IDO-14505

Chemistry - General
(TID-4500, Edition 15)

MECHANISM OF ELECTROREDUCTION OF CHROMIC ION AT THE MERCURY CATHODE

M. E. McLain, Jr.

May 20, 1960

AEC RESEARCH AND DEVELOPMENT REPORT

PHILLIPS PETROLEUM CO.
ATOMIC ENERGY DIVISION
(UNDER CONTRACT NO. AT (10-1)-205)
IDAHO OPERATIONS OFFICE
U. S. ATOMIC ENERGY COMMISSION

PRICE $1.50

Available from the
Office of Technical Services
U. S. Department of Commerce
Washington 25, D. C.

Printed in USA.

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by

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Chemical Development Section
CPP Technical Branch

This Report is Based on a Thesis Submitted in
Partial Fulfillment of the Requirements
for the Master of Science Degree
from the University of Idaho

PHILLIPS PETROLEUM COMPANY
Atomic Energy Division
Idaho Falls, Idaho
Contract AT(10-1)-205

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ABSTRACT

The mechanism of reduction for chromium (III) ion to chromium (II) at the mercury cathode was studied in 0.1M KNO_3. Data obtained at varying temperature and solution composition from polarograms gave values for ΔH^*, ΔS^*, and ΔF^* which indicated that two mechanisms were involved. At potentials more positive than the polarographic half-wave potential the mechanism appeared to be simple electron transfer from the electrode to the chromium (III) ion in solution. When the potential was more negative than the half-wave potential electron exchange between the reduced chromium ion near the electrode surface and a chromium (III) ion in solution became appreciable. Values for the heat of activation for the reduction of chromium (III) to chromium (II) in 0.1M KNO_3 for the electron transfer and exchange reaction mechanisms were determined to be 34.7 and 27.0 kcal $mole^{-1}$, respectively.

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MECHANISM OF ELECTROREDUCTION OF CHROMIC ION AT THE MERCURY CATHODE

by

Milton Eccles McLain, Jr.

I. INTRODUCTION

Mercury cathode electrolysis is a well-known separations method in analytical chemistry for removing electroreducible ions from solution. The removal of iron, nickel, and chromium by electrolysis from stainless steel-type wastes may be useful in developing a treatment process for wastes resulting from the processing of nuclear fuels.

The mechanisms of electroreduction of iron and nickel are well defined, but basic information pertaining to the electroreduction of chromium in solutions containing nitrate ion is inadequate for developing a waste treatment process.

II. PURPOSE

The purpose of this study is to establish the mechanism of the reduction of chromium (III) to chromium (II).

Chromium is the most difficult of the three alloy constituents - iron, nickel, and chromium - to remove electrolytically. Defining a mechanism for the electroreduction of chromium (III) in nitrate solution at the mercury cathode would be of considerable help in developing an electrolytic separation process.

III. LITERATURE SURVEY

The mechanism for the reduction of chromium (III) to chromium (II) at the mercury cathode was studied by Lewis(25). He concluded that in perchloric acid solution, the rate-determining step involves the transfer of an electron from the mercury electrode surface to a chromium (III) ion in solution. A study by Elving and Zemel(7), of parameters affecting the thermodynamic values for the reduction in perchloric acid, indicated that at low negative potential the mechanism seemed to be simple electron transfer. However, with increasing negative potential, an electron exchange between the chromium (II) and the chromium (III) ions appeared to enter into the mechanism.

IV. THEORY

The rate of the electrode reaction:

$$\text{oxidized} + n\,e^- \longrightarrow \text{reduced} \qquad (1)$$

is expressed by the current, i, at an applied potential, E. By convention, positive values of i are used for reduction and negative values for oxidation. The potential, E, is usually given in reference to the normal hydrogen electrode.

An equation to represent the net rate of reaction has been developed by Volmer$^{(3)}$:

$$\frac{i}{A} = [\mathrm{Ox}]_o \exp\left(-\frac{\Delta F_1^* + \alpha n \mathcal{F} E}{RT}\right) - [\mathrm{Red}]_o \exp\left(-\frac{\Delta F_2^* - \alpha' n \mathcal{F} E}{RT}\right) \qquad (2)$$

where A is a proportionality constant;

$[\mathrm{Ox}]_o$ and $[\mathrm{Red}]_o$ are concentrations (actually activities) of the oxidized and reduced species near the electrode surface;

ΔF_1^* and ΔF_2^* are the free energies of activation of the rate-determining step for the reduction and oxidation reactions, respectively;

α and α' are the fractions of the total potential across the electrode-solution interface that are effective in the reduction and oxidation;

$\mathcal{F}$ is the Faraday constant;

n is the number of Faradays per mole of ion reduced or oxidized;

R is the gas constant;

T is the absolute temperature.

The first term on the right side of Equation (2) expresses the rate of the reduction process, and the second the rate of the oxidation reaction. At equilibrium, both processes are considered to occur simultaneously. The potential determines the relative rates of oxidation and reduction. Equation (2) describes the relationship between current and potential, regardless of the specific mechanism controlling the reaction. When experimental data for current, potential, and concentration are inserted in Equation (2), values of A, $\triangle F_1^*$, $\triangle F_2^*$, α and α' can be calculated. These quantities have meaning in selecting a feasible mechanism.

The proportionality constant, A, in Equation (2) is not necessary for the determination of the heat of activation, although some assumptions concerning this constant are necessary to calculate the entropy and the free energy of activation. When the absolute reaction rate theory of Eyring(9) is extended to electrochemical processes by Kimball(20), it may be used to clarify the significance of A. There is some doubt whether Gurney's picture(16) of the electron transfer process is accurately described when A is evaluated by Eyring's theory. The activated state in the adsorption and desorption mechanisms are possibly more accurately described by the Eyring treatment.

An activation step may be postulated regardless of the mechanism chosen for the electroreduction. For example, an electron and an oxidized ion may move along a potential energy surface until they reach a saddle point (see Figure 1). Further motion along the reaction coordinate results in reduction of the ion. The intermediate configuration of the electron and the ion at this saddle point is the activated state. The velocity with which these activated complexes cross the saddle point or energy barrier from the oxidized to the reduced form

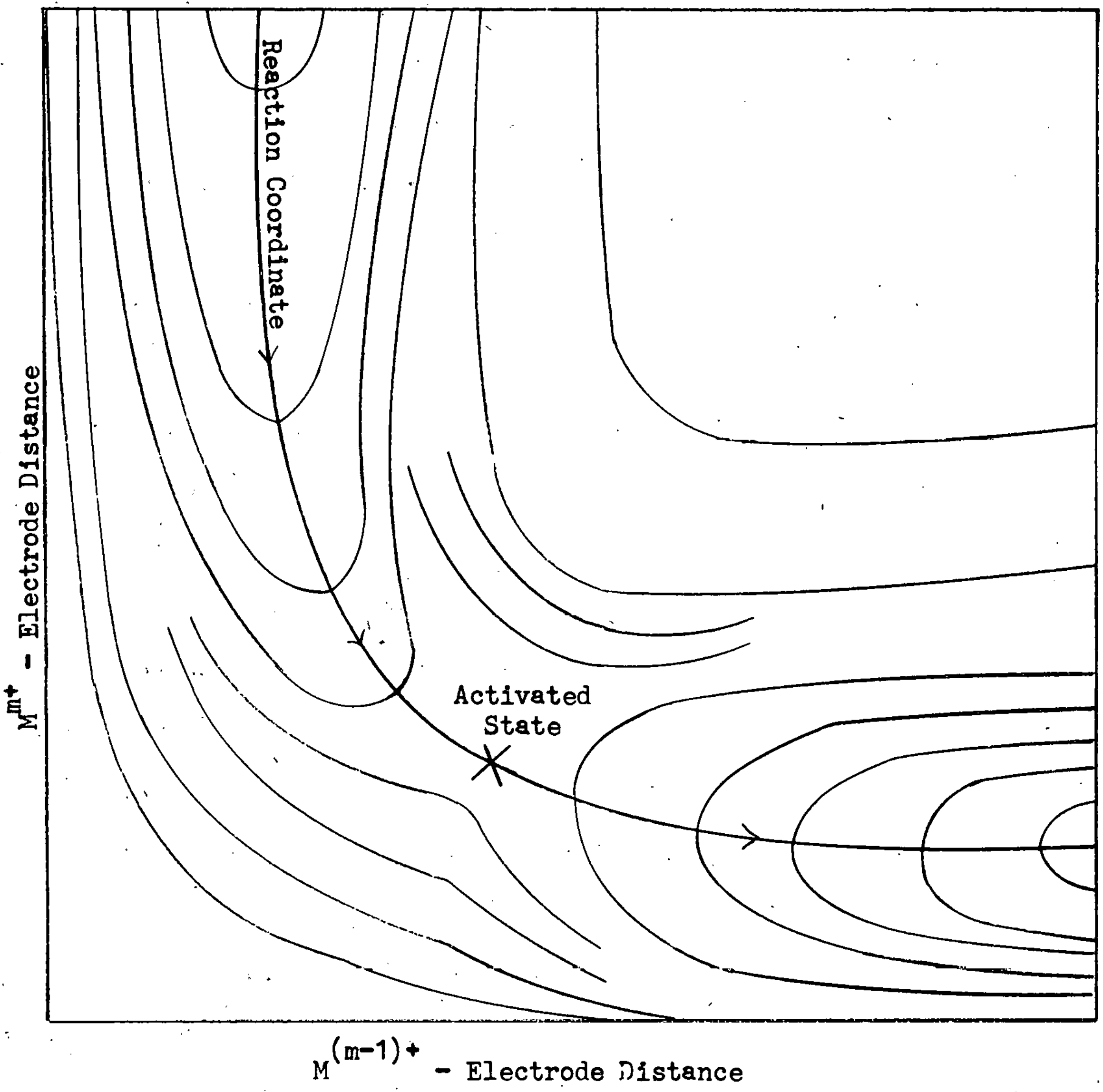


FIGURE 1

POTENTIAL ENERGY SURFACE
FOR
ELECTROREDUCTION OF METAL ION

can be expressed by $\frac{kT}{h}$, where k is the Boltzmann constant, T the absolute temperature, and h represents Planck's constant. This universal frequency is dependent only on temperature and is independent of the reactants and the type of mechanism for the reaction. Thus, from Equation (2), the rate of reduction is given by:

$$\text{rate of reduction} = \kappa \frac{kT}{h} [0x]_o \exp \left(- \frac{\Delta F_1 + \alpha n \mathcal{F} E}{RT}\right) \qquad (3)$$

where κ is the fraction of the activated complexes yielding the reaction product, and ΔF_1^* is the free energy change involved in producing the activated state. Thus, the term A in Equation (2) consists of a frequency factor and a transmission coeficient, κ. The free energy of activation, ΔF_1^*, is the difference in free energy between the normal and activated states of the ion. In the electron transfer mechanism this may be a particular configuration of an ion, its associated water molecules, and an electron which may exist a small distance from the electrode surface. The activated state in the electron exchange mechanism is probably an appropriate spatial orientation of the oxidized and reduced ions relative to one another. For the adsorption and desorption mechanisms the activated state consists of an ion adsorbed on the electrode surface.

The choice of an electrode with a known geometry and surface allows the current-concentration relationships of Equation (2) to be derived, and from these the determination of the thermodynamic properties of the activation reaction follows. The polarographic method with the dropping mercury electrode meets these requirements. In this study it was used to examine the reduction of chromium (III) to chromium (II).

Bockris(2) summarized a number of theories which have been advanced to explain the details of electroreduction and oxidation. Three general categories are evident in which the rate-determining step in the mechanism is thought of as occurring before, during, or after the transfer of electrons from the electrode to the ion.

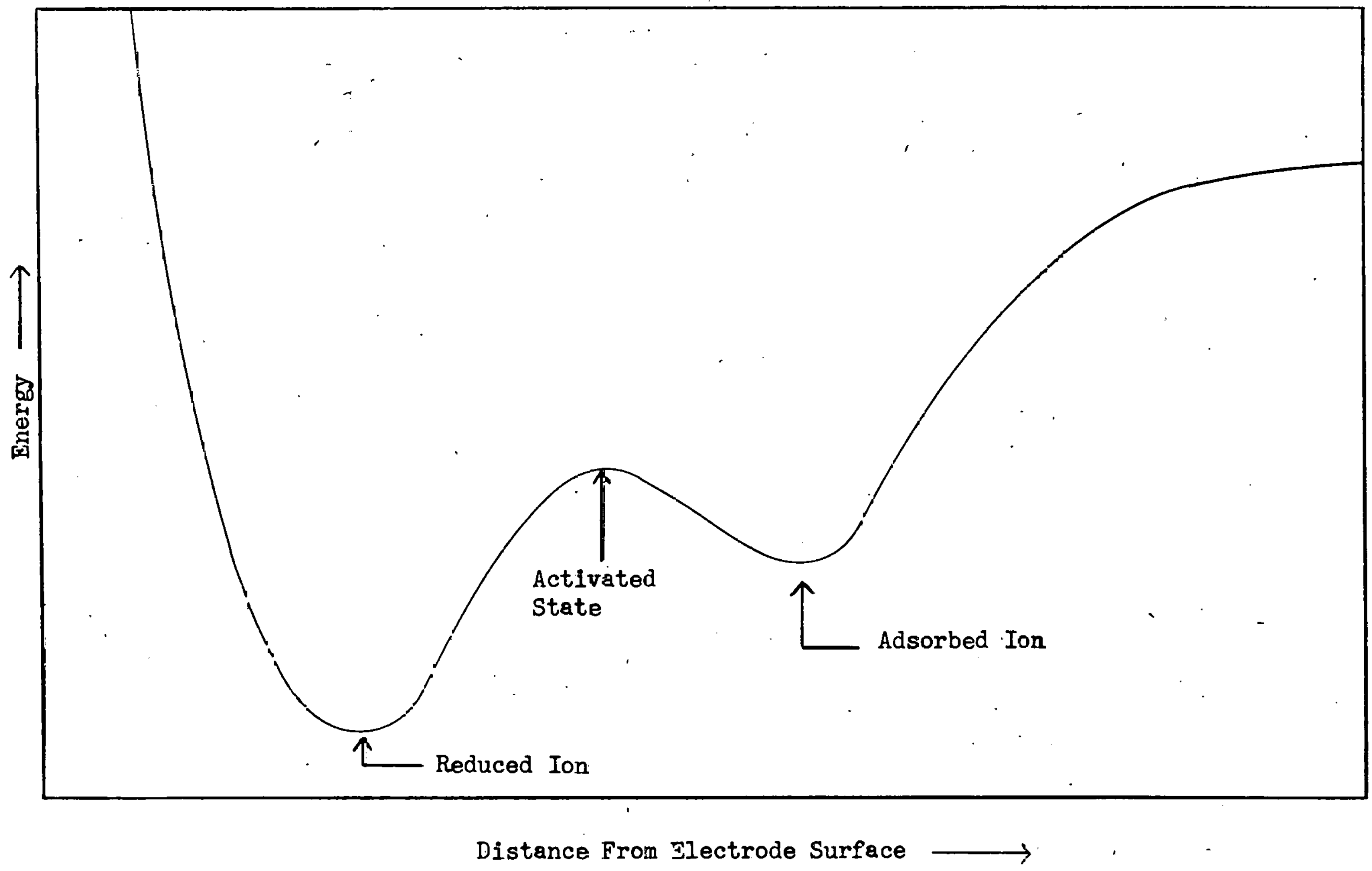
The Electron Transfer Mechanism: Gurney(16), Fowler(11), Butler(6), and Grahame(15) suggested that the rate-determining step in the reduction of hydrogen ions is the transfer of electrons between the electrode and the hydronium ion. Orlemann(29) showed that a similar mechanism explained the experimental data obtained when iodate or bromate was reduced at the dropping mercury electrode. The potential in the electron transfer mechanism raises or lowers the energy level of the electrons in the electrode relative to the level in the ions. This enables electrons to transfer from levels of higher energy to those of lower energy whether this is from the electrode to the ions or vice versa.

The Adsorption Mechanism: A second possible mechanism has as the rate-determining step the transfer of the ion from the solution across the double layer to an adsorption position on the electrode surface. This mechanism has been proposed by Erdy-Gruz and Volmer(8), Frumkin(12), Eyring, Glasstone, and Laidler(10), Kimball, Glasstone, and Glassner(21), and Kimball(20) in connection with the reduction of the hydrogen ion. Their treatments of the theory differ, but there is agreement in assuming that the double layer constitutes a potential barrier, which the hydrogen ion must cross to be reduced. Figure 2 is a graphical representation of such a potential barrier. The adsorption mechanism can be explained in terms of Equation (2) as follows:

ΔF_1^* is the difference in free energy between the normal and activated states at zero potential. Increasing the negative potential of the electrode does work on the positive ions in

FIGURE 2

POTENTIAL ENERGY OF ION AS A FUNCTION OF DISTANCE FROM ELECTRODE SURFACE



solution and elevates them to an activated or adsorbed state. α is the fraction of the total applied potential used in this process. In like manner, ΔF_2^* and α' apply to the oxidation of reduced ions.

The Desorption Mechanism: Theories have been presented, which assume the escape of adsorbed hydrogen atoms from the electrode surface to be the rate-determining step. Bowden and Rideal(5), Bowden(4), Heyrovsky(17), and Bockris and Ignatowicz(3) suggest various mechanisms for this desorption process. The application of the general equation (Equation (2)) is similar, except that the energy barrier exists for the removal of ions from the electrode surface.

The Electron Exchange Mechanism: Another possible mechanism, which cannot occur alone, but only concurrently with one of the previously mentioned processes, is the reduction of a chromium (III) ion by a chromium (II) ion. This electron exchange reaction becomes more probable as the potential increases and the concentration of chromium (II) ions near the electrode becomes greater. This mechanism was mentioned by Elving and Zemel(7) in connection with the reduction of chromium (III) to chromium (II) in perchloric acid.

V. THE POLAROGRAPHIC METHOD

Since the polarograph and its use have become commonplace in the research laboratory, the description here will be brief. More detailed descriptions of the method and apparatus used may be found in Kolthoff's and Lingane's treatment(22).

Basically, the polarograph consists of a dropping mercury electrode, A (Figure 3), whose potential is varied by a potential divider circuit, D. The dropping mercury electrode (D.M.E.) is immersed in the cell, C, containing the solution of the reducible ions in contact with a reference electrode, B. The negative potential of the D.M.E. is increased and the current between the D.M.E. and the reference electrode is measured by the galvanometer, G. In a recording instrument, the potential divider is driven by a motor, and the galvanometer is replaced by a microampere recorder.

A typical current-voltage curve obtained by the polarographic technique is shown in Figure 4. This curve is a tracing of the average value of the current as it fluctuates with the dropping electrode. Until a potential sufficient to reduce the ion is attained, a very small increase in current with increasing potential is observed. This "residual current" is due to impurities in the solution and to capacitance effect at the solution-electrode interface. At more negative potentials, electrolysis begins as some of the oxidized ion is reduced at the mercury surface. In the case of the chromium (III) to chromium (II) reduction, the reduction product diffuses back into the bulk of the solution. A concentration gradient is established, which increases as the electrode potential becomes more negative. Soon, a point is reached where the concentration of the oxidized ion at the D.M.E. surface becomes negligible compared to the concentration in the body of the solution. If a sufficient quantity of an indifferent electrolyte, e.g. potassium nitrate, is present to lower the transference number of the reducible ion to zero, a limiting or diffusion current is reached with increasing potential at which the rate of reduction, indicated by the current, is

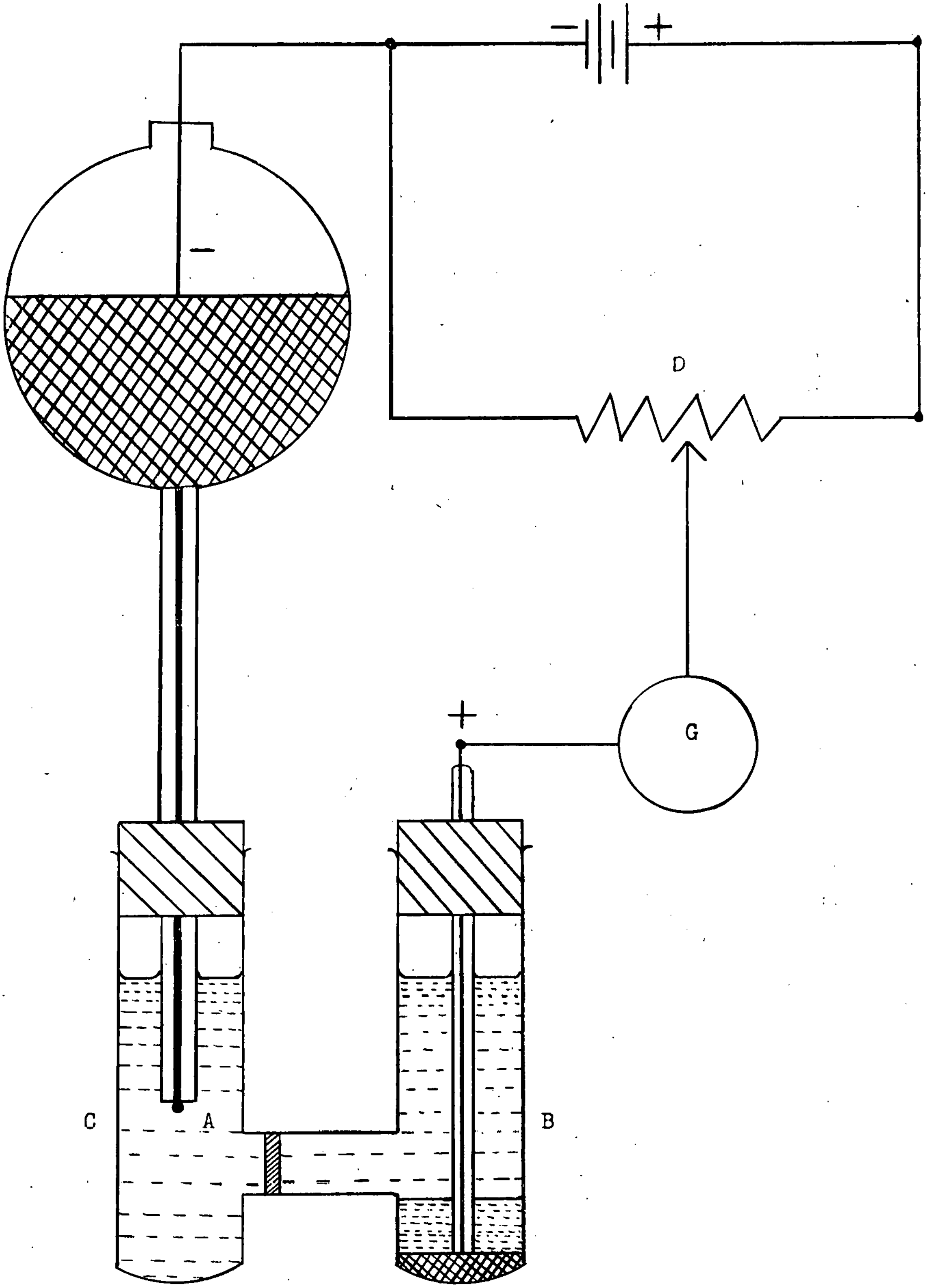


FIGURE 3

POLAROGRAPHIC CIRCUIT

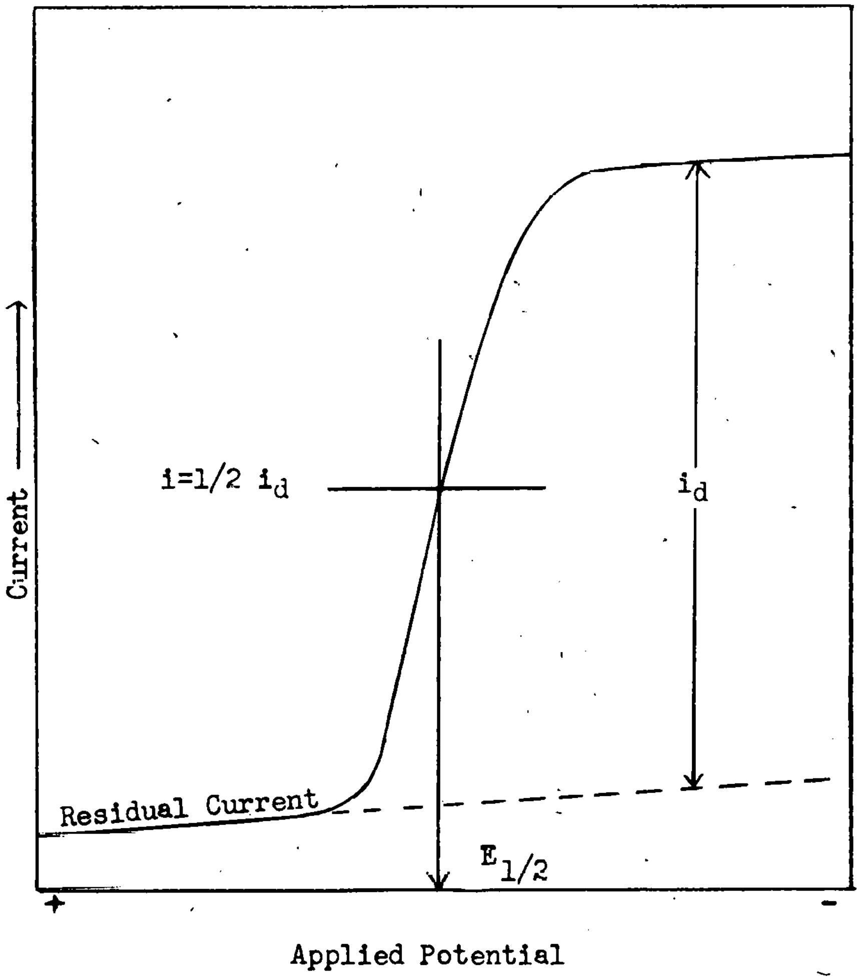


FIGURE 4

CURRENT VOLTAGE CURVE OBTAINED WITH THE

DROPPING MERCURY ELECTRODE

controlled by the rate at which the reducible ion can diffuse from the body of solution, across the concentration gradient, to the electrode surface.

Maxima often occur in the current-voltage curves. These are thought to be due to a stirring phenomenon at the dropping electrode surface(1,13). They may be eliminated by increased dilution or the addition of as little as 5×10^{-4} percent of a surface active agent such as gelatin or methyl red. In this investigation, however, the total absence of surface active agents was necessary in several instances. Therefore, the problem was eliminated by reducing the concentration of chromium (III) to a point where the maximum disappeared.

An equation for the diffusion current has been derived by Ilkovic(19) and MacGillavry and Rideal(27) from Fick's law of diffusion. An explanation of their derivation is presented by Kolthoff and Lingane(22). The Ilkovic equation is:

$$i_d = 607\, n\, D^{1/2}\, m^{2/3}\, t^{1/6}\, C \qquad (4)$$

where i_d is the diffusion current in microamperes;

n is the number of electrons transferred per molecule;

D is the diffusion coefficient of the reducible substance in square centimeters per second;

m is the mass of mercury flowing from the capillary in milligrams per second;

t is the drop time in seconds;

C is the concentration of the reducible substance in millimoles per liter.

Several terms in the Ilkovic equation are often combined to give:

$$i_d = KC \qquad (5)$$

where K is the Ilkovic or diffusion current constant expressed in microamperes per millimole per liter.

The Ilkovic equation was checked experimentally by Kolthoff and Lingane(22) and proved accurate provided the drop time was from three to six seconds, sufficient indifferent electrolyte was present to reduce the transference number of the reducible ion to 0.01 or less, and a correction was made for the residual current.

The Current-Potential Relationship for Reversible Systems: By definition, the reactants in a reversible system are at equilibrium at all times. Taking the electrolytic system:

$$M^{m+} + ne^- \longrightarrow M^{(m-n)+} \qquad (6)$$

to be at equilibrium, the net rate of the reaction is zero, since the rates of reduction and oxidation are equal. Setting i equal to zero in Equation (2) gives:

$$[M^{m+}]_0 \exp\left(-\frac{\Delta F_1^* + \alpha n \mathcal{F} E}{RT}\right) = [M^{(m-n)+}]_0 \exp\left(-\frac{\Delta F_2^* - \alpha' n \mathcal{F} E}{RT}\right) \qquad (7)$$

or

$$\frac{[M^{m+}]_0}{[M^{(m-n)+}]_0} = \exp\left(-\frac{\Delta F_2^* - \Delta F_1^*}{RT}\right) \exp\left(\frac{n\mathcal{F}E(\alpha + \alpha')}{RT}\right) \qquad (8)$$

Converting to logarithms:

$$\Delta F_1^* - \Delta F_2^* + n\mathcal{F}E(\alpha + \alpha') = RT \ \ln \frac{[M^{m+}]_0}{[M^{(m-n)+}]_0} \qquad (9)$$

For a reversible reaction, the electrical work done in the reduction, $\alpha n \mathcal{F} E$, plus the work done in the oxidation, $\alpha' n \mathcal{F} E$, must equal the total work done in the system. Therefore, the sum, $\alpha + \alpha'$, must be equal to unity. Also, if the forward and reverse reactions pass through the same activated state, as is necessary for a reversible process,

$$\frac{\triangle F_1^* - \triangle F_2^*}{n\mathcal{F}} = \frac{\triangle F^o}{n\mathcal{F}} = - E^o \tag{10}$$

where E^o is the potential for the reaction (Equation (6)) at unit activity. Substituting into Equation (9):

$$E = E^o + \frac{RT}{n\mathcal{F}} \ln \frac{\left[M^{m+}\right]_o}{\left[M^{(m - n)+}\right]_o} \tag{11}$$

Equation (11) was applied to polarography by Heyrovsky and Ilkovic(18):

$$E = E_{1/2} + \frac{RT}{n\mathcal{F}} \ln \frac{(i_d)_c - i}{i - (i_d)_a} \tag{12}$$

where $E_{1/2}$ is the potential at which the current, i, is equal to one-half the diffusion or limiting current, i_d,

$(i_d)_c$ and $(i_d)_a$ are the diffusion currents for the cathodic and anodic processes, respectively.

They assumed that the average rate of diffusion of ions to the mercury drop is proportional to the concentration gradient, and that the rates of change of the surface concentrations are zero at a single potential.

It is obvious from Equation (12) that the half-wave potential, $E_{1/2}$, is identical for reduction and oxidation in a reversible system. Even in the absence of one of the species, corresponding to $(i_d)_c$ or $(i_d)_a$ equal to zero, $E_{1/2}$ for the other form is unchanged. Figure 5 illustrates this principle for the reversible reduction and oxidation of metal ions. Equation (12) has been verified by Stackelberg and Freyhold(30) and Lingane(26) in their studies of the reversible ferric-ferrous oxalate system. Curve D in Figure 5 illustrates the result when an irreversible system such as the chromium (III)-chromium (II) pair is electrolyzed. The following section discusses this system.

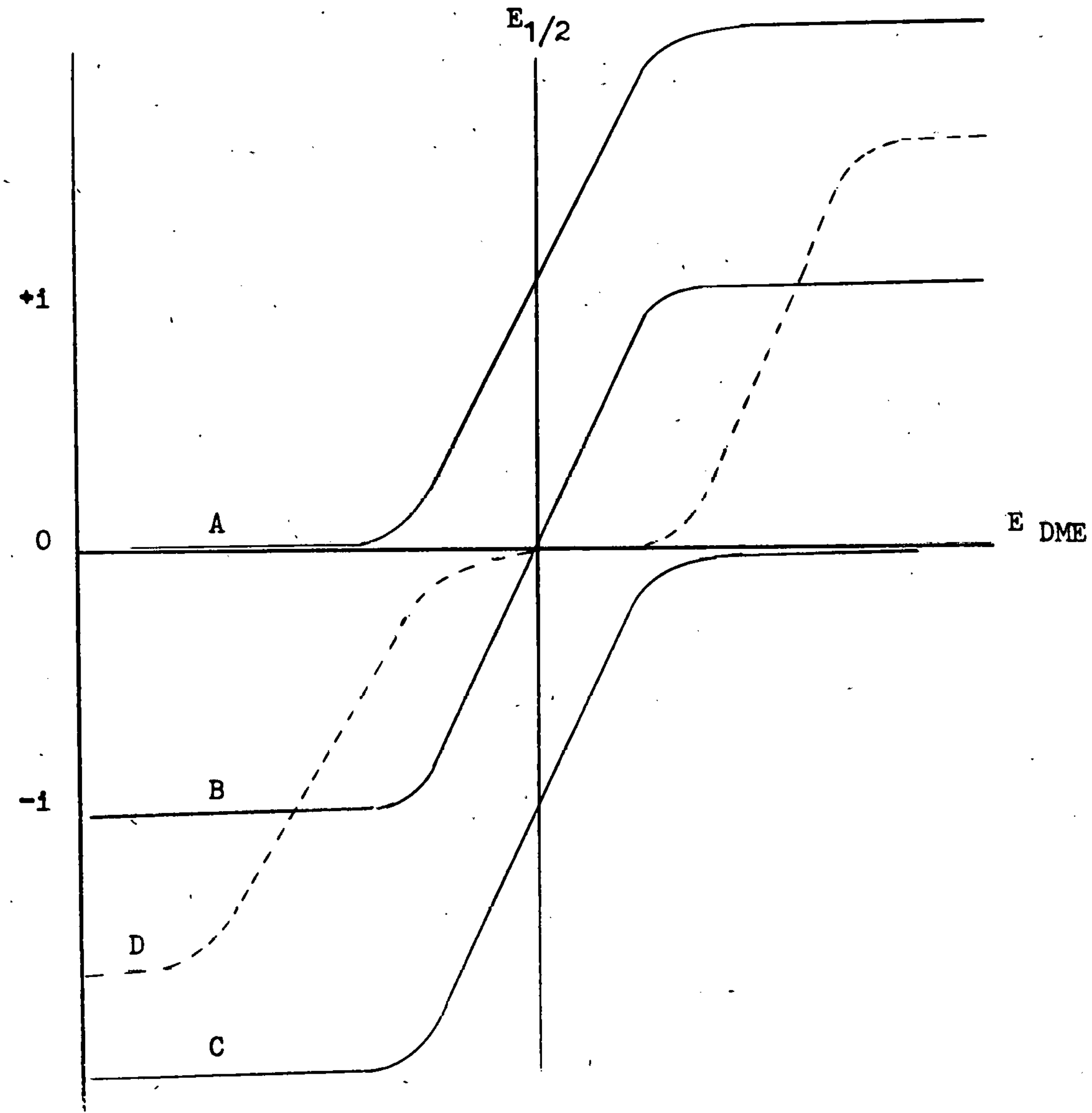


FIGURE 5

POLAROGRAPHIC WAVES DUE TO REDUCTION OR OXIDATION OF METAL IONS OR OTHER SUBSTANCES

A. Cathodic Wave of Oxidized Form.

B. Composite Cathodic-Anodic Wave of an Equal Mixture of Oxidized and Reduced Forms.

C. Anodic Wave of Reduced Form.

D. Composite Cathodic-Anodic Wave When the Electrode Reaction is Irreversible.

The Current-Potential Relationship for Irreversible Systems: At any potential during the electrolysis of an irreversible system, e.g. the chromium (III)-chromium (II) pair, the net current is the algebraic sum of the reduction and oxidation currents. The potential at any point in the solution is a function of the distance from the electrode, being a maximum at the electrode surface. A schematic representation of this effect is shown in Figure 6. The steepest portion of the potential gradient is near the electrode surface. For each of the mechanisms described in the previous section, the activated state exists at a distance, x, from the electrode. This varies with α, the fraction of the potential required to produce the activated state. This distance should be larger for the electron transfer mechanism than for adsorption or desorption mechanisms and should be even greater for the electron exchange process. The net reaction rate, then, is a sum of all the oxidation and reduction occurring from the electrode surface out to an infinitely large distance, X. The net polarographic current at any instant, i_t, may be expressed by an equation similar to Equation (2):

$$i_t = \int_0^X n\mathcal{F}A_t \mathcal{K} \frac{kT}{h} \exp\left(-\frac{\Delta F_x^* + \alpha n\mathcal{F}E_x}{RT}\right) \left[Cr^{+++}\right]_x dx - \int_0^X n\mathcal{F}A_t \mathcal{K} \frac{kT}{h} \exp\left(-\frac{\Delta F_x^{*\prime} - \alpha' n\mathcal{F}E_x}{RT}\right) \left[Cr^{++}\right]_x dx \qquad (13)$$

where A_t is the surface area of the drop at time t,

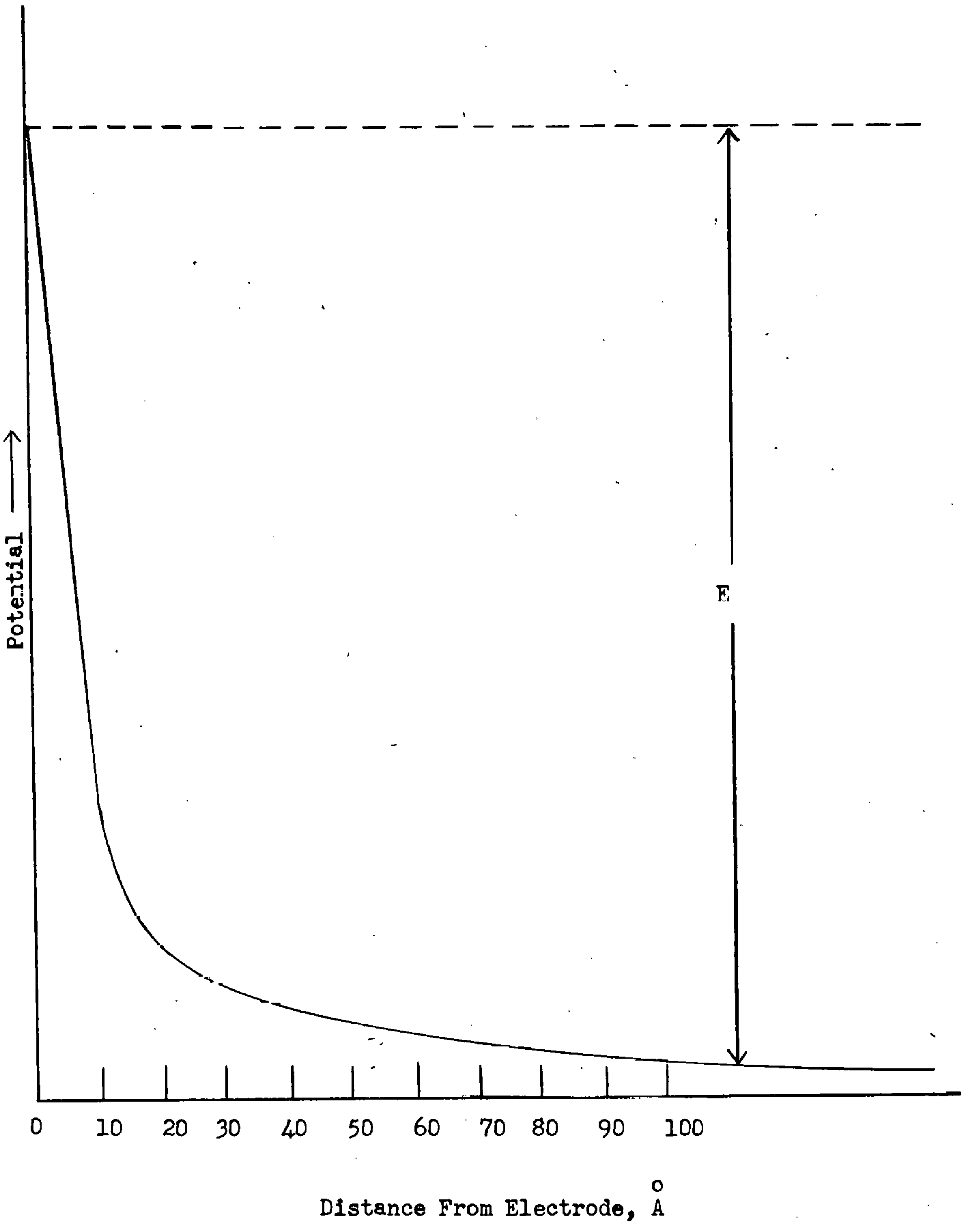
ΔF_x^* is the free energy of activation of an ion at distance x from the electrode surface,

E_x is the potential at distance x,

$\left[Cr^{+++}\right]_x$ and $\left[Cr^{++}\right]_x$ are the concentrations of chromium (III) and chromium (II), respectively, at distance x.

FIGURE 6

POTENTIAL GRADIENT NEAR ELECTRODE SURFACE



The primed quantities refer to chromium (II) ion.

Integration of Equation (13) gives:

$$i_t = n\mathcal{F}A_tX\kappa\frac{kT}{h}\exp\left(-\frac{\Delta F^* + \alpha n\mathcal{F}E}{RT}\right)\left[Cr^{+++}\right]_o - n\mathcal{F}A_tX\kappa'\frac{kT}{h}\exp\left(-\frac{\Delta F^{*\prime} + \alpha' n\mathcal{F}E}{RT}\right)\left[Cr^{++}\right]_o \qquad (14)$$

where ΔF^* is the average of all ΔF^*_x from 0 to X,

E is the difference in potential between the electrode and the body of the solution,

α is the fraction of the potential effective in reducing the ion,

$\left[Cr^{+++}\right]_o$ and $\left[Cr^{++}\right]_o$ refer to the average values for chromium (III) and chromium (II) in the surface layer.

Primed terms again refer to chromium (II) oxidation. At increasing negative values of E, the second term on the right side of Equation (14) becomes negligible, and the current is essentially a reduction current. Lewis(25) has shown this to be true by the fact that chromium (II) solutions give only a residual current at potentials corresponding to the reduction of chromium (III) ion. According to Heyrovsky and Ilkovic(18):

$$\left[Cr^{+++}\right]_o = \frac{i_d - i}{K_{Cr^{+++}}} \qquad (15)$$

where i_d is the diffusion or limiting current,

$K_{Cr^{+++}}$ is the Ilkovic constant for chromium (III) ion in this particular system.

Substituting this into Equation (14) we get at large negative values of E:

$$i_t = \frac{n\mathcal{F}A_tX\kappa}{K_{Cr^{+++}}}\frac{kT}{h}\exp\left(-\frac{\Delta F^* + \alpha n\mathcal{F}E}{RT}\right)(i_d - i) \qquad (16)$$

The value of A_t as a function of the mass of mercury flowing per second from the capillary, m, and its density, d, may be expressed by:

$$A_t = 4\pi\left(\frac{3m}{4\pi d}\right)^{2/3} \quad t^{2/3} \tag{17}$$

The Ilkovic constant may be written (Kolthoff and Lingane(22)):

$$K_{Cr^{+++}} = 4\left(\frac{7\pi}{3}\right)^{1/2} n\mathcal{F}\left(\frac{3m}{4\pi d}\right)^{2/3} D_{Cr^{+++}}^{1/2} \quad t^{1/6} \tag{18}$$

Incorporating Equations (17) and (18) into Equation (16) we obtain:

$$i_t = \left(\frac{3\pi}{7}\right)^{1/2} \frac{t^{1/2}}{D^{1/2}} \, X \mathcal{K} \frac{kT}{h} \exp\left(- \frac{\Delta F^* + \alpha n \mathcal{F} E}{RT}\right)(i_d - i) \tag{19}$$

The average value of the current is given by:

$$i = \frac{1}{t_{max}} \int_0^{t_{max}} i_t \, dt \tag{20}$$

where t_{max} is the drop time (hereafter called t), then:

$$i = \frac{2}{3}\left(\frac{3\pi}{7}\right)^{1/2} \frac{t^{1/2}}{D^{1/2}} \, X \mathcal{K} \frac{kT}{h} \exp\left(- \frac{\Delta F^* + \alpha n \mathcal{F} E}{RT}\right) \quad (i_d - i) \tag{21}$$

Converting to logarithms:

$$\ln i = \ln 0.77 \frac{t^{1/2}}{D^{1/2}} \mathcal{K} X \frac{kT}{h} - \frac{\Delta F^*}{RT} - \frac{\alpha n \mathcal{F} E}{RT} + \ln (i_d - i) \tag{22}$$

or

$$E = - \frac{\Delta F^*}{RT} + \frac{RT}{\alpha n \mathcal{F}} \ln 0.77 \frac{t^{1/2}}{D^{1/2}} \mathcal{K} X \frac{kT}{h} - \frac{RT}{\alpha n \mathcal{F}} \ln \frac{i}{i_d - i} \tag{23}$$

When i equals 1/2 i_d, E equals $E_{1/2}$ and:

$$E_{1/2} = - \frac{\Delta F^*}{\alpha n \mathcal{F}} + \frac{RT}{\alpha n \mathcal{F}} \ln 0.77 \frac{t^{1/2}}{D^{1/2}} \mathcal{K} X \frac{kT}{h} \tag{24}$$

So E may be given by:

$$E = E_{1/2} - \frac{RT}{\alpha n \mathcal{F}} \ln \frac{i}{i_d - i} \tag{25}$$

The preceding derivation was presented by Lewis(25). A more exact expression has been derived by Koutecky(24) from the equation

$$i_d = 607\ n\ CD^{1/2}\ m^{2/3}\ t^{1/6}\ (1 + Am^{-1/3}\ t^{1/6} \cdot D^{1/2}) \qquad (26)$$

where A is a constant given the value 34 by Koutecky,

C is the concentration of reducible ion in millimoles per liter, which allows for expansion of the mercury drop and curvature of its surface. The only change produced in the expression as used by Lewis is that the term "ln 0.77" is replaced by "ln 0.87". In the calculation of the experimental data in this study, Koutecky's value of 34 was used.

Plots of E vs ln $\frac{i}{i_d - i}$ for the polarograms obtained in this investigation for chromium (III) reduction to chromium (II) in 0.10<u>M</u> potassium nitrate often gave two straight lines intersecting at the half-wave potential. This indicates two mechanisms are involved with a change in mechanism occurring near the half-wave potential. The values of α corresponding to each stage in the mechanism are calculated from the slopes of the E vs ln $\frac{i}{i_d - i}$ plots. These values lie between zero and one. Other irreversible systems were found by Kolthoff and Lingane(22) and Orlemann(29) to fit Equation (25).

For convenience, Equation (24) can be written:

$$E_{1/2} = -\frac{\Delta F^*}{\alpha n \mathcal{F}} + \frac{RT}{\alpha n \mathcal{F}} \ln B \qquad (27)$$

where B equals ln 0.87 $\frac{t^{1/2}}{D^{1/2}}\ \mathcal{H}\ X\ \frac{kT}{h}$ (using Koutecky's constant).

Substituting $\Delta H^* - T\Delta S$ for ΔF^*, Equation (26) becomes:

$$E_{1/2} = -\frac{\Delta H^*}{\alpha n \mathcal{F}} + T\left[\frac{\Delta S^*}{\alpha n \mathcal{F}} + \frac{R}{\alpha n \mathcal{F}} \ln B\right] \qquad (28)$$

If we assume ΔH^* to be temperature independent, this equation has the form a + bT. Plotting $E_{1/2}$ vs temperature enables one to determine values for "a", the intercept on the $E_{1/2}$ axis at T equal zero, and "b", the slope of this plot. The thermodynamic properties for the rate-determining step may be expressed in terms of "a" and "b":

$$\Delta H^{*} = -\alpha n \mathcal{F} a \tag{29}$$

$$\Delta S^{*} = \alpha n \mathcal{F} b - R \ln B \tag{30}$$

$$\Delta F^{*} = \Delta H^{*} - T \Delta S^{*} \tag{31}$$

Similar expressions may be developed for the oxidation of the chromium (II), but were not considered within the scope of this investigation.

The experimentally determined values for ΔH^{*}, ΔS^{*}, ΔF^{*}, and α are discussed in a later section in regard to the various suggested mechanisms. The quantities are numerically the same regardless of the mechanism, but the effect on the values with changing solution and electrode surface conditions has significance in choosing a most reasonable mechanism.

VI. EXPERIMENTAL WORK

Consideration of the foregoing theories of possible mechanisms leads to the conclusion that investigation of the effect of temperature and surface active agents may offer evidence favorable to a particular mechanism. The study of temperature effect on the half-wave potential yields a value for the heat of activation. Changes in this value may permit the choice of a "most reasonable" reaction path.

Apparatus: Figure 7 is a photograph of the laboratory apparatus. The equipment used included:

1. A Leeds and Northrup Electro-Chemograph, Type E. The recorder

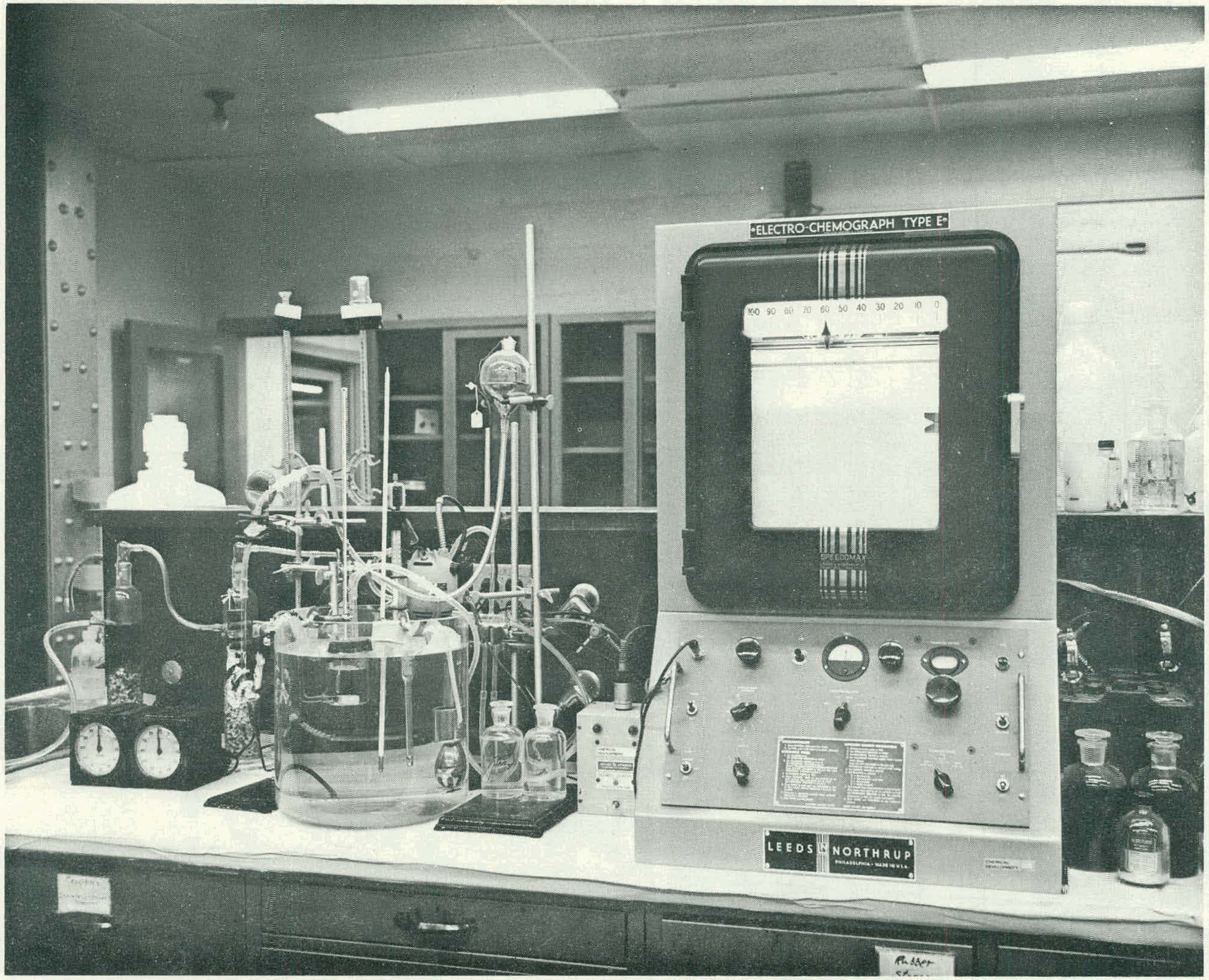


FIGURE 7

LABORATORY APPARATUS USED IN POLAROGRAPHIC STUDY OF THE MECHANISM OF ELECTROREDUCTION OF CHROMIUM (III) sensitivity used in these studies was 2 microamperes full scale. The damping control on this polarograph was used at the first position (minimum damping) without effecting the half-wave potential or distorting the current-voltage curve. The polarizing slidewire was calibrated against an Eppley Laboratories standard cell using a Leeds and Northrup K-2 potentiometer.

2. A dropping mercury electrode was prepared by connecting a Fisher Electropode capillary (approximately 0.05 millimeter bore diameter) to a leveling bulb by a length of Tygon tube. The drop time was regulated by adjusting the level of the mercury in the bulb relative to the capillary tip. This difference was 45.4 centimeters in all experiments. The quantity $m^{2/3}$ $t^{1/6}$ for this capillary was 2.00 ± 0.01 milligrams$^{2/3}$ seconds$^{-1/2}$ over the range of temperature and potential examined.
3. The reference electrode was prepared by grinding calomel with mercury and covering this mixture with saturated potassium chloride containing solid potassium chloride. The reference electrode temperature remained at 20 ± 1°. The saturated calomel reference electrode (S.C.E.) and bridge were shielded with aluminum foil and grounded to eliminate erratic currents in the cell circuit.
4. The polarographic cell was of the modified Carritt type(28) to permit rapid deaeration, yet exclude the diffusion of agar and chloride ion into the area around the dropping mercury electrode. Figure 8 shows the construction of the cell. The dimensions were: diameter, 4 centimeters; height, 8 centimeters. The resistance

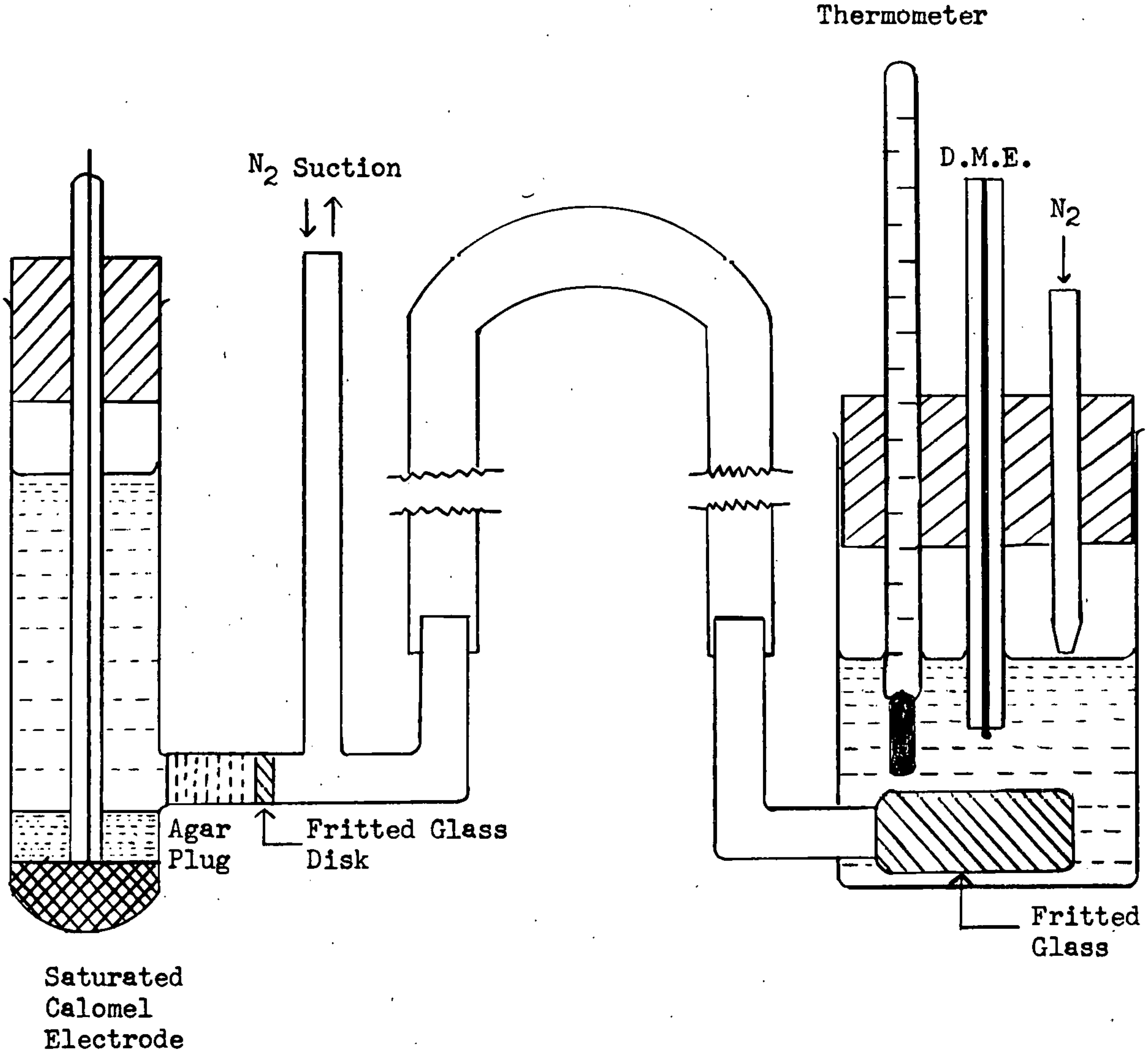


FIGURE 8

POLAROGRAPHIC CELL ASSEMBLY

of the cell assembly was measured with a Wheatstone bridge for use in correcting the measured potential for ohmic drop.

5. The cell temperature was regulated to ± 0.05 degree by a constant temperature bath controlled by a Bronwill Scientific, Inc. regulator. Sodium chromate was added to the bath water and the stirrer grounded to minimize the pickup of extraneous currents by the cell circuit.

Reagents: All reagents were prepared with reagent grade chemicals and distilled water. The chromium (III) nitrate and potassium nitrate were Baker Analyzed Reagent Grade. A 0.487M solution of chromium (III) nitrate was used in preparing all chromium solutions. In all experiments the chromium (III) concentration was 2.43×10^{-4}M and the potassium nitrate concentration 0.10M. Agar solutions were prepared by dissolving an appropriate weight of Difco Bacto-Agar in hot water and heating on a boiling water bath for one hour to insure complete hydrolysis. The indifferent electrolyte was then added, the solution cooled, an aliquot of the chromium (III) nitrate stock solution added, and the solution made up to volume.

Experimental Procedure: The cell was filled with 2.43×10^{-4}M chromium (III) nitrate, 0.01M potassium nitrate solution and deaerated by passing nitrogen (freed of oxygen by chromium (II) sulfate scrubbing) into the cell through the salt bridge and fritted glass cylinder. Purge time was fifteen minutes. The nitrogen flow was then changed to sweep the solution surface and suction applied to the nitrogen inlet to fill the bridge tube with cell solution. The dropping mercury electrode was placed in the cell following cleaning with 9M nitric acid and distilled water, in that order. Three polarograms were made each time the conditions were varied. The temperature was then adjusted and/or the solution changed and additional data taken.

Accuracy and Precision of Data: The current was measured from the polarograms with a standard deviation between the measurements of ± 1% including correction for the residual current. The values calculated for the Ilkovic constant, $K = \frac{i_d}{Cm^{2/3}\ t^{1/6}}$, for chromium (III) ions in this system are given with their standard deviation in Table I. Each of the values is the average of three determinations at agar concentrations varying from zero to 0.005 percent by weight. The temperatures are also averages of three values.

The diffusion constant for the chromium (III) ion at 25°, $D_{Cr^{+++}}$, calculated from the equation:

$$K = 607\ nD^{1/2}$$

where K is the Ilkovic constant, was found to be 5.4×10^{-6} cm^2 sec^{-1}. This is in good agreement with Lewis' value(25) of 5.6×10^{-6} cm^2 sec^{-1} in 0.1M perchloric acid and that of Lingane and Pecsock(26) who found 5.8×10^{-6} cm^2 sec^{-1} for the 0.5M sodium perchlorate system.

All potentials were measured against a saturated calomel electrode at room temperature (20 ± 1°). The stability of this reference electrode was checked periodically by determining the half-wave potential for cadmium reduction and was found to be constant within the precision of the graphical measurement which was ± 3 millivolts.

Chromium (III) concentrations are precise to ± 1% and agar to ± 0.2%. The drop time was constant at 4.52 ± 0.04 seconds at -1.0 volt vs the saturated calomel electrode. Cell temperature was controlled to ± 0.05°.

Potassium nitrate concentration was 0.10M ± 0.1%.

The Current-Voltage Curves: Figure 9 shows typical current-voltage curves obtained for the chromium (III)-chromium (II) reduction in 0.10M potassium nitrate. These curves are tracings of the average of the current fluctuations with the dropping electrode as recorded by the polarograph.

Analysis of the Data: The theories described in a preceding section all predict the following current-voltage relationship:

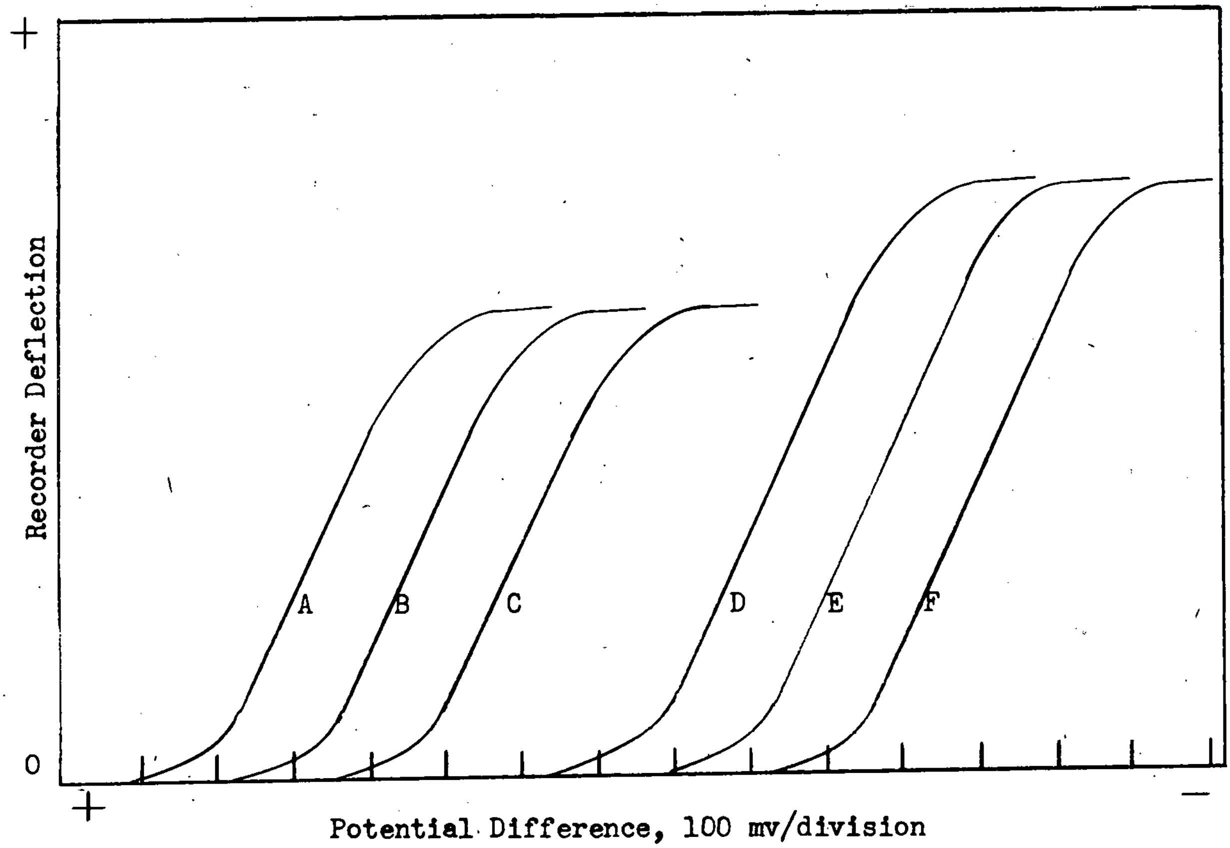
$$E = E_{1/2} - \frac{RT}{n} \ln \frac{i}{i_d - i} \tag{32}$$

Using this equation, all polarograms were analyzed by plotting the potential vs the logarithm of $\frac{i}{i_d - i}$. Figure 10 shows some typical results. Below 30.0° a strict linear relationship was observed in accordance with Equation (32). At 30.0° and above, however, two straight lines, intersecting at log $\frac{i}{i_d - i}$ equals zero, became apparent.

The half-wave potential, $E_{1/2}$, was determined as the value of E at which the logarithm of $\frac{i}{i_d - i}$ was zero. Numerical values for $E_{1/2}$, slopes of the straight line or lines, and the corresponding values of α are given in Table 2. In the cases where two straight lines were obtained, $E_{1/2}$ was determined by their point of intersection with the logarithm term equal zero line. Slope and α values for the two lines were calculated separately. In Table 2, values for the line to the positive side of $E_{1/2}$ are denoted by the subscript I, those on the negative side of $E_{1/2}$ by II.

Values were obtained from:

$$\alpha = - \frac{2.303\ RT}{n \mathcal{F} (\text{slope})} \tag{33}$$



A. No Agar, 25°.

B. 2.5 x 10^{-3}% Agar, 25°.

C. 5.0 x 10^{-3}% Agar, 25°.

D. No Agar, 40°.

E. 2.5 x 10^{-3}% Agar, 40°.

F. 5.0 x 10^{-3}% Agar, 40°.

FIGURE 9

CURRENT-VOLTAGE CURVES FOR REDUCTION OF CHROMIUM (III) AT THE DROPPING MERCURY ELECTRODE IN 0.10M POTASSIUM NITRATE AND VARYING AGAR CONCENTRATIONS

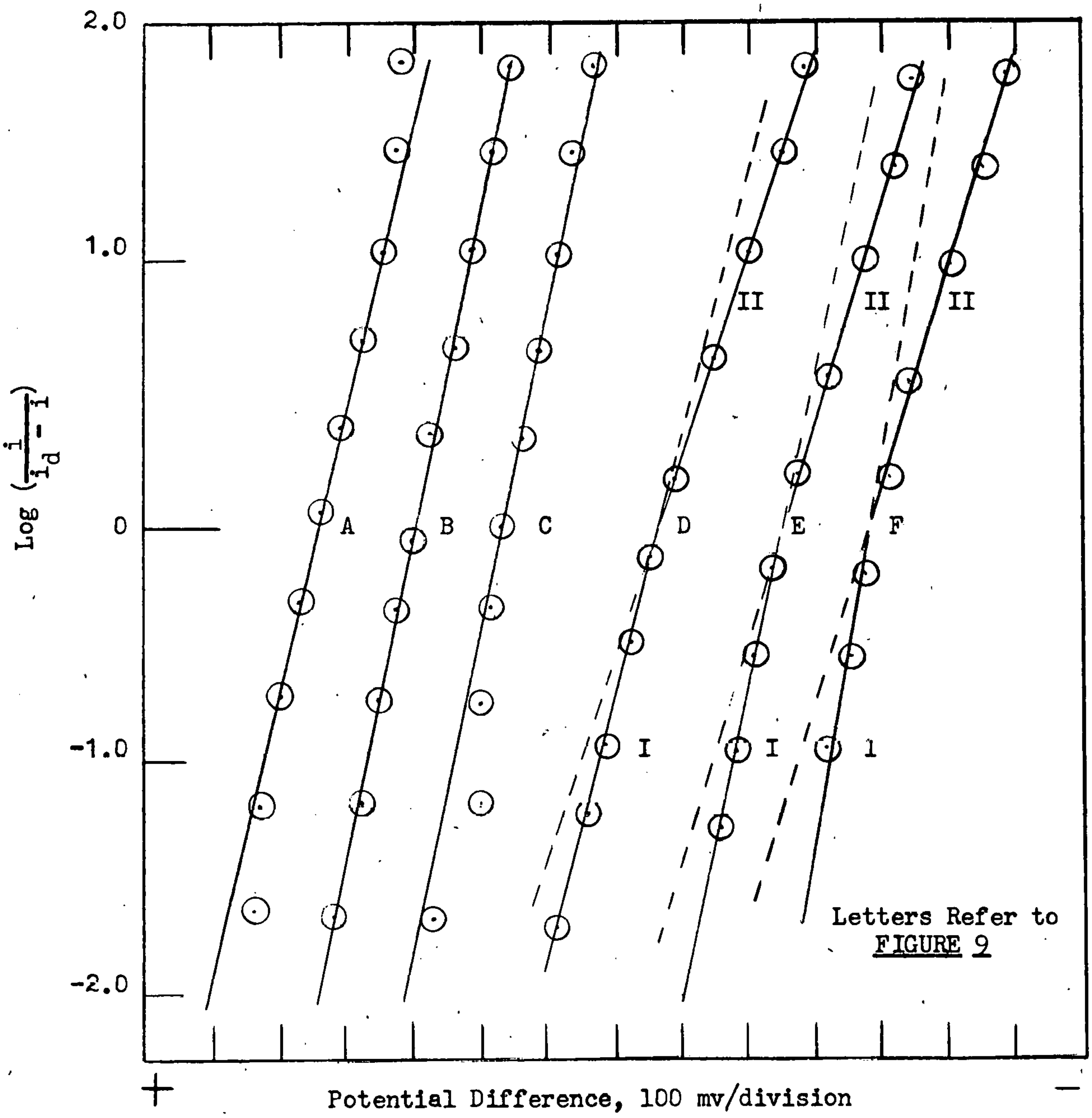


FIGURE 10

POTENTIAL VERSUS LOG $(\frac{i}{i_d - i})$ FOR THE REDUCTION OF CHROMIUM (III) IONS AT THE DROPPING MERCURY ELECTRODE IN 0.10M POTASSIUM NITRATE AND VARYING AGAR CONCENTRATIONS.

where

$$\text{slope} = \frac{dE}{d\ \log \frac{i}{i_d - i}} \qquad (34)$$

The half-wave potential for a particular agar concentration was plotted against temperature. The curves obtained were linear. Figure 11 shows this relationship for varying agar concentration. The slope of this plot corresponds to "b" in Equation (30) and the intercept at $0^{o}K$ to "a" in Equation (29). Therefore:

$$\Delta H^{*} = - a \alpha n \mathcal{F} \qquad (35)$$

$$\Delta S^{*} = b \alpha n \mathcal{F} - R \ln \frac{0.87\ t^{1/2} \kappa X}{D^{1/2}} \quad \frac{kT}{h} \qquad (36)$$

All values of "a", and therefore ΔH^{*}, were calculated in reference to the normal hydrogen electrode, N.H.E., which is -0.242 volt vs the saturated calomel electrode.

The transmission coefficient, κ, is assumed to be unity for all calculations.

The distance factor, X, of Equation (14) was assumed to be 100 Å in calculating ΔS^{*} and ΔF^{*}. This figure was chosen as a reasonable maximum distance at which reduction might occur and also so that the data of this study would be comparable with those of Lewis[25] for the perchloric acid system. The value of ΔS^{*} will differ by 4.6 cal mole^{-1} deg^{-1} for a factor of ten error in this assumption. Therefore, there is an uncertainty in ΔF^{*} of 4.6T or 13.5 kcal mole^{-1} at 25^{o} for a deviation of X from 100 Å by a factor of ten.

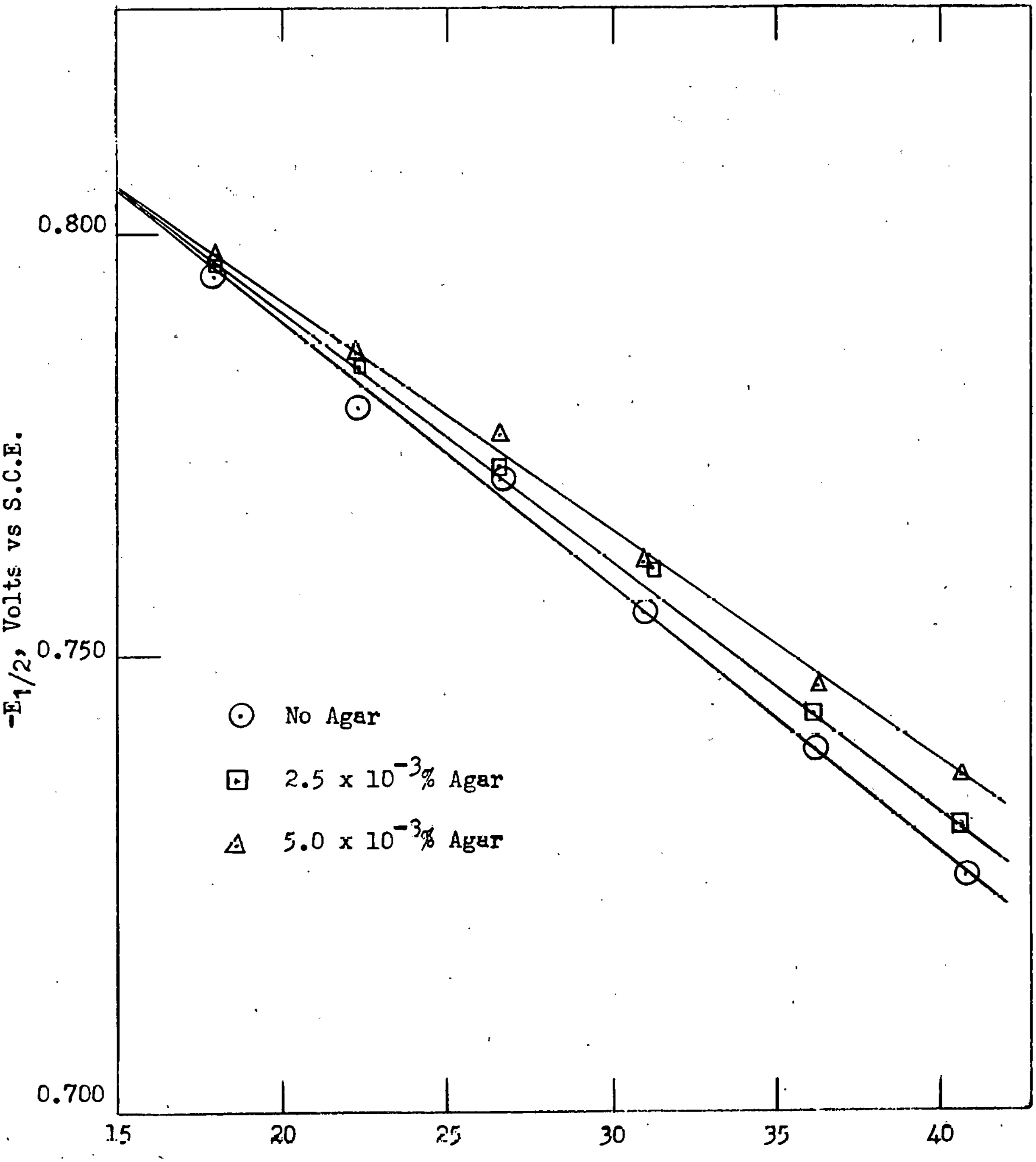


FIGURE 11

HALF-WAVE POTENTIALS FOR THE REDUCTION OF CHROMIUM (III) AT THE DROPPING MERCURY ELECTRODE IN 0.10M POTASSIUM NITRATE AS A FUNCTION OF TEMPERATURE AND AGAR CONCENTRATION.

VII. RESULTS AND DISCUSSION

In the treatment of the experimental data in which log $\frac{i}{i_d - i}$ plotted against E, two straight lines were obtained which intersected at the half-wave potential (log $\frac{i}{i_d - i}$ equals zero). The data obtained from these plots (Table 2) show two values for α suggesting the existence of two mechanisms for which the thermodynamic functions $\triangle H^*$, $\triangle S^*$, and $\triangle F^*$ were calculated and are shown in Table 3.

Similar evidence for the existence of two mechanisms was obtained in a perchloric acid system(7) and was explained by the postulation that, in addition to electron transfer, electron exchange between the reduced form near the electrode surface and the oxidized form in the diffusion layer became prominent at the half-wave potential. The application of this hypothesis to the present investigation is supported by the fact that the chromium (II) concentration at the electrode surface increases with increasing negative potential until at $E_{1/2}$ it is approximately equal to the chromium (III) concentration.

In the present study, the effect of agar on the thermodynamic functions for segments I and II of the log $\frac{i}{i_d - i}$ vs E plots (Figure 10) was investigated in the hope that the information obtained would help in the choice of reasonable mechanisms to explain the different slopes of the two segments. A maximum agar concentration of 5.0×10^{-3} weight percent was chosen for the present investigation from data by other experimenters(25) which indicated that the formation of a monomolecular layer of agar on the mercury surface is completed at this concentration (Figure 12). The elimination of maxima on polarograms obtained in this study following

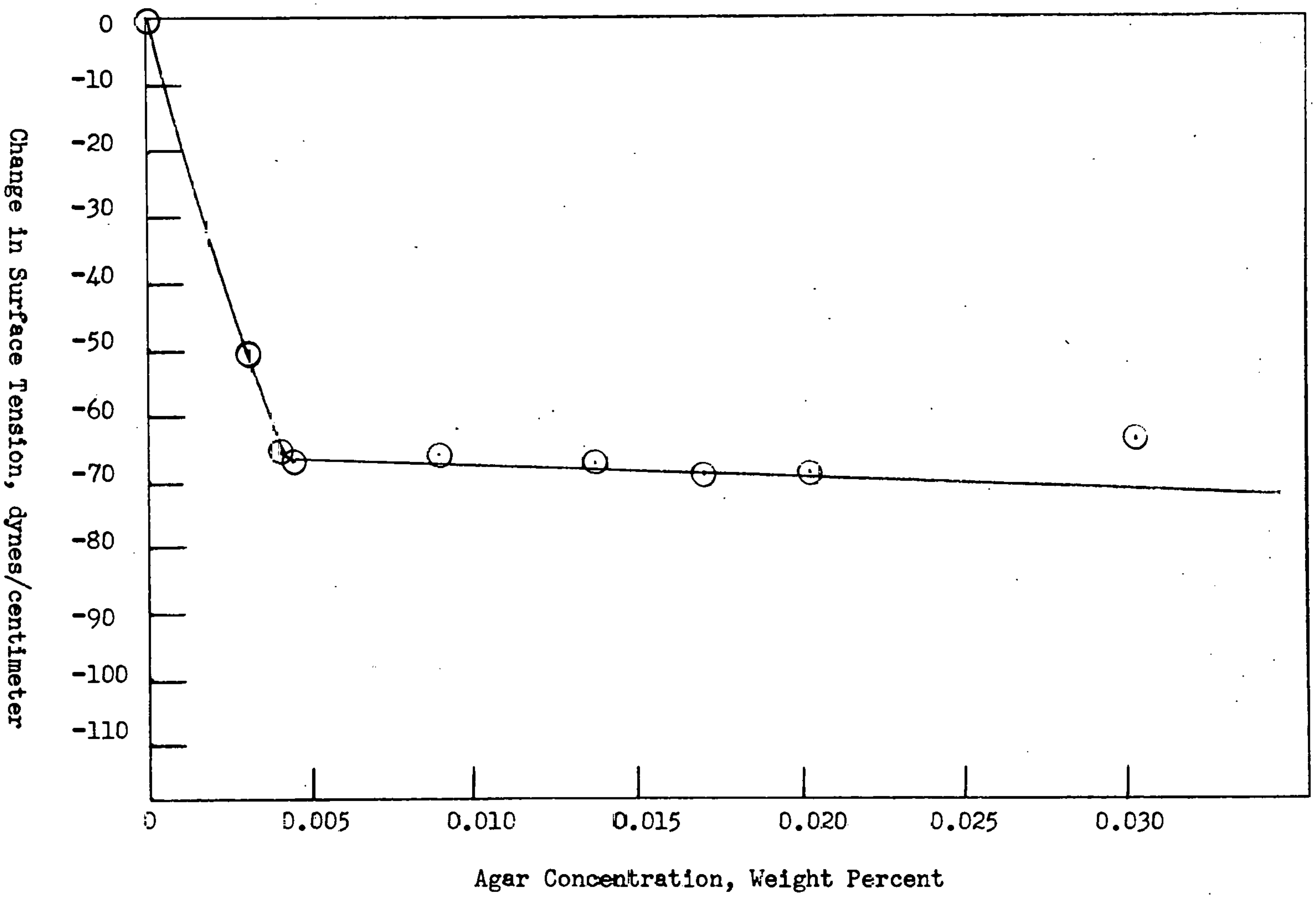


FIGURE 12

CHANGE IN THE SURFACE TENSION OF MERCURY IN AGAR SOLUTIONS AT 25° AS A FUNCTION OF AGAR CONCENTRATION.

the addition of agar indicated that the agar was still adsorbed at potentials corresponding to the reduction of chromium (III) to chromium (II). An adsorbed layer of agar on the mercury electrode would alter the mechanism of reduction and cause a change in the heat of activation, if the mechanism involves adsorption or desorption of the chromium (III) or chromium (II) ions.

The data in Table 3 indicate that the heat of activation for the reduction of chromium (III) to chromium (II) did not change within experimental error over the range of agar concentration studied. It may be concluded from the constancy of the values for the heat of activation, with and without agar, that adsorption or desorption of chromium ions on the mercury surface does not play a part in the mechanism of reduction.

A calculation of the thermodynamic values for the activation reaction in the electron transfer mechanism may be made. When a chromium (III) ion is reduced, the coordinated water sphere associated with this ion must expand to that of the chromium (II) ion. In the electron transfer mechanism, this expansion of the coordinated water sphere may be the activation or rate-determining step. From a consideration of the energy of a particle in a dielectric(25):

$$\triangle F^* = \frac{q^2}{2K}\left(\frac{1}{r} - \frac{1}{r^*}\right) \tag{37}$$

where q is the charge of an ion of radius r in a medium with the dielectric constant K. r^* in this case refers to the radius of the chromium (II) ion. Similarly, the entropy change is given by:

$$\triangle S^* = -\frac{d(\triangle F^*)}{dt} = \frac{q^2}{2K^2}\left(\frac{1}{r} - \frac{1}{r^*}\right) \frac{dK}{dT} \tag{38}$$

For example, for the change from chromium (III) (r = 0.62 Å) to chromium (II) (r^* = 0.80 Å) in an aqueous medium, $\triangle F^*$ was calculated to be 5.5 kcal mole^{-1} and ΔS^* 105 cal mole^{-1} deg^{-1}. The heat of activation ($\Delta H^* = \Delta F^* + T\Delta S^*$) using these values was calculated to be about 37 kcal mole^{-1} at 25°.

The average experimental value of ΔH^* at all agar concentrations (Table 3) for the reduction of chromium (III) to chromium (II) at potentials more positive than the half-wave potential was 34 kcal mole^{-1}. This is in good agreement with the theoretical value of 37 kcal mole^{-1} calculated from Equations (37) and (38) for an electron transfer process.

Numerical values for ΔS^* and ΔF^* are dependent on the rate theory applied in the derivation of the equations describing the rate of reduction. However, the effect of changing solution conditions on the values of ΔS^* and ΔF^* (Table 3) may be used in interpreting the mechanism.

With increasing agar concentrations ΔS^* becomes more negative (Table 3). This may be due to an increase in the distance X as the electrode becomes more heavily coated with agar or to a more precise degree of orientation required for transfer of the electron between the partially covered electrode and the ion.

At the electrode, a potential gradient exists over an appreciable distance from the electrode surface due to the quantum mechanical tunneling effect. Figure 6 shows a graphical picture of this gradient. The compact portion of the double layer has been calculated(14) to be in the order of 10 Å thick and accounts for about 90 percent of the potential drop, the diffuse portion extending out for several hundred angstroms.

Applying Figure 6 to the experimental data for the reduction of chromium (III) at potentials more positive than $E_{1/2}$, it is evident that the chromium (III) ion is reduced at a point where the potential has dropped to 92 percent ($\alpha = 0.92$) of the value at the electrode surface or at a distance of approximately 10 Å, near the outer surface of the compact double layer. Assuming this value to be correct for X in Equation (28) the values of ΔS^* and ΔF^* would be changed by +4.6 cal mole^{-1} deg^{-1} and -13.7 kcal mole^{-1}, respectively.

The α value for segment II (Figure 10) is consistently smaller than the α value for the electron transfer process (segment I), which occurs at more positive potentials. Since the transfer coefficient, α , was defined as the fraction of the total potential difference between the electrode and the body of the solution that was effective in reducing the ion, then by the exchange,

$$Cr^*(III) + Cr(II) \rightleftharpoons Cr^*(II) + Cr(III),$$

a chromium (III) ion has been effectively transported from position Cr to Cr*, i.e., closer to the electrode, across a portion of the potential gradient without the use of the potential difference. Therefore, the total process involving both electron transfer and exchange (segment II) must have a lower transfer coefficient than one in which no exchanges occur (segment I). Table 2 shows the expected difference in the transfer coefficients for the two reaction paths.

Figure 13 shows a comparison between the effect of agar on the entropy of activation for the process occurring at potentials more positive than $E_{1/2}$ and that occurring more negative than $E_{1/2}$. The two curves show an almost identical effect with increasing agar concentration as would be expected if the electron exchange occurred concurrently with electron transfer as the secondary mechanism. The heat of activation for the composite mechanism was not affected by agar adsorption on the mercury

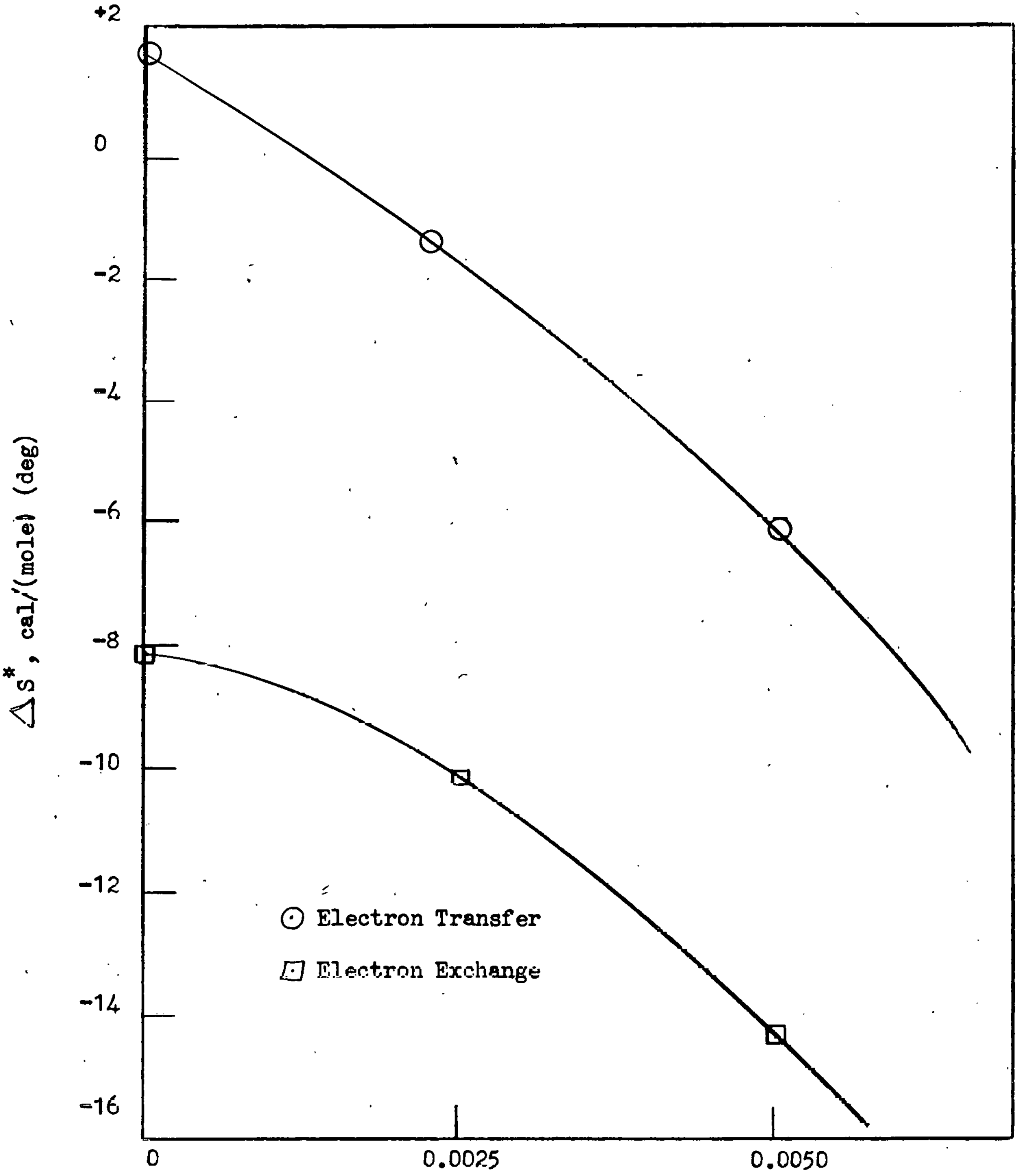


FIGURE 13

ENTROPY OF ACTIVATION FOR THE REDUCTION OF CHROMIUM (III) IN 0.10M POTASSIUM NITRATE AS A FUNCTION OF AGAR CONCENTRATION surface (Table 3). Electrode surface changes would not be expected to affect the exchange mechanism, and it has already been shown that the presence of agar had no effect on the primary mechanism, electron transfer. Thus, the dual mechanism hypothesis is in agreement with the experimental data.

VIII. SUMMARY

The reduction of chromium (III) to chromium (II) in 0.10<u>M</u> potassium nitrate at potentials more positive than the half-wave potential proceeds by a mechanism in which the transfer of an electron from the electrode to an ion near the inner limit of the diffuse portion of the double layer is the rate-determining step. The chromium (III) ion is activated by the expansion of its water sheath to the chromium (II) configuration.

At potentials more negative than the half-wave potential, the increasing ratio of chromium (II) to chromium (III) ions in the diffuse layer promotes an electron exchange mechanism which is concurrent with the electron transfer occurring nearer the electrode surface. A chromium (II) ion reduces an incoming chromium (III) ion while it is still in the vicinity of the electrode. This oxidized ion is then re-reduced through electron transfer from the electrode.

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APPENDIX

TABLE 1

The Ilkovic Constant for the Reduction of Chromium (III) to Chromium (II) in 0.10M Potassium Nitrate at Various Temperatures

Temperature °C	$K = \frac{i_d}{Cm^{2/3}\,t^{1/6}}$ microamperes second$^{1/2}$ millimole^{-1} liter^{-1} milligram$^{-2/3}$
20.1	1.41 ± 1.6%
25.0	1.49 ± 1.7%
30.0	1.60 ± 1.5%
35.0	1.70 ± 2.6%
40.0	1.84 ± 1.1%

All values of K are the average of three determinations.

Precisions are standard deviations.

TABLE 2

Reduction of Chromium (III) Ions at the Dropping Mercury Electrode in 0.10M Potassium Nitrate as a Function of Temperature and Agar Concentration

Temperature °C	Agar, Weight Percent	$-E_{1/2}$ Volts vs S.C.E.	$\alpha_{avg.}$	α_{I}	α_{II}
20.3	0	0.805	0.76	----	----
19.6	2.5×10^{-3}	0.806	0.81	----	----
20.5	5.0×10^{-3}	0.808	0.79	----	----
25.0	0	0.792	0.76	----	----
25.0	2.5×10^{-3}	0.799	0.81	----	----
25.0	5.0×10^{-3}	0.798	0.80	----	----
30.0	0	0.789	0.74	0.82	0.66
29.9	2.5×10^{-3}	0.790	0.80	----	----
30.1	5.0×10^{-3}	0.789	0.83	0.92	0.73
35.0	0	0.775	0.83	0.93	0.73
35.0	2.5×10^{-3}	0.775	0.82	0.94	0.69
35.0	5.0×10^{-3}	0.782	0.80	0.91	0.69
40.0	0	0.764	0.82	0.94	0.70
40.0	2.5×10^{-3}	0.764	0.81	0.91	0.70
39.9	5.0×10^{-3}	0.764	0.84	0.94	0.74

TABLE 3

Reduction of Chromium (III) Ions at the Dropping Mercury Electrode Over the Range 20° to 40° in 0.10M Potassium Nitrate

	Agar, Weight Percent		
	0	2.5×10^{-3}	5.0×10^{-3}
"a" (volts vs N.H.E.)	-1.673	-1.635	-1.578
"b" (mv/deg)	2.13	2.00	1.80
ΔH^{*}_{avg} (kcal/mole)	29.7	30.2	28.9
ΔH^{*}_{I} (kcal/mole)	34.7	35.1	33.5
ΔH^{*}_{II} (kcal/mole)	27.0	26.4	26.2
$\Delta S^{*}_{25^{o}I}$ (cal/(deg) (mole)	+1.7	-1.4	-6.1
$\Delta S^{*}_{25^{o}II}$ (cal/(deg) (mole)	-8.1	-12.0	-14.4
$\Delta F^{*}_{25^{o}I}$ (kcal/mole)	34.2	35.5	35.3
$\Delta F^{*}_{25^{o}II}$ (kcal/mole)	29.4	30.0	30.5


Phillips
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