIBLIOGRAPHY

1. Bredig, G., Zeit. Phys. Chem., 32, 127 (1900).
2. Burton, E.F., Phil. Mag., 11, 425 (1906).
3. Del Boca, M.C.: Electrolysis of Certain Salts of Metals in Liquid Ammonia, Helv. Chim. Acta, 16, 565 (1933).
4. Marsh G.A. and E. Scharschl: The Difference Effect and Chunk Effect, J. Electrochem. Soc., 107, 960 (1960).
5. Straumanis, M.E. and D.L. Mathis: The Disintegration of Beryllium during its Dissolution in Hydrochloric Acid, J. Less-Common Metals, 4, 213 (1962).
6. Straumanis, M.E. and D.K. Bhatia: Disintegration of Magnesium while Dissolving Anodically in Neutral and Acidic Solutions, J. Electrochem. Soc., 110, 357 (1963).
7. James, W.J., M.E. Straumanis, J.W., Johnson, and D.K. Bhatia: The Difference Effect on Magnesium Dissolving in Acids, J. Electrochem. Soc., 109, 1996 (1962).
8. Thiel, A. and J. Eckell: Korrosion U. Metallschutz, 4, 121,145 (1928).
9. Straumanis, M.E.: Korrosion U. Metallschutz, 14, 67 (1938).
10. Straumanis, M.E. and N.Y. Wang: The Difference Effect on Aluminum Dissolving in Hydrofluoric and Hydrochloric Acids, J. Electrochem. Soc., 102, 304 (1955).

11. Kroenig, W.O. and V.N. Uspensakaja: Korrosion U. Metallschutz, 11, 10 (1935).

12. Sorensen, D.T., A.W. Davidson, and J. Kleinberg: The Anodic Oxidation of Zinc and Cadmium in Aqueous Solutions, J. Inorg. Nucl. Chem., 13, 64 (1960).

13. Petty, K.L., A.W. Davidson, and J. Kleinberg: The Anodic Oxidation of Magnesium Metal, J. Amer. Chem. Soc., 76, 363 (1954).

14. Raijola, E. and A.W. Davidson: The Anodic Oxidation of Magnesium Metal, J. Amer. Chem. Soc., 78, 556 (1956).

15. Laughlin, B.D., J. Kleinberg, and A.W. Davidson: Unipositive Beryllium as a Product of Anodic Oxidation, J. Amer. Chem. Soc., 78, 559 (1956).

16. Greenblatt, J.H.: A Mechanism for the Anodic Dissolution of Magnesium, J. Electrochem. Soc., 103, 539 (1956).

17. Lake, Phyllis E. and E.J. Casey: Anodic Oxidation of Cadmium, J. Electrochem. Soc., 105, 52 (1958).

18. Hoey, G.R. and M. Cohen: Corrosion of Anodically and Cathodically Polarized Magnesium in Aqueous Media, J. Electrochem. Soc., 108, 36 (1961).

19. Stoner, G.E. and W.J. James: Valence Exhibited by Zinc Amalgam Anodically Dissolving in Nitrate Solutions, J. Amer. Chem. Soc., 85, 1354 (1963).

20. Sun, Y.C.: The Anodic Dissolution of Cadmium in Aqueous

Solutions, M.S. Thesis, Univ. of Missouri at Rolla, (1964).

21. Hoar, T.P.: Private Communication to W.J. James.

22. Kolotyrkin, J.M.: Effect of Specific Adsorption of Anions on Hydrogen Overvoltage, Fara, Soc., 55, 455 (1955).

23. Uhlig, H.H.: Corrosion and Corrosion Control, p. 70., John Wiley & Sons Inc., New York, (1963).

24. Evans, U.R.: The Corrosion and Oxidation of Metals, p. 238-39, Edward Arnold Ltd., London, (1955).

25. Krochmal, Franciszek, and Marra Beltowska: Influence of Cations on Anodic Behavior of Zinc, Zeszyty Nank, Uniw., pozuamic mat., Fiz., Chem., (1963).

26. Yoshino, Hisao: Anodic Performance of Zinc in Fresh Water at Elevated Temperatures, Tokyo Kogyo Shikenaho Hokoku, 57, 551 (1962).

27. Stern, M. and A.L. Geary: A Theoretical Analysis of the Shape of Polarization Curves, J. Electrochem. Soc., 104, 1 (1957).

28. Straumanis, M.E., S.T. Shih, and A.W. Schlechten: Hydrogen Overvoltage on Titanium in Acidic and Basic Solutions, J. Electrochem. Soc., 102, 573 (1955).

29. Johnson, J.W.: A Study of the Dissolution of Hafnium in Hydrofluoric Acid, Ph.D. Thesis, Univ. of Missouri at Rolla, (1961).

30. Deng, Eh: The Anodic Dissolution of Cadmium in Nitrate Solutions, M.S. Thesis, Univ. of Missouri at Rolla, (1965).

31. Sun, Yun-chung: The Anodic Behavior of Zinc in Aqueous Salt Solutions, Ph.D. Thesis, Univ. of Missouri at Rolla, (1966).

32. Sillen, L.G. and A.E. Martell: Stability Constants of Metal-ion Complexes, The Chemical Society, London, (1964).

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