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EFFECT OF TEMPERATURE ON THE
ELECTROCHEMICAL KINETICS OF GADOLINIUM
IN THE CURIE REGION

by

David W. DeBerry

A THESIS SUBMITTED
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REQUIREMENTS FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

Thesis Director's signature:

A handwritten signature in dark ink, appearing to read "Harold G. DeBerry", is written over a horizontal line. A vertical line descends from the left side of the signature.

Houston, Texas

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CHAPTER I

INTRODUCTION

The influence of the nature of a metal electrode on the rates of electrochemical reactions involving that electrode is of interest both in obtaining a fundamental understanding of electrochemical kinetics and in practical electrochemical applications. The practical applications include the selection of efficient fuel cell and battery electrodes and the design of corrosion-resistant materials. Fundamental research is intimately related to the complex nature of electrochemical kinetics. The comparison of results obtained for different metals is complicated by simultaneous changes in many properties which might influence the rates and occasionally by changes in reaction mechanisms. Similar problems are encountered (to a lesser extent) in the use of alloys, along with unknown variations in the surface compositions relative to the bulk compositions.

The object of the research described in this thesis was to determine the rates of electrochemical reactions involving gadolinium metal in the paramagnetic and ferromagnetic states. This represents an attempt to investigate the effect of changes primarily in the electronic structure of a pure metal on its electrochemical kinetics properties.

Changes in the reactivity of metals and alloys at their Curie points have been observed for many reactions. Much of this work has been done in the field of gas/solid catalysis. The observed variation in the temperature coefficient of the reaction rate at the Curie point is known as the magnetocatalytic or Hedvall effect^{1, 2, 3}. For example, in the decomposition of formic acid by a cobalt-palladium alloy there is a 30 percent increase in the Arrhenius activation energy and a thousandfold increase in the pre-exponential factor above the Curie point. Similar results were obtained for the oxidation of iron-chromium alloys in an oxygen atmosphere⁵. In general both the apparent activation energy and pre-exponential factor change in such a way as to give a practically smooth overall Arrhenius curve. Explanations of the effect are usually given by qualitative discussions of changes in electronic states, orientation of electron spins, d-band holes, and work function^{6, 7}.

A related area involves the study of reactions at a series of alloys with compositions ranging from ferromagnetic to paramagnetic at constant temperature. Conway determined the electrochemical rates and activation energies of the hydrogen evolution reaction (HER) at a series of Cu-Ni alloys. The apparent activation energies and exchange current densities decrease from pure Ni to pure Cu, but

beyond 60 percent Cu the relative changes were much smaller. The results were interpreted as reflecting changes in the metal-H bond energy caused by changes in the number of d-holes per atom of Ni, "although variations of the d-electron configuration can account only for about 20 percent of the M-H bond energy...". Anodic passivation studies of Ni alloys indicate anomalous changes at the critical alloy compositions^{9, 10}. These too have been attributed to changes in the d-electron configuration.

Some doubt has recently been expressed as to whether any correlation exists between d-band character and M-H bond energy¹¹. There is also evidence that even in Cu-Ni alloys the surface composition may be quite different from the bulk composition¹².

Gadolinium was chosen for this research since its Curie temperature (17°C) is in a readily accessible temperature range. Electrochemical measurements at a gadolinium electrode are complicated by the thermodynamic instability of the metal in the presence of water¹³.

The mixed potential of Gd in aqueous solutions (pH 5-6) was measured over a temperature range including the Curie point by Prall¹⁴ and later by Daire¹⁵. Below the

Curie point they both observed a rapid increase in the mixed potential to more active values as the temperature was increased. Prall assumed that changes in the work function or sublimation energy of Gd might make the ferromagnetic electrode more electropositive. Daire suggested that his results might be explained by either an abnormal increase in the anodic dissolution rate of Gd or the presence of electronic surface states different from those in the bulk metal near the Curie point. He also indicated that it was difficult to explain the changes in terms of classical thermodynamics. Earlier work by Daire did not show any abnormal changes (within the experimental error of ± 0.3 kcal) in the heat of solution of Gd in 1 N HCl from $3^{\circ} - 40^{\circ}\text{C}^{16}$.

It is impossible to draw any firm conclusions from the results given above. Mixed potential measurements in this type of system give only a rough indication of the relative rates of the anodic and cathodic reactions proceeding simultaneously at open-circuit. The specific rates of the separate reactions cannot be determined from this measurement.

Investigations of the kinetics of the hydrogen evolution reaction (HER) and the anodic dissolution of metals have led to an extensive literature. Several

reviews are available for the HER^{17, 18, 19, 20} and for the anodic dissolution reaction^{21, 22}. Much of the work relating to the influence of the electrode material has been done for the HER and is contained in the reviews cited. The rare earth metals have received relatively little attention. Greene has reported some corrosion studies in several systems²³ and polarization curves in phosphoric acid solutions for the rare earth metals^{24, 25}. No kinetic parameters could be obtained for the anodic dissolution reaction.

The experiments presented here were designed to measure the rates of anodic dissolution of Gd and hydrogen evolution at Gd separately, and to exclude other possible reactions.

CHAPTER II

EXPERIMENTAL

A. Materials

The gadolinium was obtained from Materials Research Corporation (Job No. 27426) in the form of 0.25 inch diameter cast rods prepared from the distilled metal. The typical emission spectrographic analysis supplied with the sample lists the following impurities: 0.005% Eu, Dy, Y; 0.01% Sm, Tb, Ca, Mg, Si, Fe, Al. Details of electrode construction and preparation are given in the Apparatus Section.

The water used for solution preparation was purified by distillation from a two-stage quartz still (Amersil Inc., Model Bi-4) fed with laboratory deionized water. The suitability of this water for electrochemical measurements was tested by measuring the cathodic current-potential curve at a Pt rotating disc electrode in 0.5 M H_2SO_4 solution. Reproducible linear Tafel slopes of 0.032 v were obtained, in agreement with previous investigations¹⁷.

Reagent grade chemicals were used in preparing the solutions. A Beckman Expandomatic pH meter and glass

electrode were used to measure the pH of the solutions. Standard pH 4.01 and pH 7.00 buffer solutions were used to calibrate the instrument. Glassware used in solution preparation was cleaned in alcoholic KOH, then in a mixture of 1:1 concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ followed by thorough rinsing with distilled water.

High purity grade helium was used to deaerate the test solutions. Trace oxygen was removed by passing the helium through a tube containing Ridox oxygen scavenger (Fisher Scientific Co.). The helium was bubbled through a gas washing bottle containing the test solution before entering the cell. Connections were made with glass tubing and ball joints.

B. Apparatus

A diagram of the cell is shown in Figure 1. All parts of the cell were either Pyrex glass, Teflon or platinum. Joints were lubricated only with cell solution or distilled water. Teflon standard taper adapters were used to fit the reference electrode, thermometer, and rotating electrode body to the cell. The main body of the cell was jacketed to allow circulation of water from a constant temperature bath. A large area Pt gauze auxiliary

FIGURE 1
CELL DIAGRAM

- 1a. Top View of Cell Head (Schematic); $\frac{1}{2}$ Actual
Size
- 1b. Cross Section of Rotating Electrode; Actual
Size
- 1c. Cell and Rotating Electrode; $\frac{1}{2}$ Actual Size

electrode was contained in a tube separated from the main cell solution by a fine glass frit. The reference compartment and bridge were filled with the same solution as used in the cell but were separated from the main cell compartment by a coarse frit. Helium entered the cell as shown and was discharged through a small bubbler. The working volume of the main cell body was 150 ml.

Before each series of runs the cell was cleaned in 1:1 concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ for at least 48 hours followed by thorough rinsing and soaking with distilled water. Occasionally the acid step was preceded by cleaning in alcoholic KOH.

A precision -1° to 51°C (with 0.1°C subdivisions) thermometer was used in the cell. It was found to be in agreement with an Anschutz thermometer over the temperature range studied.

The reference half-cell was a calomel, 1 N KCl electrode (normal calomel electrode). It was prepared from a commercial (Fisher Scientific Co., part number 13-639-52) porous plug calomel electrode by replacing the saturated KCl filling solution with (calomel saturated) 1.00 M KCl. The normal calomel electrode has a lower temperature coefficient near room temperature than the

usual saturated calomel electrode. The recommended potential of the normal calomel half-cell is 0.280 v vs. SHE at 25°C²⁶.

A Beckman Rotating Electrode assembly was used to drive the Gd rotating disk electrode (RDE). The RDE consisted of a Gd cylinder machined to fit very tightly in a cylindrical Teflon sheath so that only the end of the metal was exposed (Figure 1b). The other end of the Gd cylinder was drilled and tapped for connection to the drive shaft of the rotating electrode body.

Three Gd RDE's were used in this work. The diameter of each was measured using a cathetometer and used to calculate the apparent surface area. The surface areas were 0.212, 0.233, and 0.196 cm² with a mean deviation of ± 0.005 cm² in each case. The electrodes were thoroughly degreased and stored in trichloroethylene when not in use. Just before use the electrode was polished on 3 M 600 grit and Buehler 4/0 grit emery paper.

The cell temperature was regulated to within $\pm 0.03^\circ\text{C}$ by circulation of water from a constant temperature water bath. The water bath was cooled by a Sargent water bath cooler. A Bronwill mercury thermoregulator controlling a knife heater was used to maintain the desired bath temperature.

C. Electronics

Cell potentials were measured to the nearest millivolt using a Non-Linear Inc., Model 5005 digital voltmeter. A Keithley Model 610B electrometer was used for this purpose in preliminary work. There was negligible circuit loading by the more accurate digital voltmeter in the systems used.

The scanning potentiostat was constructed in this laboratory using Teledyne-Philbrick operational amplifiers. A circuit diagram of the major components is shown in Figure 2. The design is conventional²⁷. Compensation of the ohmic potential drop in the solution (IR_s) was achieved by positive feedback to the control amplifier of a signal equal to IR_s . This was done by setting R_c (Figure 2) equal to the solution resistance. The solution resistance (between the working electrode and the reference electrode probe tip) was initially obtained using galvanostatic pulse measurements (see below). Later it was found that the same value could be obtained by setting R_c just (~ 1 ohm) below the point where current oscillations began.

In use, the initial voltage source was set equal to the "open-circuit" cell potential so that there was zero current through the cell. The voltage (corrected for IR_s)

FIGURE 2
POTENTIOSTAT CIRCUIT

Rc: 1K, 10-TURN, PRECISION

R_W: IK, 0.25%

R_1, R_2, R_3, R_4 : 10K, MATCHED

applied to the working electrode was then the same as the output of the ramp generator. A Moseley 2DR-2 X-Y recorder was used to record the current-follower output versus the ramp generator output. This recorder is accurate to within 0.2% of the full-scale range. In terms of the range used to measure the ramp voltage this corresponded to an error of less than ± 1.5 mV. The repeatability was within ± 1 mV.

Galvanostatic (constant current) pulses were generated and observed using the circuit and components shown in Figure 3. The current was measured by replacing the cell with a precision resistor and measuring either the voltage output of the Tektronix Type 161 pulse generator or the voltage drop across the precision resistor. The cell response was displayed on a Tektronix 535A oscilloscope and photographed using a Tektronix model C-12 camera system. The rise time of the pulse generated by the apparatus was about one microsecond.

The ohmic potential drop between the working electrode and reference probe tip was determined from the discontinuity in the potential versus time trace at the start of a constant current pulse²⁸. The corresponding solution resistance was then calculated from the known input current (usually 2.0 mA). In most cases an oscilloscope sweep rate of 0.1 msec/division and pulse duration

FIGURE 3
GALVANOSTAT CIRCUIT

AMPLIFIERS:
1. 1021
2. QFT-5

of 0.4 msec were used. Both single and repetitive (10/sec) pulses were employed. Double layer charging curves were measured using the same apparatus and an oscilloscope sweep rate of 2μ sec/division.

The X-Y recorder and digital voltmeter were calibrated using a voltage source standardized with a Leeds and Northup Type K-3 potentiometer. The digital voltmeter was accurate to within ± 1 mV over the range used in the experiments. The potentiostat was checked using the digital voltmeter and precision resistors. The oscilloscope internal calibrator was adjusted according to the manufacturer's instructions and used to calibrate the pre-amplifier.

D. Experimental Design and Procedure

The experimental design and procedure for determining the charge-transfer reaction rates evolved from preliminary experiments and consideration of the results in terms of the goals stated in Chapter I. The apparatus was designed and purification procedures followed to reduce the chances of complications due to impurities. The electrolyte system was selected based on the results given in Chapter III. The experimental procedure was then

chosen to give reproducible and kinetically useful results for this system, in which the reaction rates are moderately high.

There are several transient or perturbation methods which are used to study fast electrochemical reactions²⁹. Even using "ideal" solid electrode systems these measurements are difficult to interpret and their precision is often low. Attempts to use a galvanostatic pulse method were unsuccessful due to both of these points.

A rotating disk electrode was employed to give high and reproducible mass transfer rates to and from the electrode surface. The RDE reduced the accumulation of reaction debris at the electrode surface and minimized mass transport control of the reaction rates at moderate current densities. A rotation rate of 50 rps was found to give satisfactory results. Higher rotation rates were tried but erratic behavior was observed.

The actual rate or current-potential measurements were made by polarizing the working electrode potentiostatically at a constant scan rate and measuring the resulting current as a function of the applied potential (the so-called potentiokinetic or potentiodynamic method). The

scan rate of 0.050 v/min was chosen as a compromise between the two goals of approaching steady state and minimal disturbance of the electrode surface. In a given run the cathodic scan was made first, followed by the anodic scan. Equivalent results were obtained for the anodic scan if it was done first, but the subsequent cathodic scan results were different and erratic.

The IR_s compensation circuit (Section C) was added to minimize the contribution of the nonfaradaic ohmic potential drop in solution to the polarization results. The reference electrode probe tip cannot be placed very close to an RDE without disturbing the solution flow.

The steps followed in making a typical run are summarized below. Details of some of the steps have been given in previous sections.

After cleaning, the cell was rinsed and filled with test solution. The solution was deaerated for at least four hours at room temperature. The cell temperature was then adjusted to the desired value. Helium was bubbled through the solution at all times during the run. The solution was stirred with a Teflon covered magnetic stirrer for efficient deaeration and uniform thermal distribution.

The electrode was polished, then rapidly attached to the rotating electrode shaft and placed in the cell. Rotation of the electrode at 50 rps was started. The open-circuit cell potential was recorded as a function of time of immersion. The ohmic cell resistance was determined and used to set the potentiostat IR compensator as previously described. After 30 minutes immersion the initial potential of the potentiostat was set to correspond to the open-circuit cell potential and the cell was switched into the potentiostat circuit. The cathodic scan was then recorded, starting at the open-circuit potential (recorded to the nearest millivolt) and continuing for about 0.35 v at 0.050 v/min. The cell was returned to open-circuit and after about 5-10 minutes the anodic scan was recorded using the same procedure. The electrode was removed, cleaned, and polished before the next run. The solution was replaced and the cell cleaned at frequent intervals.

CHAPTER III

RESULTS

A. Selection of Electrolyte System

In preliminary work the electrochemical behavior of gadolinium was studied in a number of electrolyte solutions. The aqueous acetic acid/sodium acetate, pH 5.0 - 6.5, system was finally chosen for detailed study. Before giving the results obtained in this system, the qualitative results obtained in the other systems will be briefly described.

In acidic aqueous solutions (0.2 M NaClO_4 + HClO_4 to pH 1-3) Gd undergoes very rapid attack with vigorous hydrogen evolution. The polarization curves show almost complete mass transfer control. In pH 12, 0.5 M Na_2SO_4 solution a fine white precipitate [probably $\text{Gd}(\text{OH})_3$] is formed on part of the electrode surface. The corrosion rate is substantially decreased in slightly acidic or neutral (pH 5-7) aqueous salt solutions. In this category, solutions of NaClO_4 , Na_2SO_4 , $(\text{NH}_4)_2\text{SO}_4$, GdCl_3 , and $\text{Gd}(\text{ClO}_4)_3$ were used. Reproducible and kinetically useful results could not be obtained in these unbuffered solutions. This is probably due to changes in the pH of the solution, and

especially changes near the electrode surface during polarization. The pH of the solutions was found to increase even during short (~ 30 min.) runs. In addition, localized corrosion and pitting of the electrode was usually evident, especially in solutions containing chloride ion.

Several attempts to study the Gd^{3+}/Gd reaction in nonaqueous solvents (acetonitrile and dimethylformamide) were unsuccessful. The open-circuit potential of the electrode was always much more positive (noble) than that expected for this couple. The measured potential was not reproducible and at times slow oscillation could be observed. The electrode was readily polarized at small current densities (e.g., $\Delta V \approx 0.5$ v for $i = 10 \mu\text{A}/\text{cm}^2$). This behavior is probably caused by oxidation of the metal surface by water in the solution to form a stable film. The procedure followed for the purification of dimethylformamide is said to reduce the water concentration to less than 20 ppm³⁰.

These results indicated that it was necessary to use a buffered, slightly acidic aqueous electrolyte solution. The acetic acid/sodium acetate buffer system was found to be satisfactory. Other possible systems (phosphate, carbonate, dicarboxylic acids) are expected to introduce more complications due to adsorption, side reactions, or formation of insoluble gadolinium compounds.

A relatively high (1.00 M) concentration of sodium acetate was used to reduce double layer effects, increase buffer capacity, and reduce solution resistance. The surface of the electrode is somewhat roughened in the acetate solution and appears gray-metallic after removal from solution. There is no apparent localized corrosion or pitting. An example of the open-circuit potential (V_M)-time behavior is shown in Figure 4. The fairly stable values obtained after about 25 minutes were reproducible to within an average of ± 0.011 volts.

B. Polarization Curves and Transfer Coefficients

Polarization curves were recorded at each temperature and pH using the procedure given in Chapter II. Some of the results obtained are given in Figures 5 - 8 as $\log i$ versus π , where i is the current density and π is the polarization ($\pi = V - V_M$). The most linear curves were obtained in the higher pH solutions (pH 5.94 and 6.46) since in these the open-circuit corrosion current density is relatively low compared to the current densities at which mass transfer becomes important. The linear Tafel slopes obtained in these solutions were used to obtain the anodic (α_a) and cathodic (α_c) transfer coefficients presented in Table 1.

$$\alpha_j = (\ln 10) RT/F \left| d \log |i| / d\pi \right| \quad (1)$$

FIGURE 4
MIXED POTENTIAL VERSUS TIME FOR
Gd AT 17.3°C IN pH 5.94,
1.00 M SODIUM ACETATE SOLUTION

FIGURE 5
POLARIZATION CURVES FOR Gd
IN pH 5.06 ACETATE BUFFER AT
7.3, 13.0, AND 17.3°C

FIGURE 6
POLARIZATION CURVES FOR Gd IN
pH 5.45 ACETATE BUFFER AT
7.3, 13.0, and 21.2°C

FIGURE 7
POLARIZATION CURVES FOR Gd IN
pH 5.94 ACETATE BUFFER AT
10.1, 19.0, AND 25.6°C

FIGURE 8
POLARIZATION CURVES FOR Gd IN
pH 6.46 ACETATE BUFFER AT
13.0, 17.3, AND 27.6°C

TABLE 1
EXPERIMENTAL TRANSFER COEFFICIENTS

<u>t (°C)</u>	<u>α_c</u>	<u>α_a</u>
5.6	0.31	0.38
7.3	0.33	0.41
10.1	0.30	0.41
13.0	0.33	0.40
16.2	0.34	0.40
17.3	0.35	0.40
19.0	0.34	0.39
21.2	0.36	0.40
23.3	0.34	0.38
25.6	0.33	0.41
27.6	0.35	0.38
29.7	<u>0.32</u>	<u>0.37</u>
Average	0.33	0.40

The same slopes can be seen to apply to the lower pH results at moderate current densities. The lower limit is at about pH 5.06, however, since results obtained at pH 4.70 did not show any appreciable linear region. The transfer coefficients are independent of temperature within experimental error (± 0.03 in α).

The cathodic Tafel slope of 0.170 V (at 25°C) obtained by Greene²⁵ in phosphate buffered solutions is in good agreement with the results given here. He was unable to obtain linear anodic Tafel slopes in these solutions.

C. Reaction Orders

Reaction order determinations were made at several different temperatures. The effect of solution pH on the rates of both the cathodic and anodic reactions is shown in Figures 9-11. The sodium acetate concentration was 1.00 M for all of these determinations. The dependence of anodic reaction rate on acetate ion concentration was determined at pH 5.45 by varying the sodium acetate concentration while maintaining a constant ionic strength ($I = 1.00$ M) by addition of NaClO_4 . These results are shown in Figure 12. The reaction orders were obtained from the least squares slopes of these curves. In all

FIGURE 9
CATHODIC LOG i VERSUS pH at 7.3, 17.3, 27.6°C
 i MEASURED AT -1.220 V VERSUS SHE

FIGURE 10
CATHODIC LOG i VERSUS pH 13.0, 21.2°C
 i MEASURED AT -1.220 V VERSUS SHE

FIGURE 11
ANODIC LOG $|i|$ VERSUS pH;
 i MEASURED AT -0.920 V VERSUS SHE

FIGURE 12
ANODIC LOG $|i|$ VERSUS LOG (ACETATE CONCENTRATION);
7.3°C: i MEASURED AT -0.940 V VERSUS SHE
17.3, 25.6°C: i MEASURED AT -0.920 V VERSUS SHE

cases there is no apparent temperature dependence. For the hydrogen evolution the average reaction order is given by Equation 2 (95% confidence limits):

$$\left(\frac{\partial \log i}{\partial \text{pH}} \right)_{V, (\text{Ac}^-), T} = -1.11 \pm 0.06 \quad (2)$$

Within experimental error, the Gd dissolution reaction orders with respect to both pH and acetate ion concentration are zero. The results are summarized in Table 2.

For each order determination the constant cell potential was chosen such that the corresponding current densities were in the linear $\ln i$ vs. π region. The temperature variation of the pH of these solutions was estimated using thermodynamic data³¹. The maximum change is about the same as the uncertainty of the pH values measured at 25°C (± 0.03 pH units) and no correction was attempted.

D. Temperature Dependence

1. The Hydrogen Evolution Reaction

The temperature dependence of each reaction rate was determined at a constant cell potential with respect to a reference electrode at room temperature.

TABLE 2
REACTION ORDERS

<u>Cathodic</u>		<u>Anodic</u>	
<u>t (°C)</u>	<u>p(H⁺)</u>	<u>p(H⁺)</u>	<u>p(Ac⁻)</u>
7.3	1.04 ± 0.13	0.10 ± 0.15	0.01 ± 0.14
13.0	1.20 ± 0.20	0.01 ± 0.08	-----
17.3	1.13 ± 0.13	0.02 ± 0.12	-0.03 ± 0.19
21.2	1.08 ± 0.13	0.01 ± 0.12	-----
27.6	1.11 ± 0.11	0.05 ± 0.15	-----
25.6	-----	-----	0.04 ± 0.12

The thermal liquid junction potential (TLJP) developed in the solution (1.00 M NaAc/HAc) salt bridge was estimated from published data³² and found to be negligible (0.02 mV/deg) over the temperature range used. Most other electrochemical activation energy determinations have been carried out in acidic or alkaline solutions in which the TLJP's are large and not accurately known. This has led to the use of isothermal working and reference electrodes. This introduces additional uncertainties since the temperature dependence of the reference electrode-solution potential difference is unknown⁸. Further discussion of the desirability of using the measurements at constant cell potential is given in Chapter IV.

Current densities corresponding to a constant cell potential of -1.220 v vs. SHE (25°C) were obtained from the experimental polarization curves for all temperatures and pH values used. This cell potential was chosen so that for each run the current density would be in the linear region of the $\ln i$ vs. π plot. The $\ln i$ values obtained in the pH 5.06, 5.45, and 6.46 solutions were then converted to the corresponding values for pH 5.94 using Equation 2.

The results are shown in Figure 13 as a plot of the average values of $\ln i$ vs. $1/T$. This graph represents

FIGURE 13
CATHODIC LOG i AT -1.220 V VERSUS SHE
VERSUS $1/T$

a total of 63 runs at 12 temperatures. The mean deviation is indicated for each point. Values of the slopes, intercepts, and standard deviations calculated for the overall curve and indicated high and low temperature intervals using a replicated data linear least squares method are given in Table 3. An analysis of variance of regression was carried out following a known procedure³³. There is a significant reduction in the amount of deviation using the two individual lines compared to the overall regression line (ratio of mean squares = 4.13; $F_{0.05,2/59} = 3.15$). The difference between the slopes of the individual lines is significant at the $F_{0.01}$ level.

2. The Gadolinium Dissolution Reaction

The data treatment was analogous to the HER except that no pH normalization was necessary since the reaction order is zero. The current densities were measured at -0.920 v vs. SHE (25°C) and were in the linear $\ln i$ vs. π region. The results are shown in Figure 14 as a plot of the average values of $\ln i$ vs. $1/T$. This graph represents a total of 65 runs at 12 temperatures. The resulting weighted least squares values are given in Table 3. A highly significant reduction in the amount of deviation is obtained by using the high and low temperature

TABLE 3

ACTIVATION ENERGIES AND PRE-EXPONENTIAL FACTORS

	Cathodic Temperature Range, ($^{\circ}\text{C}$)		Anodic Temperature Range, ($^{\circ}\text{C}$)	
	(5.6-16.2)	(17.3-29.7)	(5.6-16.2)	(17.3-29.7)
E (kcal/mole)	8.89 $\pm$ 2.40	16.21 $\pm$ 2.88	14.51 $\pm$ 1.39	12.11 $\pm$ 2.05
$\ln B$	8.87 $\pm$ 8.75	21.77 $\pm$ 4.90	18.87 $\pm$ 2.42	15.02 $\pm$ 3.65
No. of Runs	29	34	63	30
OSS ^a	1.93627667	1.39671461	3.7997982	0.36008640
E ^o (kcal/mole) ^b	18.2	25.5	23.8	24.7
			17.6	21.0

Notes: 95% Confidence Limits Shown

a: Overall Sum of Squares of Deviations

b: E Referenced to Standard Potentials

FIGURE 14
ANODIC LOG $|i|$ AT -0.920 V VERSUS SHE
VERSUS $1/T$

intervals as compared to the overall regression line (ratio of mean squares = 10.41; $F_{0.01,2/61} = 4.98$). This is due primarily to the significant difference in the two individual slopes for which ratio = 19.20, $F_{0.01,1/61} = 7.08$.

The activation energy of an electrochemical charge-transfer reaction depends upon the potential at which it is measured. This study is concerned only with changes in the activation energy at a given potential so that it is not necessary to consider the potential dependence. For completeness, however, the approximate activation energies at the standard potentials, V_j^0 , of the H^+/H_2 and Gd^{3+}/Gd electrodes were calculated by adding $|\alpha_j F(V - V_j^0)|$ to the experimental activation energies obtained at V . These values are given in Table 3.*

*The V^0 value of the Gd/Gd^{3+} electrode was taken as -2.29 V vs. SHE for these calculations. This value is based on the heat of solution of Gd measurements given by Spedding³⁴ and by Daire¹⁶ which are in good agreement. The V^0 value usually quoted (-2.40 V) is based on the heat of solution measurements by Bommer³⁵ which have been criticized by Spedding. Experimental values at 25°C for S_{Gd}^0 (16.267 eu)³⁶ and $S_{Gd^{3+}}^0$ (-48.0 eu)³⁷ were used in the calculation of the V^0 proposed here.

E. Other Results

Some double layer capacity results were obtained using the galvanostatic single pulse method³⁸. No systematic study was attempted. In pH 6.46 NaAc/HAc solution the measured double layer capacity is about $40 \mu\text{F}/\text{cm}^2$ at the open circuit potential. There is a small increase on cathodic polarization to about $46 \mu\text{F}/\text{cm}^2$ at $\pi = -0.5 \text{ v}$. The apparent surface area of the electrode was used in the calculations.

The concentration of Gd^{3+} was determined in each solution used for a series of runs by titration with standard EDTA using Eriochrome Black T indicator. The solutions were buffered to pH 7 using triethanolamine. The concentration of Gd^{3+} ranged from about $1.0 \times 10^{-4} \text{ M}$ to $4.0 \times 10^{-4} \text{ M}$ depending on the solution pH and duration of electrode immersion. This is approximately the concentration range expected for the observed corrosion currents. Other results given here are apparently insensitive to this amount of Gd^{3+} in solution since results obtained in fresh solutions agreed with those obtained after several runs in the same solution.

True steady state mixed potentials were not obtained. The mixed potentials given here represent those measured about 25 minutes after the electrode was placed in solution. The results obtained at all pH values were referenced to pH 5.94 using Equation 3 and the experimental transfer coefficients and reaction order (1.11).

$$\left(\frac{\partial V_M}{\partial \text{pH}} \right)_T = \frac{-1.11(\ln 10)RT}{(\alpha_a + \alpha_c)F} \quad (3)$$

The results are shown in Figure 15.

FIGURE 15
MIXED POTENTIAL VERSUS TEMPERATURE

CHAPTER IV

DISCUSSION

The results given in Chapter III can be divided into two groups: (1) transfer coefficients and reaction orders relating to the mechanisms of the hydrogen evolution reaction (HER) on gadolinium and the anodic dissolution of Gd, (2) the rates of these reactions as a function of temperature. There is no detectable change in the quantities of the first group over the temperature range studied. This indicates that the mechanisms of these reactions are the same for paramagnetic and ferromagnetic gadolinium. A brief analysis of the possible mechanisms of the two reactions is given first. This is followed by a discussion of the variation of the reaction rates with temperature and degree of magnetic order. In both cases the discussion will apply mainly to the sodium acetate/acetic acid electrolyte.

A. Mechanisms

1. Anodic Dissolution of Gadolinium

The zero reaction orders with respect to pH and acetate ion indicate that no complexing by either OH^- or Ac^- is involved during the formation of Gd^{3+} at

the electrode surface. The ion therefore must be stabilized by hydration. The linear Tafel plots of slope $(\ln 10)RT/0.40^\circ\text{F}$ indicate charge-transfer control at low to moderate current densities. At high current densities the reaction becomes mass transfer controlled.

The Gd^{3+} ion is the only stable species observed in solution³⁹. This does not preclude the possibility of formation of lower valent short-lived species at the electrode surface. Single electron transfer reactions are usually considered much more probable than multi-electron transfers. A simple stepwise mechanism can be written for the dissolution reaction (omitting the water of hydration).

If all steps but one are at equilibrium the experimental transfer coefficient can be expressed in terms of n_d , the number of electrons exchanged in the rate-determining step, n' , the number of electrons exchanged after the RDS, and v_d , the stoichiometric number⁴⁰.

$$\alpha_a = (1-\beta)n_d + n'/v_d \quad (2)$$

The symmetry factor is usually considered to be $\approx \frac{1}{2}$. On this basis the rate-determining step would be (1c) which gives $\alpha_a = 0.40$ for $\beta = 0.6$. If, however, two steps have similar activation energies, the same apparent transfer coefficient may result at the high overpotentials necessarily used in these experiments. Although the transfer coefficient of 0.40 does not permit an unambiguous determination of the rate determining step, it does indicate that electron transfer to the metal is involved in this step.

2. Hydrogen Evolution Reaction

In the buffered acetic acid (HAc) solutions used here, the actual HER is probably preceded by the chemical reaction given in Equation 3.

The limiting reaction current density for which the production of H^+ by reaction (3) would become the overall rate determining step can be calculated from Equation 4¹.

$$i_r = F[k_D(\text{HAc})(\text{H}^+)D_{\text{H}^+}]^{\frac{1}{2}} \quad (4)$$

For the range of (H^+) and (HAc) used, i_r is much greater than the measured current densities in the Tafel region and reaction (3) is not rate limiting.

The following reactions are usually considered in discussing the mechanism of the HER:

followed by either

or

There are two reaction paths: discharge (5) followed by electrodic desorption (6a), or discharge followed by chemical desorption (6b). Either step may be rate-determining within each path or dual control by both steps can exist.

The observed Tafel slope is $(\ln 10)RT/0.33 F$ and the reaction order with respect to H_3O^+ is 1.11. These

values rule out the mechanism of discharge followed by rate-determining chemical desorption. Discharge followed by rate-determining electrodic discharge at low or intermediate coverage by atomic hydrogen is also ruled out. None of the other mechanisms can be clearly eliminated solely on the basis of the experimental results. Other considerations, however, indicate that electrodic desorption at high coverage of H $\cdot$ is the rate-determining step.

The Gd-H bond dissociation energy can be estimated using the Pauling equation (7).

$$D_{MH} = \frac{1}{2}(D_{MM} + D_{HH}) + 23.06 (X_M - X_H)^2 \quad (7)$$

Calculations based on several different methods of estimating D_{GdH} based on this equation all give values of D_{GdH} in the range 75-85 kcal/mole. The value estimated from experimental data for the Gd-H system is also in this range. The high value of D_{GdH} indicates that ΔH_{adsH} has a large negative value. This leads to both a high surface coverage with absorbed H $\cdot$ and an increase in the activation energy of Step (6a) relative to Step (5). A more detailed analysis by Krishtalik indicates that electrodic desorption is the rate-determining step for metals having D_{MH} similar to that of Gd¹⁹.

B. Temperature Dependence of the Reaction Rates

The results presented in Chapter III show that there is a significant difference in the electrochemical reactivity of paramagnetic and ferromagnetic gadolinium. This difference is observed for both the HER on Gd and for the electrochemical dissolution of the metal. A unified theory describing this behavior must take into account both the experimental results given here and the experimental and theoretical aspects of the magnetic behavior of Gd. In this section it is first shown how the unusual behavior shown by the experimental temperature dependence can be rationalized and used to interpret the results. Then the deficiencies of a model based solely on changes in the bulk energy of the electrode are discussed. Finally, a model based on both changes in the electronic structure of Gd on magnetic ordering and changes in this structure near the surface of the metal is proposed.

Two observations based on the $\ln i$ vs. $1/T$ curves appear to be especially pertinent:

- (1) The magnitudes of the apparent changes in the activation energies of the HER and Gd dissolution reaction at the Curie

point are almost the same (but in opposite directions).

- (2) For both reactions there is a simultaneous change in the pre-exponential or frequency factor in such a way as to give a practically smooth overall $\ln i$ vs. $1/T$ curve.

These observations seem to be anomalous, especially considering the different nature of the two reactions. They can be rationalized, however, if it is recognized that any possible contribution to the activation energies due to "magnetic" order in the ferromagnetic state will decrease as the Curie point is approached. It then seems natural to take the paramagnetic state as the "normal" case and to assume that any such contributions are absent in that state. It may then be proposed that the ferromagnetic contribution to the overall activation energy below the Curie temperature can be written in the form:

$$E_f = |\kappa f(T/T_c) E_f^0| \quad (8)$$

where $f(T/T_c) \rightarrow 0$ as $T \rightarrow T_c$ (the Curie temperature), κ is a constant, and E_f^0 is the energy contribution at $T = 0$. The assumed form of Equation 8 implies that κ can be identified with the symmetry factor or Bronsted coefficient

appearing in linear free energy relationships^{43, 44}. To this approximation, κ is a constant for reactions of similar type and can take on the values $0 < \kappa < 1$. It is often found that $\kappa \approx \frac{1}{2}$.

The magnitude of E_f is apparently the same for the HER and Gd dissolution reaction, but the contribution is such that the overall activation energy of the HER is decreased while that of the anodic reaction is increased in the ferromagnetic state. The cathodic and anodic current densities can then be expressed as:

$$i_c = B_c e^{-(E_{c,p} - E_f)/RT} e^{-\alpha_c FV/RT} \quad (9a)$$

$$i_a = -B_a e^{-(E_{a,p} + E_f)/RT} e^{\alpha_a FV/RT} \quad (9b)$$

in which temperature independent terms are contained in the B factors and $E_{c,p}$ and $E_{a,p}$ are the "paramagnetic" cathodic and anodic activation energies. Rearrangement yields Equations 10a and 10b.

$$\ln i_c - E_f/RT = -1/RT(E_{c,p} + \alpha_c FV) + \ln B_c \quad (10a)$$

$$\ln |i_a| + E_f/RT = -1/RT(E_{a,p} - \alpha_a FV) + \ln B_a \quad (10b)$$

Application of these equations to the experimental data with suitably chosen values of κ , E_f^0 , and the function $f(T/T_c)$ should result in $(\ln i \pm E_f/RT)$ vs. $1/T$ plots linear over the entire temperature range. Further discrimination of mechanisms is based on the estimation of E_f and prediction whether the overall activation energies should be increased or decreased by its application.

At a given potential versus a reference electrode, the electronic energy levels in different metal electrodes are considered to be equal. Under this condition there is essentially no explicit dependence of the rates of an electrode reaction on the work functions of different metals⁴⁵. For reactions in which there is strong interaction with the electrode, differences in these rates from one metal to another are thought to be due primarily to differences in the adsorption energy of reactants on the metal^{19, 20, 45, 46}. The HER involving the adsorption of hydrogen atoms is the best known example of this type of dependence. For metal deposition and dissolution reactions the free energies of ionic solvation, ionization of the metal atom, and cohesion of different metals must also be taken into account.

The results for gadolinium might be considered to be those for two "different" metals, paramagnetic Gd

and ferromagnetic Gd. As seen in the previous section, it is probably better to consider the results at each temperature below the Curie point to correspond to different metals. Therefore the HER results might be interpreted as being due to changes in the energy of adsorption of hydrogen atoms. For the Gd dissolution reaction, the metal cohesion energy and the energy of adsorption of intermediate adatoms or adions might be affected by the degree of magnetic order.

It would be very difficult to calculate the energies of adsorption and cohesion in detail. These energies can be estimated, however, if it is assumed that they are due solely to the bulk exchange energy of the metal. The Weiss molecular field theory is the simplest model that can be expected to give a reasonable estimate of the overall exchange energy of gadolinium. In this approximation the total exchange energy contribution to the internal energy of the solid is⁴⁷:

$$U_M = -\frac{1}{2}\gamma M_S(0)^2 \delta^2 \quad (11a)$$

where γ is molecular field constant, $\delta = M_S(T)/M_S(0)$ and $M_S(T)$ is the saturation magnetization at the temperature T . Using γ calculated from the Curie temperature and the experimental value of $M_S(0)$ ⁴⁸, U_M can be estimated as:

$$U_M \approx -7.0 \times 10^2 \delta^2 \quad (\text{cal/mole}) \quad (11b)$$

The experimental temperature variation of δ near the Curie temperature of Gd is represented fairly well by the Brillouin function with $J = 7/2$:

$$\delta = \frac{2J+1}{2J} \coth \frac{2J+1}{J} x - 1/2J \coth(x/2J) \quad (12a)$$

where

$$x = (3J/J+1) (T_c/T) \delta \quad (12b)$$

For the experimental temperature range discussed here, $T \rightarrow T_c$ and a series expansion of the coth y terms of Equation 12a can be used to obtain an explicit expression for δ in terms of T/T_c .

Using the above assumptions and Equations 8 and 11 the magnitude of the exchange contribution to the activation energies can be expressed as:

$$E_f = (\kappa\gamma/2) M_s(0)^2 \delta^2 \quad (13a)$$

$$E_f \approx 7.0 \times 10^2 \kappa \delta^2 \quad (\text{cal/mole}) \quad (13b)$$

where $f(T/T_c)$ is identified as δ^2 . The corresponding contributions to $\ln i$ are quite small even with $\kappa = 1$. At the lowest temperature (5.6°C) E_f/RT is 0.10, and decreases rapidly at higher temperatures. There is little effect on the experimental $\ln i$ vs. $1/T$ plots, and there is still a significant difference between the high and low temperature slopes. Since these calculations represent an expected upper limit, a model based solely on overall changes in the bulk metal energy as influencing the energies of adsorption and cohesion appears to be inadequate.

Consideration of the probable surface properties of a ferromagnetic substance also leads to difficulties in the interpretation given above. Although little is known about these properties, the collective nature of ferromagnetism alone leads to an expected decrease in the degree of magnetic order near the surface of a ferromagnet. A recent analysis based on a molecular field model indicates that near the Curie temperature the relative magnetization near the surface is⁴⁹:

$$\delta \propto (1-T/T_c) \quad (14)$$

while the bulk value is

$$\delta \propto (1-T/T_c)^{\frac{1}{2}} \quad (15)$$

Therefore near T_c the molecular field quantity U_M should be much smaller near the surface than in the bulk. Experimental observations of the magnetic properties of thin evaporated films of nickel indicate that the apparent Curie temperature decreases with decreasing film thickness⁵⁰. A 20A thick Ni film has no spontaneous magnetization at room temperature, and the magnetization versus temperature curves are considerably flatter than those of the bulk metal. A similar decrease in magnetization with decreasing film thickness has been reported for electroplated nickel, iron, and cobalt. These observations indicate that very near the surface the electronic structure of a ferromagnetic metal must change more or less abruptly to the corresponding paramagnetic structure. This is expected to be especially true near the Curie temperature of the bulk material.

The magnetic ordering in rare earth metals is thought to occur through an indirect exchange mechanism between the highly localized magnetic 4f electrons by way of the spin polarized conduction electrons. Gadolinium is one of the simpler examples of this effect and shows only ferromagnetic behavior below the Curie point. Conduction band and Fermi surface calculations have been made for Gd^{51, 52}. The calculated conduction bands are quite

different from those of the free-electron model and resemble those of the transition metals. There is a high density of states near the Fermi level. Ordering of the 4f moments is thought to introduce energy gaps in the conductance bands at or near the Fermi surface and "destroy" large segments of the surface⁵³. These gaps are about the same magnitude as the exchange coupling, j_{sf} , between the 4f and conduction electrons. There is then an exchange splitting of the conduction bands. This splitting has been used to explain an experimentally observed infrared absorption peak of ferromagnetic Gd^{54, 55, 56}. This peak occurs at about 0.70 eV at low temperature, shifts to longer wavelengths as the temperature is increased, and disappears above the Curie point. The shift correlates with the spontaneous magnetization - temperature curve of Gd within the accuracy limits of the measurements⁵⁶. The value of j_{sf} estimated from the "excess" moment of Gd (i.e., $7.55 \mu_B$ instead of $7.0 \mu_B$) and the calculated density of states at the Fermi level is 0.087 eV⁵³. The value calculated from the absorption peak at 0.70 eV is 0.10 eV.

It is proposed that the existence of such energy gaps at or near the Fermi level of the ferromagnetic bulk metal, relative to the paramagnetic surface layers, may introduce an energy gradient for the transport of electrons

near the metal surface. The qualitative features of the experimental results could be explained if this gradient is such that the transport of electrons to the electrode surface (as in the HER) is favored below the Curie temperature while the transport of electrons to the bulk metal (as in Gd dissolution) is simultaneously retarded. The magnitude of the effect should be the same for the two reactions, in accordance with the results. Furthermore, if it is assumed that E_f^0 can be identified with j_{sf} and $f(T/T_c)$ with δ , Equation 8 becomes, with $\kappa = \frac{1}{2}$:

$$E_f = \frac{1}{2}\delta j_{sf} \quad (16)$$

The application of this equation with $j_{sf} = 0.10$ eV to the experimental points using Equation 10 is shown in Figures 16 and 17. There is no significant difference (even at the 30% t test confidence level) between the slopes of the paramagnetic and ferromagnetic curves. The lines drawn in Figures 16 and 17 correspond to the pooled high and low temperature slopes and intercepts. Although the pooled slopes fit the data quite well, there appears to be small residual changes in the intercepts ($\ln B_j$) at the Curie point. Due to the approximate nature of the model it is not at present possible to comment on the reality of these changes.

FIGURE 16
CATHODIC LOG $i - E_f/RT$ VERSUS $1/T$
POOLED ACTIVATION ENERGY = 15.71 KCAL/MOLE
POOLED LOG B = 20.75

FIGURE 17
ANODIC LOG $|i| + E_f/RT$ VERSUS $1/T$
POOLED ACTIVATION ENERGY = 5.49 KCAL/MOLE
POOLED LOG B = 3.60

An expression for the extrapolated mixed potential of the electrode can be obtained from Equation 9 by setting i_c equal to $|i_a|$. Using E_f from Equation 16, V_M is given by:

$$V_M = \frac{1}{(\alpha_a + \alpha_c)F} [j_{sf}\delta + E_{a,p} - E_{c,p} + RT \ln \frac{B_c}{B_a}] \quad (17)$$

In terms of the pooled activation energies (both referenced to the SHE) and pooled intercepts, V_M can be evaluated as:

$$V_M = 0.137 \delta - 1.663 + 2.025 \times 10^{-3} T \quad (\text{volts}) \quad (18)$$

Calculated values of V_M as a function of temperature are shown in Figure 18. The magnitude of the changes and shape of the curve agrees well with the experimental curve (Figure 15). Even better agreement is obtained with Daire's¹⁵ more precise data in 0.1 M GdCl₃ after fitting the second and third terms of Equation 18 to the "paramagnetic" part of his data.

The deduction of Equation 16 is admittedly rough and intuitive. One of the major assumptions concerns the direction of the proposed energy gap gradient. Photoemission results for Gd indicate that the energy distribution curves at -80°C and 25°C are identical in shape (the resolution was 0.1 eV)⁵⁷. The curve at -80°C

FIGURE 18
CALCULATED MIXED POTENTIAL
VERSUS TEMPERATURE

TEMPERATURE (°C)

is shifted to higher energies by about 0.03 eV from the 25°C curve. Intermediate temperature results lie between these two curves. This gives a rough indication that the Fermi level is higher in the ferromagnetic state than the paramagnetic state. This supports the proposed direction of the energy gradient. The identification of $j_{sf}\delta$ as the overall energy change may be a gross oversimplification. The experimental results are, however, adequately represented by the magnitude and temperature dependence of this quantity.

C. Conclusions and Implications

The proposition given above is an attempt to explain the experimental results in terms of the magnetic properties of gadolinium. The proposition is in part contrary to most of the commonly accepted notions of the role of a metal electrode in electrochemical reactions. It is difficult to rationalize all of the observations in terms of accepted theories. Although Gd may represent a special case, it is felt that attempts to apply free-electron models to real metals and ignorance of possible changes in electron structure very near the metal surface cannot be expected to yield a quantitative description of the electrochemical behavior of a metal electrode.

Acceptance of the proposed model implies that similar considerations may also apply to iron, cobalt, and nickel electrodes. All of these metals are ferromagnetic at temperatures normally encountered in electrochemical measurements, and thermal behavior similar to that considered here is not expected. Although highly speculative, it is possible that some peculiarities of their electrochemical behavior may be partially explained in terms of the model given here. It is well-known that chemisorption of some species can alter the magnetization of very small "superparamagnetic" particles⁵⁸. Chemisorption on Fe, Co, and Ni electrodes might also modify the "magnetic" properties of the surface relative to the bulk metal and influence any existing gradient. It is likely that the initial stage of anodic passivation of these metals is accompanied by the adsorption of an oxygen anion⁵⁹. The adsorption of this species may result in an increase in the gradient (and increase in activation energy) for metal dissolution. The consequent "electronic inhibition" could be partially responsible for the abrupt and pronounced onset of passivity for these metals when only a very thin "film" is present.

The discussion given here might also be applicable to the magnetocatalytic effects observed in gas phase catalysis. In almost all of these cases, however, the chemistry of the surface reactions is much more complicated than that considered here.

REFERENCES

1. Hedvall, J. Arvid, "Solid State Chemistry," Elsevier Publishing Co., Amsterdam, 1966, pp. 78-93.
2. Selwood, P. W., "Magnetochemistry," 2nd ed., Interscience, New York, pp. 404-407.
3. Roca, F. F., Ann. Chim., 2, 255 (1967).
4. Cohn, G., and J. A. Hedvall, J. Phys. Chem., 46, 841 (1942).
5. Uhlig, H. H., and A. de S. Brasunas, J. Electrochem. Soc., 97, 448 (1950).
6. Dowden, D. A., J. Chem. Soc., 1950, 242.
7. Lielmezs, J., and J. P. Morgan, Chem. Eng. Sci., 22, 781 (1967).
8. Conway, B. E., E. M. Beatty, and P. A. D. DeMaine, Electrochim. Acta, 7, 39 (1962).
9. Börggrafe, P., and H. G. Feller, Corros. Sci., 7, 265 (1967).
10. Osterwald, J., and H. H. Uhlig, J. Electrochem. Soc., 108, 515 (1961).
11. Vijh, A. K., and A. Bélanger, Z. Physik. Chem. Neue Folge, 83, 173 (1973).
12. Clark, Alfred, "The Theory of Adsorption and Catalysis," Academic Press, New York, 1970, p. 338.
13. Pourbaix, M., "Atlas of Electrochemical Equilibria," Pergamon Press, London, 1966, p. 185.
14. Prall, J. K., and P. R. Doidge, Nature, 199, 800 (1963).
15. Daire, M., Electrochim. Acta, 15, 211 (1970).
16. Daire, M., C. R. Acad. Sci. Paris, 266 (Ser. C), 1111 (1968).
17. Kita, Hideaki, J. Electrochem. Soc., 113, 1095 (1966).

18. Vetter, K. J., "Electrochemical Kinetics," Academic Press, New York, 1967, pp. 516-614.
19. Krishtalik, L. I., "Advances in Electrochemistry and Electrochemical Engineering," Vol. 7, P. Delahay, Ed., Interscience, New York, 1970, pp. 283-339.
20. Bockris, J. O'M., A. Damjanovic, and R. J. Mannan, J. Electroanal. Chem., 18, 349 (1968).
21. Hoar, T. P., "Modern Aspects of Electrochemistry," No. 2, J. O'M. Bockris, Ed., Academic Press, New York, 1959, pp. 262-342.
22. Bockris, J. O'M., and A. R. Despić, "Physical Chemistry," Vol. 9B H. Eyring, D. Henderson, and W. Jost, Eds., Academic Press, New York, 1970, pp. 661-730.
23. Lee, L., and N. D. Greene, Corrosion, 20, 145t (1964).
24. Lee, L., and N. D. Greene, "Rare Earth Research II," K. S. Vorres, Ed., Gordon and Breach, New York, 1964, p. 531.
25. Morse, S. L., and N. D. Greene, Electrochim. Acta, 12, 179 (1967).
26. Hills, G. J., and D. J. G. Ives, "Reference Electrodes," D. J. G. Ives and G. J. Janz, Eds., Academic Press, New York, 1961, p. 160.
27. Brown, E. R., T. G. McCord, D. E. Smith, D. D. DeFord, Anal. Chem., 38, 1119 (1966).
28. Vetter, K. J., "Electrochemical Kinetics," Academic Press, New York, 1967, p. 407.
29. Yeager, E., and J. Kuta, "Physical Chemistry," Vol. 9A, H. Eyring, D. Henderson, and W. Jost, Eds., Academic Press, New York, 1970, pp. 661-730.
30. Ritchie, R. L., J. Am. Chem. Soc., 89, 1447 (1967).
31. Harned, H. S., and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd ed., Reinhold, New York, 1950.
32. de Bethune, A. J., J. Electrochem. Soc., 107, 829, (1960).

33. Lark, P. D., B. R. Craven, and R. C. L. Bosworth, "The Handling of Chemical Data," Pergamon Press, Oxford, 1968, p. 170.
34. Spedding, F. H., and J. P. Flynn, J. Am. Chem. Soc., 76, 1474 (1954).
35. Bommer, H., and E. Hohmann, Z. Anorg. Allgem. Chem., 248, 357 (1941).
36. Jelinek, F. J., B. C. Gerstein, M. Griffel, R. E. Shochdople, and F. H. Spedding, Phys. Rev., 149, 489 (1966).
37. Bertha, S. L., and G. R. Choppin, J. Inorg. Chem., 8, 613 (1969).
38. Riney, J. S., G. M. Schmid, and N. Hackerman, Rev. Sci. Instr., 32, 588 (1961).
39. Cotton, F. A., and G. W. Wilkerson, "Advanced Inorganic Chemistry," 3rd ed., Interscience, New York, 1972, p. 1057.
40. Bockris, J. O'M., and A. R. Despić, "Physical Chemistry," Vol. 9B, H. Eying, D. Henderson, and W. Jost, Eds., Academic Press, New York, 1970, p. 628.
41. Vetter, K. J., "Electrochemical Kinetics," Academic Press, New York, 1967, p. 241.
42. Study, G. E., R. N. R. Mulford, J. Am. Chem. Soc., 78, 1083 (1956).
43. Gardiner, W. C. Jr., "Rates and Mechanisms of Chemical Reactions," W. A. Benjamin, Menlo Park, California, 1969, p. 163.
44. Levich, V. G., "Physical Chemistry," Vol. 9B, H. Eying, D. Henderson, and W. Jost, Eds., Academic Press, New York, 1970, p. 988.
45. Frumkin, A. N., J. Electroanal. Chem., 9, 173 (1965).
46. Parsons, R., Surface Sci., 2, 418 (1964).
47. Martin, D. H., "Magnetism in Solids," Iliffe, London, 1967, p. 225.

48. Nigh, H. E., S. Levgold, and F. H. Spedding, Phys. Rev., 132, 1092 (1963).
49. Wolfram, T., and R. D. Dewames, Prog. in Surface Sci., 2, 234 (1972).
50. Crittenden, E. C. Jr., and R. W. Hoffman, Revs. Modern Phys., 25, 310 (1953).
51. Dimmock, J. O., and A. J. Freeman, Phys. Rev. Letters, 13, 750 (1964).
52. Keeton, S. C., and T. L. Loucks, Phys. Rev., 168, 672 (1968).
53. Watson, R. E., A. J. Freeman, J. P. Dimmock, Phys. Rev., 167, 497 (1968).
54. Schüler, C. C., "Optical Properties and Electronic Structure of Metals and Alloys," F. Abeles, Ed., North-Holland, Amsterdam, 1965, p. 221.
55. Hodgson, J. N., and B. Cleyet, Proc. Phys. Soc., London, Solid St. Phys., Ser. 2, 2, 97 (1969).
56. Knyazev, Yu. V., M. M. Noskov, Phys. Metals, Metallography, 31, 211 (1971).
57. Blodgett, A. J. Jr., W. E. Spicer, and A. Y-C. Yu, Revs. Modern Phys., 25, 254 (1953).
58. Selwood, P. W., "Adsorption and Collective Paramagnetism," Academic Press, New York, 1962.
59. Hackerman, Norman, Z. Elektrochem., 62, 632 (1958).