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The anodic dissolution of cadmium in aqueous solution

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THE ANODIC DISSOLUTION OF CADMIUM

IN AQUEOUS SOLUTION

BY

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I INTRODUCTION

The increasing importance of prevention of corrosion in industry has stimulated extensive studies on the fundamental behavior of metals in corrosive media.

The basic mechanism of the anodic dissolution of metals such as cadmium, magnesium, and zinc in salt solutions is not completely known. Several mechanisms have been proposed by different investigators, but evidence is still lacking to draw unquestionable conclusions to explain the discrepancies which often arise between coulometric data and weight loss of metal electrodes in certain salt solutions.

The purpose of this investigation was to obtain experimental data for anodic dissolution of cadmium in various electrolytes and to arrive at a mechanism consistent with the results.

II LITERATURE REVIEW

When either zinc or cadmium dissolves anodically in aqueous neutral salt solution in the absence of oxidizing agents, a normal oxidation state of plus two is obtained. However, in the presence of certain oxidizing agents, such as nitrate, the number of coulombs required to dissolve one gram equivalent weight of zinc or cadmium is always less than the amount calculated from Faraday's Law, assuming zinc and cadmium have normal valences of plus two. This abnormal anodic dissolution has been investigated and several mechanisms have been proposed.

As early as 1933, Del Boca (1) proposed a mechanism for zinc and cadmium under anodic dissolution. He suggested that a portion of the anode is dissolved as atoms and is transported to the cathode in the form of $Cd.Cd^{++}$. More recently, March and Schaschl (2) suggested that when steel dissolves anodically at a high rate, the corrosion proceeds by the removal of "chunks of iron" containing several atoms. Therefore, the anodic metal does not dissolve as predicted by Faraday's Law because of the expulsion of metallic particles.

In 1955, Epelboin (3) reported that the anodic dissolution of zinc in the presence of perchlorate ion took place with an apparent valence number of 1.40. This value was obtained by weighing the zinc electrode after electrolysis and determining the amount of chloride ion formed from the reduction of the perchlorate ion.

Davidson, Kleinberg, and Sorensen (4-7) have given support to the concept of "uncommon valence". Using platinum as a cathode they calculated the initial mean valence number of the active metals under-

going anodic dissolution in various electrolytes. The electrolytic
cell was connected in series with a variable voltage, full-wave, mer-
cury tube rectifier, a silver coulometer, and an ammeter. The initial
valence number, V_i, of metallic ions formed was calculated by means of
the equation:

$$V_i = \frac{\text{(Wt. of silver deposited in coulometer) (At. Wt. of metal)}}{(107.88) \text{ (Wt. of metal lost from anode)}}$$

The value of V_i for cadmium dissolving in 0.2 M $NaNO_3$ solution at
30° C. was found to be 1.55, decreasing linearly with increasing temp-
erature. Cadmium exhibited an initial mean valence of plus two not
only in NaCl, KCl solution but also in 0.2 M $KClO_3$. In the latter med-
ium, however, zinc did enter solution with an initial mean valence num-
ber less than two.

The results were explained on the hypothesis that the primary reac-
tion at the metal anode consists of a stepwise oxidation, the first
step being the oxidation of the metal to the unipositive ion:

$$\text{Metal} = \text{Metal}^+ + e^- \text{ (at the electrode)} \qquad (1)$$

The unipositive ion would be expected to be very unstable and
would readily form the normal bipositive ion. There are two ways in
which this second step can occur:

1) by further electrolytic oxidation at the anode:

$$\text{Metal}^+ = \text{Metal}^{++} + e^- \text{ (at the electrode)} \qquad (2)$$
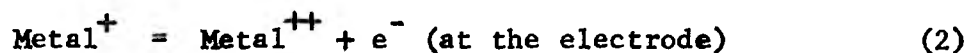
2) by chemical oxidation by the oxidizing agent in solution:

$$\text{Metal}^+ + \text{oxidant} = \text{Metal}^{++} + \text{reductant (in solution)} \quad (3)$$
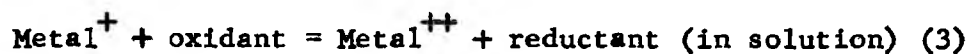
With nonreducible electrolytes reaction (3) cannot occur, and con-
sequently an initial mean valence number of two would be observed.
With reducible electrolytes, however, the two possible mechanisms of
the step are competitive; which one will predominate depends on the

nature of the oxidizing electrolyte and the conditions of the experiment. The initial mean valence might then range from +1 to +2, depending upon the relative extents of the reactions (2) and (3) which in turn depend upon the concentration of the oxidizing electrolyte and the temperature. Reaction (3) would be expected to increase with increasing concentration of the oxidant and temperature.

Analysis at the end of a run carried out in 3 Per cent $NaNO_3$ revealed the presence of nitrite ion, thus proving the reducing power of the initial corrosion product. Attempts to detect the presence of the unipositive species were unsuccessful. The formation of a grey-black film on the surface of the zinc anode after electrolysis in $NaNO_3$ was reported but no further mention was made of its possible significance. No attempt was made to explain the anomalous behavior of cadmium in chlorate solution.

Another mechanism suggested by Greenblatt (8) for anodic dissolution of magnesium was that as magnesium ions leave the metal lattice a finite time is required for them to diffuse through the oxide film, 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 through the film which fill anion vacancies. This results in a greater amount of metal being dissolved than the number of coulombs passing through the external circuit would indicate.

In 1958, using X-ray diffraction analysis, Hoey and Cohen (9) identified a film of $Mg(OH)_2$ which formed at the surface of the Mg anode during electrolysis. They further observed, using a microscope, free Mg metal particles in the film. They suggested that reactions such as:

$$2Mg = Mg.Mg^{++} + 2e^-$$
$$Mg.Mg^{++} + 2H_2O = Mg^{++} + Mg(OH)_2 + H_2$$
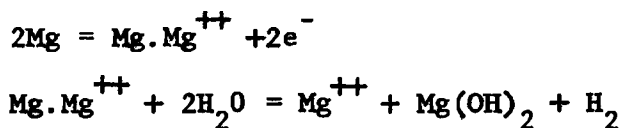
are energetically possible.

Furthermore, Robinson and King (10) concluded that the electrochemical behavior of magnesium can be satisfactorily explained solely on the basis of divalent ion formation. The magnesium hydroxide film on magnesium in aqueous environments is extremely protective, but quite responsive to electrochemical and environmental changes. This fact leads to the film control of the electrochemistry of magnesium in aqueous environments.

Straumanis and Mathis (11), using optical methods with high magnification, established that beryllium metal aggregates in the anolyte did not originate from nucleation but from anodic disintegration of metal. Under a high-power microscope, they observed large numbers of deformation twins in the metallic residue and on the surface of the electrode. Since deformation twins arise in the castings as a consequence of stresses set up due to temperature gradients and do not occur in nucleation, their studies provided conclusive proof of the origin of the particles.

Later Straumanis and Bhatia (12) showed that magnesium disintegrated partially into very 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 magnesium particles held in a matrix of $Mg(OH)_2$, as confirmed under high magnifications employing both reflected and transmitted light.

James and Stoner (13) reported that when zinc amalgam was electrolyzed in nitrate solution, there was no evidence of univalent ions; the agreement between the faradaic equivalent and the amount of zinc dissolved, based on bi-Positive ions was excellent. This showed that the concept of uncommon valence was inadequate to explain the anodic dissolution of zinc in oxidizing electrolytes.

Another electrochemical phenomenon related to the apparent valence of metals undergoing anodic dissolution is called the "difference effect". This was first recognized and named by Thiel and Eckell (14). They reasoned that when a metal is made an anode in an electrolytic cell, its rate of corrosion should be the sum of (a) local action as observed in the absence of external current, and (b) the corrosion rate equivalent to the applied current. In actual tests with metals, however, they found the observed corrosion rate to be less or more than the sum of the components (a) and (b). This positive or negative deviation value was given the name "difference effect". The negative difference effect has been attributed by some investigators to uncommon valencies (15-16).

A report of a positive and negative difference effect occurring simultaneously for the same metal-acid system (Mg-acid) was made by James et al (17). They suggested that for magnesium dissolving in acids, the difference effects result 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 in plots of the difference effect versus current density was attributed to the increased effect of anodic disintegration.

III EXPERIMENTAL

The experimental plan consisted of the following major phases:

A. The effect of various electrolytes on the apparent valence of cadmium undergoing anodic dissolution.

B. The effect of a nitrate solution on an amalgamated cadmium anode.

C. The study of surface films formed on a cadmium anode while dissolving in nitrate solution.

D. The effect of current density on the apparent valence of cadmium undergoing anodic dissolution.

The description of each phase will include apparatus, method of procedure, results, and sample calculations.

The list of materials used is given in the Appendix, Page 37.

A. The Effect of Various Electrolytes on the Apparent Valence of Cadmium Undergoing Anodic Dissolution.

Apparatus: The apparatus consisted of a reactor beaker of 250 milliliter capacity, an electric stirrer, and an electrolytic cell consisting of a cadmium electrode, a sensitive milliammeter, a decade-type resistance box with graduations from 0 to 9999 ohms in one-ohm divisions, two general purpose dry cells (1.5 volt), a knife switch, and a carbon cathode, all connected in series. A timer in one-second divisions was used for measuring the number of coulombs (amp. sec.) passed. Pipettes with capacities of 5, 10, and 25 milliliters were used to withdraw aliquots from the reactor and a microburette of 10 milliliter capacity with 0.05 milliliter graduations was employed

to measure the cadmium content of the aliquots by E.D.T.A. titration. The reactor beaker was immersed in a constant temperature water bath, described in the Appendix, which was controlled to within $\pm 1.0^\circ$ C.

Procedure: A specimen with a cross-sectional area of about 0.91 square centimeters was cut from a bar of cadmium metal of 99.99 per cent purity. It was then mounted in lucite by means of a metallographic mounting press. The cadmium electrode was prepared by drilling a hole in the lucite and inserting a copper wire. The wire was fastened to the metal to provide a good electrical contact. A glass rod was then placed over the wire and sealed to the lucite with beeswax. The electrode was polished immediately before each run according to the procedure listed in the Appendix. Two hundred milliliters of a three per cent solution of the electrolyte was quantitatively transferred to the reactor beaker by means of a 100 milliliter volumetric flask. The reactor beaker was then placed into the constant temperature bath in such a position as to insure complete submergence of the solution. The solution was allowed to remain in the water bath for about half an hour to bring the system to constant temperature before starting a run. The mounted metal anode and the carbon cathode were then immersed into the reactor flask and connected in series with the external circuit. The knife switch was closed and the current was kept at a steady rate by means of the resistance box. A timer and the milliammeter were used for measuring the number of coulombs passed. A 5 milliliter aliquot was withdrawn from the electrolyte at the end of a run, diluted to approximately 100 milliliters with distilled water, heated to about 80° C., buffered to a pH of 10, and titrated with a

standard E.D.T.A. solution using the organic dye Erichrome Black-T as an internal indicator. The E.D.T.A. solution had been previously standardized against a weighed amount of pure cadmium obtained from the same bar as the mounted specimen. The time was recorded in seconds, the current in amperes, and the weight loss of the cadmium (determined by the E.D.T.A. titration described above) in grams. The procedure employed was the same for all electrolytes. The treatment of the white precipitate formed during electrolysis is described in the Appendix. A detailed description of the procedure for standardizing the E.D.T.A. is in the Appendix.

Data and Results: As the valence studies were carried out in potassium chloride, potassium chlorate, and potassium nitrate, a brief summation of the results for each electrolyte follows separately.

Potassium Chloride: The anodic dissolution of cadmium in potassium chloride was carried out in a three per cent (by weight) solution at a current density of 0.055 ± 0.001 amps cm^{-2} and a temperature of $25.0 \pm 1.0°$ C. Data for this run are shown in Table I. The average value for the apparent valence is 1.99, indicating that cadmium anodically dissolves in its normal oxidation state of +2 in potassium chloride solution.

TABLE I

Apparent Valence for Cadmium Dissolved Anodically in Three Per cent
KCl at 25°C.

Time	*Current Density	Wt. of Cadmium		Apparent Valence
(sec)	(amp/cm^2)	Calcd. (g)	Expt. (g)	
900	0.055	0.0262	0.0263	1.99
900	0.055	0.0262	0.0265	1.98
1800	0.055	0.0524	0.0511	2.05
1800	0.055	0.0524	0.0529	1.98
2800	0.055	0.0815	0.0828	1.97
2800	0.055	0.0815	0.0820	1.99
3600	0.055	0.1048	0.1057	1.98
3600	0.055	0.1048	0.1052	1.99
				Average 1.99

* electrode surface area = 0.91 cm^2

Potassium chlorate: Cadmium was anodically dissolved in a
three per cent solution of potassium chlorate at a temperature of
25.0 ±1.0°C. and a current density of 0.055 ± 0.001 amps cm^{-2}. The
average value for the apparent valence of cadmium under these con-
ditions was 1.98. Table II includes the data taken during this run.
These indicate that cadmium anodically dissolves in its normal
oxidation state of +2 in potassium chlorate solution.

TABLE II

Apparent Valence for Cadmium Dissolved Anodically in Three Per cent $KClO_3$ at 25°C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
900	0.055	0.0262	0.0266	1.97
900	0.055	0.0262	0.0261	2.01
1800	0.055	0.0524	0.0530	1.98
1800	0.055	0.0524	0.0522	2.00
2800	0.055	0.0815	0.0825	1.98
2800	0.055	0.0815	0.0829	1.97
3600	0.055	0.1048	0.1053	1.99
3600	0.055	0.1048	0.1066	1.96
				Average 1.98

* electrode surface area = 0.91 cm^2

Potassium Nitrate: The anodic dissolution of cadmium in a three per cent potassium nitrate solution was observed at four different temperatures (5.0, 25.0, 40.0, 60.0 $\pm$ 1.0° C.) and at a current density of 0.055 $\pm$ 0.001 amps cm^{-2}. The data are shown in Tables III and IV. The apparent valence decreases with increasing temperature, ranging from 1.55 at 5.0° C. to 1.41 at 60.0° C. A graphical representation of these results (Figure I, Page 14) shows a linear relationship between the apparent valence and the temperature at the stated current density. A qualitative test for nitrite ion at the end of the run indicated the presence of nitrite ion. The nitrite ion content was determined by titration with potassium permanganate. The results are presented in Table V.

TABLE III

Apparent Valence for Cadmium Dissolved Anodically in Three Per cent KNO_3 at 25° C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
900	0.055	0.0262	0.0360	1.46
900	0.055	0.0262	0.0357	1.47
900	0.055	0.0262	0.0354	1.48
1800	0.055	0.0524	0.0726	1.44
1800	0.055	0.0524	0.0715	1.47
1800	0.055	0.0524	0.0718	1.46
				Average 1.46

* electrode surface area = 0.91 cm^2

TABLE IV

Effect of Temperature on the Apparent Valence of Cadmium Dissolved Anodically in Three Per cent KNO_3

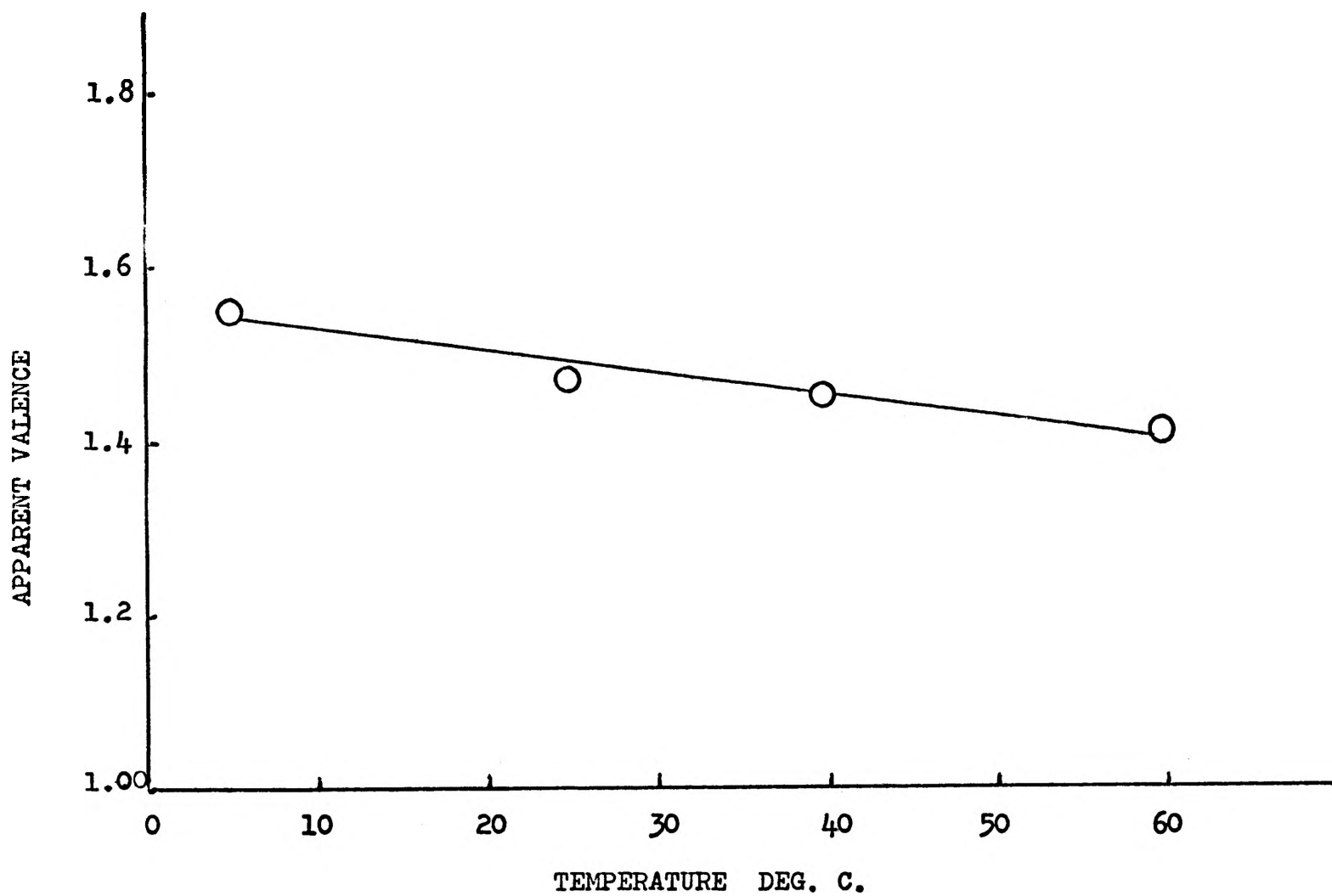| Time (sec)	*Current Density (amp/cm^2)	Temp. deg. C.	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
900	0.0550	5.0	0.0262	0.0338	1.55
1100	0.0550	25.0	0.0320	0.0437	1.47
900	0.0550	40.0	0.0262	0.0361	1.45
1200	0.0550	60.0	0.0291	0.0413	1.41

* electrode surface area = 0.91 cm^2

Figure I. Apparent valence as function of temperature for cadmium
dissolving anodically in 3 percent KNO_3 at a current
density of 0.055 amp cm^{-2}

TABLE V

Weight of Nitrite Ion Formed during Electrolysis of Cadmium in
Three Per cent KNO₃ at 25° C.

| Wt. of Cadmium | | Cd in Excess | Wt. of NO₂⁻ Produced From Cd in Excess | Wt. of NO₂⁻ Determined From Titration |
| Calcd. | Expt. | | | |
(g)		(g)		(g)
0.0262	0.0360	0.0098	0.00403	0.00435
0.0262	0.0365	0.0103	0.00422	0.00483
0.0175	0.0242	0.0067	0.00275	0.00311

During the runs in potassium nitrate, the current decreased steadily for approximately 3 minutes. This was corrected by decreasing the resistance of the external circuit using the resistance box. Removal of the cadmium anode at the end of a run revealed the presence of a gray film which turned completely white after about five minutes exposure to the atmosphere. A white precipitate was observed in the reaction beaker at a position directly below the cadmium anode.

This precipitate was shown to be Cd $(OH)_2$ by means of X-ray diffraction as shown in Table VII.

Sample Calculations: The method used for calculation of the apparent valence in potassium chloride, potassium chlorate, and potassium nitrate was the same.

Calculation of Apparent Valencies: The data for the anodic dissolution of cadmium in three per cent potassium chloride at 25.0° C. (Table I) have been used to illustrate the calculations involved in this part of the experimentation.

Calculation of the Apparent Weight of Cadmium Dissolved from

Coulombic Data: The apparent weight of cadmium dissolved according

to Faraday's Law, assuming the normal valence of +2 was calculated

as follows:

Wt. of Cadmium (apparent) = $\dfrac{(I)\ (t)\ (\text{Atomic Wt. of Cadmium})}{(F)\ (n)}$

where:

    t = time interval of run = 3600 sec

    I = current = 0.05 amp

    Atomic Wt. of Cadmium = 112.41 gm

    F = Faraday constant = 96,500 amp sec

    n = normal cationic charge of cadmium = 2

therefore:

Wt. of cadmium (apparent) = $\dfrac{(0.05)\ (3,600)\ (112.41)}{(96,500)\ (2)}$

= 0.105 gm

Calculation of the Apparent Valence: The apparent valence was

calculated simply by means of the equation:

V (apparent valence) = $\dfrac{(\text{Wt. of Cadmium apparent})(\text{normal valence})}{(\text{Wt. of cadmium experimental})}$

= $\dfrac{(0.105)\ (2)}{(0.106)}$

= 1.98

where:
    Wt. of cadmium experimental = Wt. of cadmium determined
                                   by E.D.T.A. titration

    (see Appendix for detailed procedure)

Calculation of the   Amount of Nitrite Ion Formed After Electrolysis:

The amount of nitrite ion formed during electrolysis was deter-
mined by titration with 0.0455 N $KMnO_4$. If equation 1 (Page 32) holds,
each atom of cadmium should produce one nitrite ion. Thus, the weight
of cadmium determined experimentally in excess of the amount calculated
from the coulombic data should produce an equivalent amount of nitrite
ion. The data for the anodic dissolution of cadmium in three per cent
KNO_3 at 25° C. have been used to illustrate the calculation.

Wt. of cadmium calculated by coulombic data = 0.0262 gm

Wt. of cadmium calculated by experiment = 0.0360 gm

Wt. of cadmium in excess = 0.0360 - 0.0262

$$= 0.0098 \text{ gm}$$

Wt. of nitrite ion = (Wt. Cd in excess) $\dfrac{\text{(Mol. Wt. Nitrite ion)}}{\text{(At. Wt. Cd)}}$

$$= (0.0098) \ \frac{(46.00)}{(112.41)} \ = \ 0.00403 \text{ gm}$$

Wt. of nitrite ion by $KMnO_4$ titration = 0.00435 gm

B.   The Effect of a Nitrate Solution on an Amalgamated Cadmium Anode:

Apparatus: The apparatus was the same as described in the
previous section.

Procedure: The cadmium electrode was ground and polished as
described previously, then amalgamated by bringing the exposed metal
surface in contact with a few drops of chemically pure mercury on a
watch glass. In order to insure coverage of the entire surface of
the cadmium by the mercury, a backward and forward motion was employed
until observation under a microscope revealed the absence of any
exposed portions of cadmium metal surface.

Runs were then made in three per cent solutions of potassium nitrate at 25.0* C. and a current density of 0.055 amp cm^{-2}. The same procedure as described in the previous section was used for each run. The cadmium anode was ground, polished, and freshly amalgamated before each run.

Data and Results: The data collected are shown in Table VI. The average value for the apparent valence of cadmium is 1.99 at 25.0° C. Observation of the amalgamated cadmium electrode at the end of a run indicated the absence of any film on the surface of the metal. Qualitative tests for nitrite ions proved negative.

TABLE VI

Apparent Valence for Cadmium Amalgam Dissolved Anodically in Three Per cent KNO$_3$ at 25* C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
900	0.055	0.0262	0.0268	1.96
900	0.055	0.0262	0.0264	1.99
1800	0.055	0.0524	0.0529	1.98
1800	0.055	0.0524	0.0520	2.02
				Average 1.99

* electrode surface area = 0.91 cm^2

Sample Calculations: The same method for calculating the apparent valence was used as in the first section.

C. The Study of Surface Films Formed on a Cadmium Anode While Dissolving in Nitrate Solution.

During the anodic dissolution of cadmium in aqueous potassium nitrate, it has been reported that a grey-black film was formed on the surface of the metal. Qualitative studies were carried out to produce the grey-black film, to determine its composition, and to observe its behavior during electrolysis.

Electrolysis was carried out in three per cent potassium nitrate solution. The current density was varied from 0.055 amps cm^{-2} to 0.10 amps cm^{-2}. The metal surface became completely covered with the film after about thirty seconds. Then the grey film turned to white gradually. At a high current density, 0.10 amps cm^{-2}, small portions of the white deposit were spalled off the metal surface. An X-ray analysis of this white deposit was made using a Straumanis asymmetric powder diffraction camera and copper $K\alpha$ radiation. The sample was irradiated for 60 minutes. Comparison of the experimental values for the "d" spacings with values in the A.S.T.M. file, shown in Table VII, revealed that the white precipitate was $Cd(OH)_2$.
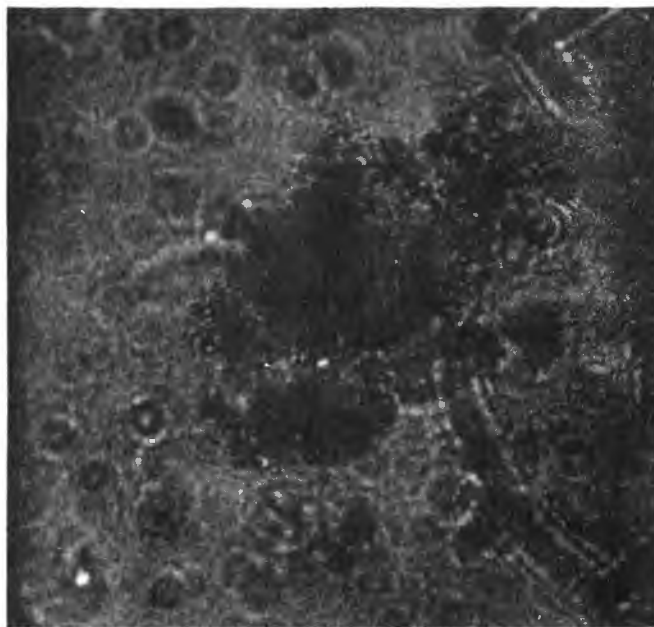
TABLE VII

Identification of White Residue Formed During the Anodic Dissolution of Cadmium in Three Per cent KNO_3 at 25° C.

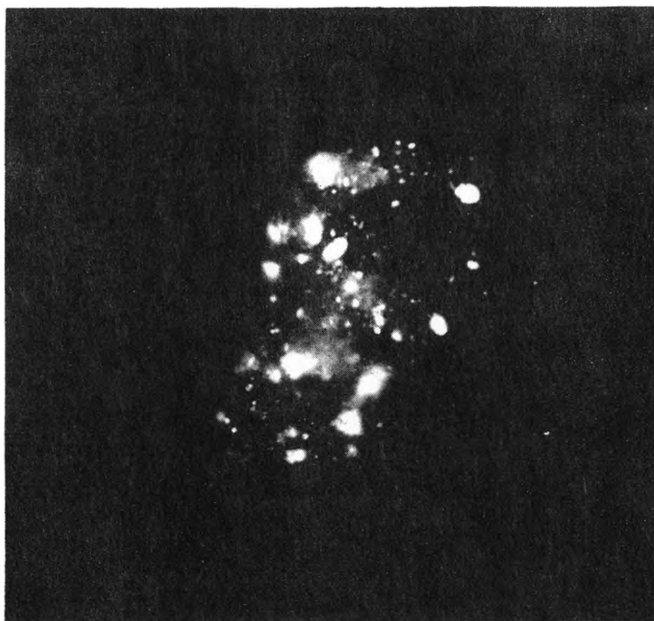| Experimental Values		A.S.T.M. Values for $Cd(OH)_2$	
"d" Spacings A	I/I_o	"d" Spacings °A	I/I_o
4.70	30*	4.71	100
2.58	100	2.56	100
3.03	65	3.03	63

* fluorescence shielded lines

In order to isolate the grey film, it was necessary to immerse the electrode in dry acetone. This removed the moisture which readily reacts with the grey film, turning it white. After immersion in acetone, the grey film partially flaked off the electrode and remained stable. This portion which flaked off the electrode was collected and viewed under a high power microscope, using oil immersion, at 1430X magnification. In reflected light, a multitude of bright metallic particles was observed in a matrix of the corrosion product. The accompanying photomicrograph (Figure II, Page 21) shows these metallic particles in the corrosion product. In transmitted light, parts of the sample appeared black, whereas in reflected light the corresponding parts appeared as bright, highly reflecting particles (Figure III, Page 21).

As another means of identification, the grey flakes were subjected to X-ray analysis. Copper $K\alpha$ radiation was used. An aluminum screen was employed to eliminate fluorescence which obscured several lines. The analysis yielded values for "d" spacings corresponding to the values for metallic cadmium and $Cd(OH)_2$ in the A.S.T.M. file, shown in Table VIII, revealing that the grey film consisted of metallic cadmium particles and $Cd(OH)_2$.

1430x

Figure II. Cadmium Particles as They Appear in Transmitted Light.

1430x

Figure III. Cadmium Particles as They Appear in Reflected Light.

TABLE VIII

Identification of Dark Corrosion Product Formed During the Anodic

Dissolution of Cadmium in Three Per cent KNO_3 at 25° C.

Experimental Values			A.S.T.M. Values for Cadmium and $Cd(OH)_2$	
"d" Spacings° A		I/I_o	"d" Spacings° A	I/I_o
Cd	2.35	65*	2.35	100
Cd	2.81	55	2.81	65
Cd	2.60	30	2.58	32
$Cd(OH)_2$	4.71	100	4.71	100
$Cd(OH)_2$	2.60	40*	2.56	100
$Cd(OH)_2$	3.01	75	3.03	63

* fluorescence shielded lines

D. The Effect of Current Density and Temperature on the Apparent

Valence of Cadmium Undergoing Anodic Dissolution

Apparatus: The apparatus was the same as described in the pre-

vious section except that an ice bath was used for the 5.0° C. run.

Procedure: The same procedure was used as described in the

previous section.

Data and Result: The anodic dissolution of cadmium in a three

per cent potassium nitrate solution was observed at three different

temperatures (5.0, 25.0, 60.0° C.) and at various current densities,

ranging from 0.001 to 0.140 amps cm^{-2}. The data collected are shown

in Tables IX, X, and XI.

TABLE IX

Effect of Current Density on the Apparent Valence of Cadmium Dissolved Anodically in Three Per cent KNO_3 at 25° C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Wt. of Cadmium Expt. (g)	Apparent Valence
19800	0.0011	0.0115	0.0116	1.99
15000	0.0011	0.0087	0.0088	1.98
14400	0.0017	0.0126	0.0132	1.91
6500	0.0055	0.0170	0.0179	1.88
4100	0.0110	0.0239	0.0265	1.81
4000	0.0110	0.0233	0.0261	1.78
200	0.0220	0.0233	0.0275	1.69
1300	0.0330	0.0227	0.0286	1.59
1230	0.0440	0.0285	0.0374	1.48
1100	0.0550	0.0320	0.0437	1.47
1000	0.0660	0.0349	0.0472	1.48
700	0.0770	0.0285	0.0395	1.44
750	0.0880	0.0349	0.0494	1.41
500	0.0990	0.0315	0.0453	1.39
500	0.1100	0.0291	0.0430	1.35
700	0.1320	0.0481	0.0696	1.38
600	0.1650	0.0524	0.0746	1.40

* electrode surface area = 0.91 cm^2

TABLE X

Effect of Current Density on the Apparent Valence of Cadmium Dissolved
Anodically in Three Per cent KNO_3 at 5° C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
8700	0.0055	0.0253	0.0268	1.89
2700	0.0110	0.0157	0.0167	1.88
2000	0.0220	0.0233	0.0266	1.75
1400	0.0330	0.0245	0.0288	1.70
900	0.0550	0.0262	0.0338	1.55
881	0.0770	0.0353	0.0471	1.50
754	0.0990	0.0395	0.0526	1.50
747	0.1100	0.0435	0.0583	1.49
500	0.1200	0.0320	0.0419	1.53
500	0.1530	0.0400	0.0516	1.55

* electrode surface area = 0.91 cm^2

TABLE XI

Effect of Current Density on the Apparent Valence of Cadmium Dissolved
Anodically in Three Per cent KNO_3 at 60°C.

Time (sec)	*Current Density (amp/cm^2)	Wt. of Cadmium Calcd. (g)	Expt. (g)	Apparent Valence
7515	0.0055	0.0219	0.0235	1.86
2180	0.0110	0.0127	0.0148	1.72
2000	0.0220	0.0233	0.0282	1.65
1070	0.0330	0.0184	0.0243	1.52
900	0.0440	0.0210	0.0294	1.42
1200	0.0550	0.0291	0.0413	1.41
900	0.0770	0.0367	0.0533	1.38
631	0.0990	0.0325	0.0477	1.37
600	0.1100	0.0349	0.0518	1.35
500	0.1320	0.0349	0.0513	1.36
500	0.1650	0.0437	0.0643	1.36

* electrode surface area = 0.91 cm^2

The apparent valence approaches its normal valence of +2 at a very low current density (0.001 amps cm^{-2}) and decreases with increasing current density. It seems to have a tendency to stay around 1.45 (25° C) with current densities larger than 0.06 amp cm^{-2} (Figure IV, V, and VI, Page 27 and 29).

Sample Calculation: The same method for calculating the apparent valence was used as in the previous section.
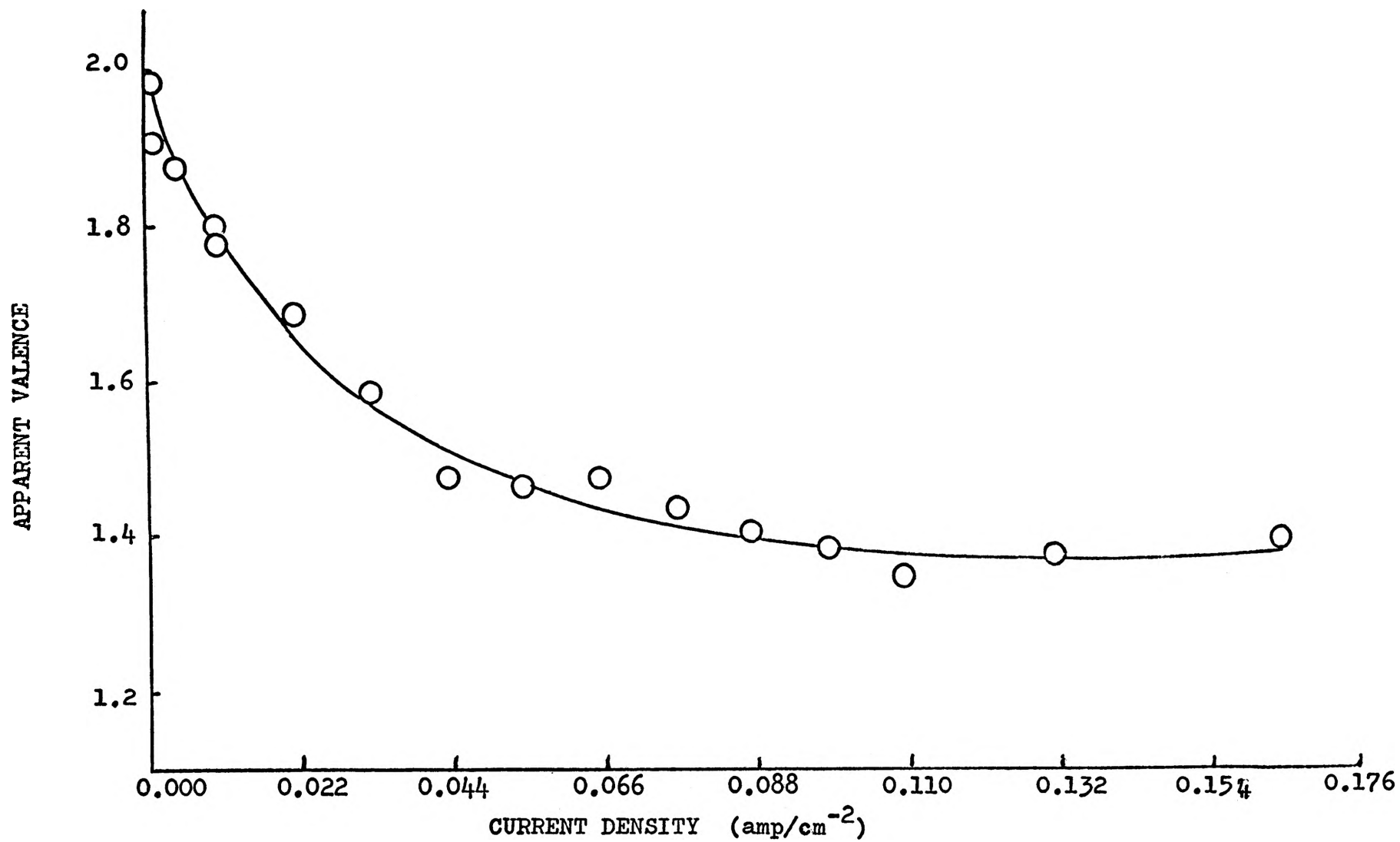
Figure IV. Effect of current density on the apparent valence of cadmium

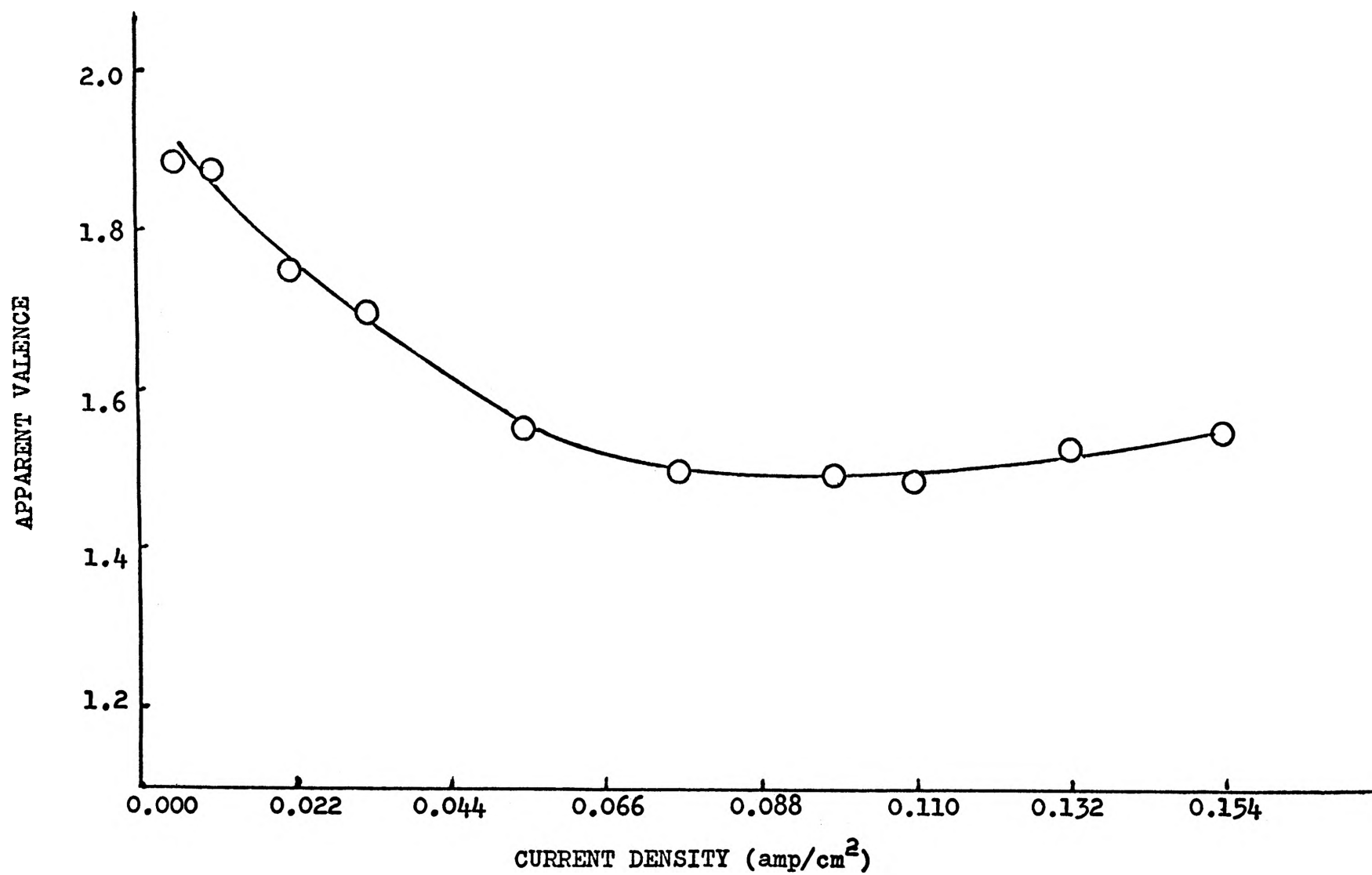dissolved anodically in 3 percent KNO_3 at 25° C.

Figure V. Effect of current density on the apparent valence of cadmium

dissolved anodically in 3 percent KNO_3 at $5°$ C.

Figure VI. Effect of current density on the apparent valence of cadmium
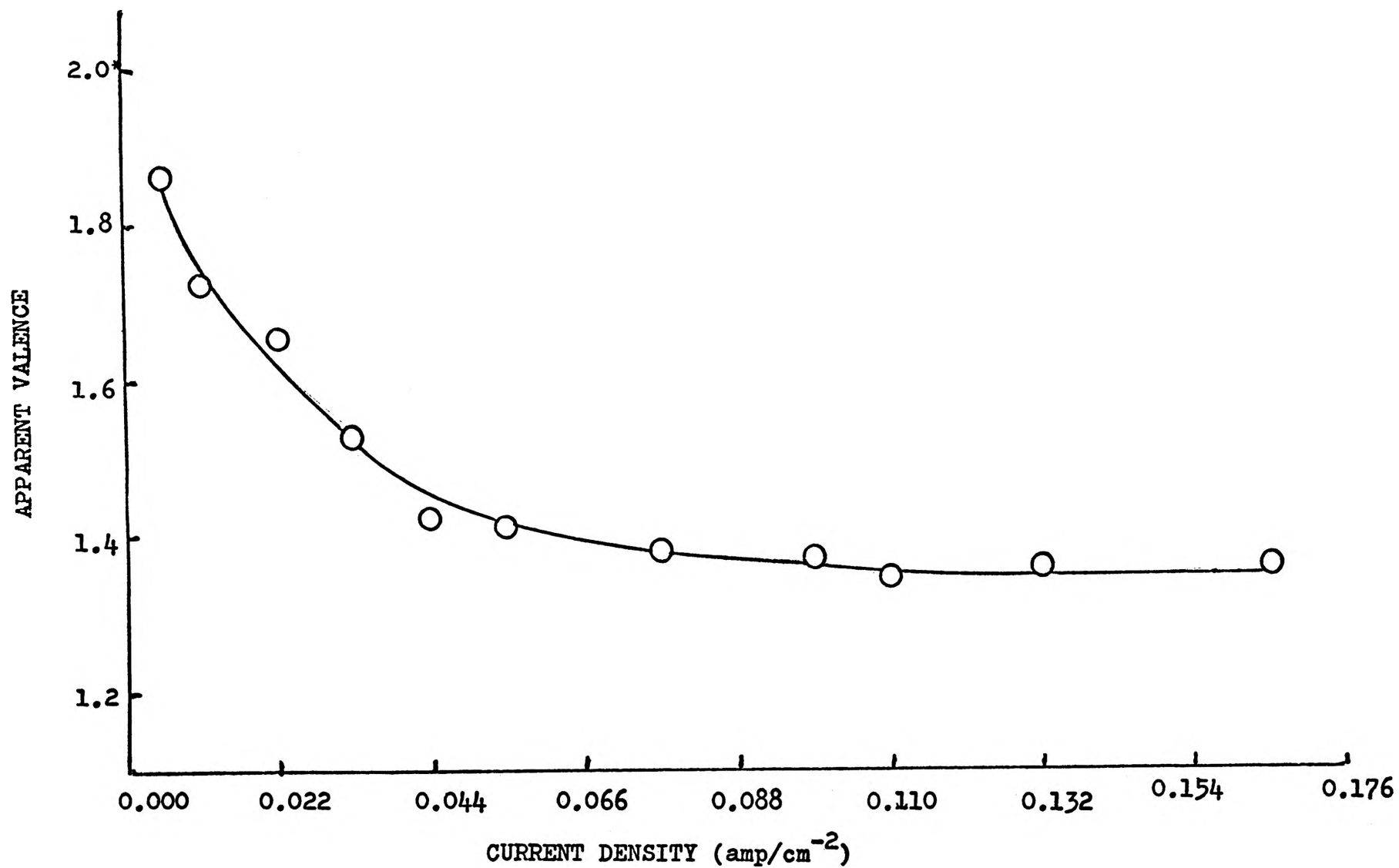dissolved anodically in 3 percent KNO_3 at 60° C.

IV DISCUSSION

Sorenson, Davidson, and Kleinbert (4-7) have proposed that zinc and cadmium dissolve anodically in certain oxidizing salt solutions with an initial mean valence between one and two.

The purpose of this investigation was to obtain experimental data for anodic dissolution of cadmium and to determine whether cadmium enters solution with valencies less than two. Preliminary studies were made to obtain values for the apparent valence of cadmium dissolving anodically in three per cent solutions of potassium chloride, chlorate, and nitrate.

In potassium chloride and chlorate, values of mean apparent valencies are 1.99 and 1.98 (Tables I and II, Pages 11 and 12). Anodic dissolution of cadmium in three per cent potassium nitrate, however, results in valences which are less than +2 (1.46 at 25° C.) and which decrease linearly with increasing temperature (Table III, Page 13 and Figure I, Page 14). These results are in agreement with Sorenson et al, for cadmium dissolving in sodium chloride, chlorate and nitrate.

During electrolysis in potassium nitrate, a grey film formed on the surface of the cadmium electrode but was not present in either potassium chloride or potassium chlorate solution. The interesting fact is that this film is present only when electrolysis is performed in certain oxidizing salt solutions where it is also found that the apparent valence is less than +2. It was suspected that this film formed on the metal anode (Cd and Zn) was in some manner responsible for the abnormal behavior of the anodic dissolution.

As a means of determining the behavior of this film in dissolution, Hoar (18) suggested that the mechanism of anodic dissolution of zinc and cadmium be studied by the use of amalgamated electrodes. The amalgamation would prevent the disintegration of the electrode and the formation of films such as are observed on pure zinc and cadmium electrodes in nitrate solution. 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.
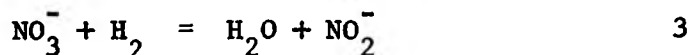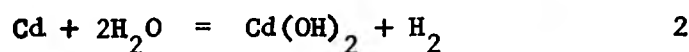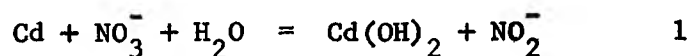
Accordingly, an amalgamated cadmium electrode was prepared and electrolyzed in three per cent potassium nitrate. Values obtained for the mean apparent valence (1.99 and at 25° C.) showed agreement between the faradaic equivalent obtained from the current based on bi-positive cadmium ions and the amount of cadmium dissolved as determined by titration with E.D.T.A. Further tests showed that nitrite ions were absent. The results prove, as in the case of zinc (13), that the concept of uncommon valence states is inadequate to explain the anodic dissolution of cadmium in oxidizing electrolytes.

The studies carried out with a cadmium amalgam electrode aroused interest in the grey corrosion product formed on pure cadmium. The corrosion product was only present when apparent valencies of less than +2 occurred, namely in nitrate solution in the absence of an amalgamated surface.

The grey corrosion product was produced by electrolyzing cadmium in three per cent potassium nitrate at 25° C. and a current density of 0.055 to 0.10 amps per square centimeter surface area.

The metal surface became completely covered with the grey film after about thirty seconds. Then the grey film turned to white gradually. At higher current densities the dark deposit was continually spalled off the surface in small portions. An X-ray analysis of this white deposit was made and proved it was $Cd(OH)_2$ (Table VII, Page 19). The dark grey film could be preserved by removal of all moisture, otherwise it turned white. It was necessary to immerse the electrode in dry acetone; this caused small portions of the grey deposit to flake off the electrode. Observation of those portions, which were spalled off into the acetone, in reflected light at high magnifications revealed many bright metallic particles in the matrix of the dark deposit. In transmitted light, this portion of particles was black. (Figure II, Page 21). An X-ray analysis of this dark deposit produced diffraction lines for cadmium and $Cd(OH)_2$. (Table VIII, Page 22).

Thus it appears that a more likely mechanism is 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 cadmium anode. These particles, possibly due to their size, are very active and are oxidized immediately by nitrate ion or by water to form insoluble $Cd(OH)_2$ followed by the oxidation of hydrogen to water:

$$Cd + NO_3^- + H_2O = Cd(OH)_2 + NO_2^- \qquad 1$$

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

$$NO_3^- + H_2 = H_2O + NO_2^- \qquad 3$$

The rate at which the film is expelled from the surface of the

metal might be expected to increase with temperature, explaining the lower values for the apparent valence of cadmium at higher temperature.

Several quantitative studies were made to determine how much nitrite ion formed after electrolysis in potassium nitrate. Results confirmed that the amount of nitrite ion formed was enough to account for the difference between the amount of cadmium dissolved based on a valence of plus two and actual weight loss of the cadmium electrode, assuming equation (1) holds. This mechanism is more probable than that of Sorenson (4-7), because it not only accounts for the experimental measurement of valence and nitrite ion but also for the presence of metallic particles in the hydroxide film. It also accounts for the film turning white in the presence of water because of the hydrolysis of the metallic particles with the water.

Sorenson indicates that there is no effect of current density on the apparent valence. Actually, the current density is a vital factor affecting the apparent valence. The apparent valence approaches its normal oxidation state of two at a very low current density $(0.001 \text{ amp cm}^{-2})$ and decreases with increasing current density. With current densities larger than 0.06 amp cm^{-2}, the apparent valence remains almost constant within electrochemical side reaction range. This means that the metallic disintegration is proportional to the current density when it is less than 0.06 amp cm^{-2}; after this value the rate of disintegration will remain constant. This proves once again that the electrochemical behavior of cadmium can be satisfactorily explained solely on the basis of divalent ion formation, otherwise this current density affecting the apparent valence cannot be readily explained.

The results in apparent valence which were found to be less than two, and which decrease linearly with increasing temperature during anodic dissolution of cadmium in potassium nitrate solution aroused interest in the evaluation of the activation energy. Using the Arrhenius equation, a plot was made of logarithm of normal valence minus apparent valence versus the reciprocal of absolute temperature at current densities 0.055 and 0.077 amp cm^{-2}, values which lie in the horizontal range of the plot of current density versus apparent valence. From the slopes, an activation energy of a mean value of 0.5 kilocalorie per gram mole was obtained. The small value of the activation energy suggests some controlling step of a physical nature, possibly of an absorptive or desorptive nature rather than a chemical reaction.

The results are in accord with Greenblatt's conclusions (8) wherein he states that the dipositive ion formation is the only posibility consistent with the electrochemical behavior of the anodic dissolution. However, his proposed mechanism does not take into consideration the formation of the grey film and the ejection of the metallic particles during electrolysis. The mechanism proposed in this thesis is consistent with the experimental observations of all investigators of this phenomenon.

RECOMMENDATIONS

Studies using an electrode in a separating compartment and measuring the volume of gas evolved during electrolysis might give some information concerning anodic and cathodic reactions and the mechanism of the metal electrode dissolution in the oxidizing electrolyte.

A closed cell investigation in which atmospheric oxygen would be absent might help to clarify the effect of atmospheric oxygen on the rate of metallic disintegration.

V SUMMARY AND CONCLUSIONS

The purpose of this investigation was to obtain experimental data for anodic dissolution of cadmium and to determine whether cadmium enters solution with valencies less than two.

The anodic dissolution of cadmium was studied in potassium chloride, chlorate and nitrate. A titration with disodium E.D.T.A. was used to determine the weight loss of the cadmium electrode during electrolysis. The temperature was controlled by means of a constant-temperature water bath or an ice bath. The current was measured by means of a sensitive milliammeter. In potassium nitrate solutions, the temperature was varied from 5.0° C. to 60.0° C. and an amalgamated cadmium electrode was used for several runs. The surface film formed on cadmium while dissolving anodically in potassium nitrate was studied. This led to the following results:

(1) In potassium chloride and potassium chlorate, cadmium exhibits a normal valence of plus two; in potassium nitrate, however, apparent valence less than two occur, becoming smaller with increasing temperature.

(2) When amalgamated cadmium is anodically dissolved in potassium nitrate, valencies of only plus two are exhibited.

(3) A grey film forms on cadmium during electrolysis in nitrate solutions but does not form when the electrode is amalgamated or in chloride and chlorate solutions. This grey film is composed of many tiny metallic cadmium particles embedded

in a matrix of $Cd(OH)_2$. At higher current densities this film is partially spalled off the electrode, turning white.

On the basis of the above, it is concluded that the normal valence of cadmium ions does not change during anodic dissolution in nitrate solution. The apparent valence of less than two arises as consequence of a partial disintegration of the anode. The tiny metallic particles embedded in a hydroxide matrix constitute the dark film which flakes off into the electrolyte, where the cadmium particles react with the oxidizing agent. The dissolution of cadmium outside the electrical circuit thus accounts for the lower coulombic equivalent.

LIMITATIONS

Temperature When runs were made at higher temperature, the volume of the reacting solution was assumed to remain the same. However, at temperature around 60° C., some evaporation will occur, changing the concentration of solution from time to time.

When runs were made at a temperature of 5° C., an ice bath was used; however, the temperature of the electrolyte was 5°C. ± 2°C. because of the poor conduction of the glass beaker.

E.D.T.A. Titration As the runs at higher temperature had to be made at shorter time intervals, the total volume of the E.D.T.A. was sometimes less than one milliliter. Thus, even using a microburette, an error of one drop in titration could introduce a relative error of from 2 to 4 per cent.

VI APPENDIX

MATERIALS

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

1. (Ethylenedinitrilo) Tetraacetic acid, Disodium salt. Reagent grade. Distillation Products, Eastman Organic Chemicals, Rochester 3, New York.

2. Triethanolamine, N.F. Reagent grade, Fisher Scientific Company, Fair Lawn, N.J.

3. Potassium Chloride. Reagent grade, meets ACS specifications. J.T. Baker Chemical Co., Phillipsburg, N.J.

4. Potassium Chlorate. Reagent grade, meets ACS specifications. Allied Chemical Corporation, New York, N.Y.

5. Potassium Nitrate. Reagent grade, meets ACS specifications. J.T. Baker Chemical Co., Phillipsburg, N.J.

6. Mercury. Redistilled. Fisher Scientific Company, Fair Lawn, N.J.

7. Cadmium. 99.99 per cent purity, obtained by Dr. M.E. Straumanis.

APPARATUS

Mounting and Surface Preparation of Cadmium Specimens

1. **Belt Surfacer.** Buehler No. 1255, Buehler Ltd., Evanston, Ill.

2. **Hand Grinder.** Handimet, 4 stage, Buehler No. 1470, Buehler Ltd., Evanston, Ill.

3. **Centermet Press.** One-inch mold, Buehler No. 1303, Buehler Ltd., Evanston, Ill.

Constant Temperature Bath Apparatus

1. **Heater, Immersion.** 115 v 500 w, ac, Central Scientific Co., Chicago, Ill.

2. **Motor, Stirrer.** Pensky-Martins Motor Stirrer, 115v, 60c, ac, Fisher Scientific Co., Pittsburg, Pa.

3. **Switch, Relay.** Type SR600A, 115v, ac, Philadelphia Scientific Glass, Quakertown, Pa.

4. **Thermoregulator.** Type SE-712, Philadelphia Scientific Glass, Quakertown, Pa.

Electrolysis Apparatus

1. **Ammeter.** Model 931, Weston Electric Instrument Corporations, Newark, N.J.

2. **Cells, Dry.** General Purpose, 1.5v.

3. **Motor, Stirrer** (Reactor). Fultork Labmotor, 115v, 60c, ac, Fisher Scientific Co., Pittsburg, Pa.

4. **Resistance Box.** Decade type, Graduated from 0 to 9999 ohms in one ohm division, Central Scientific Co., Chicago, Ill.

Miscellaneous Special Equipment

1. __Beakers, Pyrex.__ 50, 100, 250, 400, and 600 ml capacity.

2. __Burette, Micro.__ Shelback, 10 ml, 0.05 ml graduations, Fisher Scientific Co., Pittsburgh, Pa.

3. __Pipettes.__ 2, 5, 10, 25, and 50 ml.

4. __Volumetric Flask.__ 100, 250 and 500 ml capacity.

5. __Erlenmeyer Flask.__ 250 and 300 ml capacity.

6. __Graduated Cylinder.__ 10 and 100 ml capacity.

MISCELLANEOUS EXPERIMENTAL PROCEDURES

Standardization of Disodium E.D.T.A.

The procedure for this part of the experimentation follows
as a step-by-step operation.

1. Accurately weigh out approximately three-tenths of a
   gram of cadmium metal of 99.99 per cent purity.

2. Transfer to a 100 milliliter volumetric flask and dissolve
   in 1.3 diluted HCl: mix thoroughly.

3. Withdraw 5 ml aliquot by means of a pipette.

4. Dilute to 100 ml with distilled water and heat to about
   80° C.

5. Add 5 ml pH 10 buffer solution.

6. Add one drop of Erichrome Black-T indicator solution.

7. Titrate with 0.05 M disodium E.D.T.A. in a micro burette
   until one drop turns solution blue.

8. Determine the cadmium equivalent of the disodium E.D.T.A.
   solution in gm cadmium/ml.

Surface Preparation of Cadmium Specimens

The following procedure was used for the cadmium metal surface
preparation.

1. Remove all pits and irregularities from the surface with a
   belt surfacer equipped with a No. 150 grit abrasive cloth belt.

2. Finish the sample surface on a water-flushed four-stage
   hand grinder equipped with numbers 240, 320, 400, and 600
   abrasive strips, proceeding from the coarsest to the finest.

3. Wash the sample with distilled water.

Treatment of White Precipitate and Grey Film Formed on the Cadmium Electrode

The following procedure was used for treating the grey film formed during the anodic dissolution of cadmium in aqueous potassium nitrate.

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

2. Then the film surface is massaged with a rubber policeman until it completely flakes off the electrode into a beaker containing 10 ml 1:1 HCl.

3. The combined acid solution is added to the electrolyte where it dissolves the white precipitate.

Quantitative Test for Nitrite Ion

1. Pipette 5 ml of 0.0455 N $KMnO_4$ solution into a flask.

2. Add one ml of concentrated sulfuric acid.

3. Heat to about 40°C.

4. Titrate with electrolyte to the end point.

5. Determine the equivalent weight of nitrite ion in the electrolyte.

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VIII ACKNOWLEDGEMENTS

IX VITA

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