

by the loss of active sites by the readsorption of impurities and other species.

When the ultrasonic waves were turned off, the overvoltage did not recover its original value. This can be explained on the basis that impurities and other particles adsorbed irreversibly on the electrode surface prior to the overvoltage measurements were not readily readsorbed at the more cathodic potential of the electrode when polarizing current was being passed. This hypothesis is supported by the fact that the overvoltage regained its original value when the polarizing current was turned off for a short time. Under these circumstances the potential of the electrode decayed to a voltage approaching the original value before passage of polarizing current.

The ability of ultrasonic waves to strip off adsorbed materials on the electrode surface can be readily appreciated if consideration is given to the fact that high intensity ultrasonic waves (10 watts/cm.<sup>2</sup>) have been used (in this Laboratory) to produce suspensions of metals such as copper and aluminum by direct irradiation of these metals as foils in liquids. An increase in the surface area through the erosion of the electrode surface might have been considered as a direct explanation for the decrease in polarization produced by ultrasonic waves if it were not that the original values for the polarization are obtained after the current has been interrupted for a short period.

Further attention would have also been given to the "stripping off" of adsorbed hydrogen through cavitation except that such an effect would modify the slope of the overvoltage-log  $I$  plot. The only apparent way such a mechanism could be a major factor without influencing the Tafel slope would be for the stripping action to be proportional to the square of the surface concentration which is unlikely. Explanations involving the formation of electroactive materials such as free radicals through cavitation have been given little consideration since the effect of such depolarizers would be dependent on current density. Likewise, it does not seem feasible to explain the effect in terms of changes in the average temperature at the electrode because such effects would be very small in a well thermostated system and would not persist after the radiations have ceased.

Thus, the two explanations involving the factor  $H$  in equation (14) and  $N$  in equations (6) and (7) seem most feasible in terms of the experimental results. Experimental work is in progress at the present time in an attempt to further substantiate these hypotheses.

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## ELECTRODE PHENOMENA AND THE THERMODYNAMICS OF IRREVERSIBLE PROCESSES<sup>1</sup>

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The thermodynamics of irreversible processes developed by De Donder, Prigogine, de Groot and others makes possible a systematic presentation of electrochemical thermodynamics in which reversible electrode processes, reversible cells, states of electrochemical equilibrium, etc., appear as limiting cases in a more general treatment. A rational thermodynamic theory of polarization can thus be constructed. The concepts of uncompensated heat, power of irreversibility, entropy production and affinity of irreversible chemical reactions are now extended to irreversible electrochemical processes. The concept of power of polarization is introduced and its connection with electrochemical affinity and overvoltage is developed and discussed. In addition to complete cells one treats single electrodes which are the seats of one or of several half-reactions. In the case of mixed electrode processes occurring not too far from reversibility, linear relations between reaction velocities (or currents) and electrochemical affinities (or overvoltages), with application of Onsager's reciprocity principle between "drag coefficients," are used. Prigogine's theorem concerning stationary states of minimum entropy production is extended to electrochemical processes. These theoretical considerations suggest experimental investigations, in particular in the field of corrosion.

### Introduction

A rational thermodynamic treatment of electrochemical systems (galvanic and electrolytic cells, single electrodes) requires the use of the thermodynamics of irreversible processes. Although by no means new this discipline is still unfamiliar to the majority of physical chemists and electrochemists. Moreover, electrochemistry has not yet been given more than scant attention by the main contributors to the field of irreversible thermodynamics. Among these we should distinguish between the authors

who are concerned with the whole range of degrees of irreversibility of chemical reactions (pressure and temperature being uniform and chemical potentials corresponding to the ordinary statistical distribution functions of the various components) and the authors who are mainly concerned with the neighborhood of equilibrium and with the linear relations between reaction velocities and affinities (or more generally between flows and forces), the phenomenological coefficients obeying Onsager's reciprocal relations.<sup>2</sup> The first group of authors consists chiefly of De Donder and his collaborators, often designated as constituting the "Brussels or Belgian

(1) Paper presented at the Symposium on Electrode Processes held by the Division of Physical and Inorganic Chemistry of the American Chemical Society at the Atlantic City, N. J., meeting, September 14 to 19, 1952.

(2) L. Onsager, *Phys. Rev.*, **37**, 405, 2265 (1931).

school." A first presentation of electrochemical thermodynamics was included in the 1936 monograph on affinity.<sup>3</sup> Prigogine<sup>4</sup> also devoted a chapter to electrochemistry in his monograph of 1947 in which the Onsager relations and their implications are systematically added to the De Donder type of presentation of chemical thermodynamics. In de Groot's recent book<sup>5</sup> will be found a very brief discussion of electrochemistry which does not go beyond the scope of Prigogine's presentation. Several other authors have made some use of irreversible thermodynamics in their electrochemical studies. Among these we wish to mention particularly Piontelli<sup>6</sup> and Pourbaix.<sup>7</sup> In a monograph now nearly completed<sup>8</sup> we present a detailed and systematic treatment of electrochemical systems and electrode processes by the methods of the theory of affinity of De Donder and taking into account the later developments contributed by Prigogine and others. In the present communication we wish to outline the essential steps of this treatment which we believe to be of fundamental importance to the progress of our understanding of electrode processes. Time and space limitations force us to postpone to later communications certain important aspects of the subject and in particular the discussion of thermo-electrochemistry, Peltier heats, etc.

The systems we shall be considering are cells, galvanic or electrolytic, and half-cells or single electrodes. In addition to heat and work against the external pressure a cell exchanges electrical work with its surroundings through the passage of an electrical current from one terminal to the other in an external circuit. Inside the cell this current causes electrode reactions to occur in accordance with Faraday's laws of electrolysis. At the same time electrolytic migration and various polarization phenomena will occur in the system, diffusion phenomena will occur at liquid junctions, etc. All these phenomena are irreversible. Perfect reversible behavior is exceptional and is theoretically possible only for zero current. Independently of polarization, diffusion, etc., the passage of current will result in the production of the Joule heat  $RI^2$  which is an ever-present item in the various contributions to the total uncompensated heat. It is clear that, beyond the inequalities and qualitative statements

(3) Th. De Donder, "L'Affinité," new presentation by P. Van Rysselberghe, Gauthier-Villars, Paris, 1936, see Chapter XVI, pp. 123-137. Th. De Donder and P. Van Rysselberghe, "Thermodynamic Theory of Affinity," Stanford University Press, 1936, see Chapter XVI, pp. 123-137.

(4) I. Prigogine, "Étude Thermodynamique des Phénomènes Irréversibles," Dunod, Paris, and Desoer, Liège, 1947, see Chapter III, pp. 29-47.

(5) S. R. de Groot, "Thermodynamics of Irreversible Processes," Interscience Publishers, Inc., New York, N. Y., 1951, see Chapter IX, pp. 181-184.

(6) R. Piontelli, see various articles and further references in "Proceedings of the Second and of the Third Meetings of the International Committee of Electrochemical Thermodynamics and Kinetics," Tamburini, Milan, 1951; Manfredi, Milan, 1952.

(7) M. Pourbaix, "Thermodynamique des Solutions Aqueuses Diluées—Rôle du pH et du Potentiel," Meinema, Delft, and Béranger, Paris, 1946. "Thermodynamics of Dilute Aqueous Solutions—with Applications to Electrochemistry and Corrosion," Longmans-Green, New York, 1949. Articles and further references in "Proceedings, etc."<sup>8</sup>

(8) P. Van Rysselberghe, "Electrochemical Affinity—Studies in Electrochemical Thermodynamics and Kinetics," a monograph in preparation.

usually found in the discussions of these irreversible phenomena, a quantitative treatment such as that available through irreversible thermodynamics appears highly desirable.

The electrical potentials we shall be dealing with are the internal ones which have been clearly defined by Lange.<sup>9</sup> We shall designate them by the Greek letter  $\varphi$ . The differences of internal potentials between two phases are *Galvani potential differences*. The external electrical potentials  $\psi$  are those taken at a distance of the order of  $10^{-4}$  cm. of the external geometrical surface of the phase. Differences of  $\psi$  potentials are *Volta potential differences*. Between the  $\varphi$  and  $\psi$  potentials pertaining to the same phase we have the relationship

$$\varphi = \psi + \chi \quad (1)$$

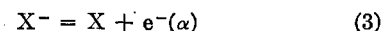
in which  $\chi$  designates the surface potential difference.

Our electrochemical systems will be of one or another of the types represented on Figs. 1 to 4: an electrode of metal  $\alpha$  and one of metal  $\alpha'$  dip in the same solution  $\beta - \beta'$  (Fig. 1) or in separate solutions  $\beta$  and  $\beta'$  connected by means of a siphon constituted in such a manner as to minimize liquid junction potential differences (Fig. 2). To metal  $\alpha$  we attach a piece of metal  $\alpha''$  identical with  $\alpha'$ . This precaution does away with several complications to be discussed later. One may also attach pieces of a common metal to  $\alpha$  and  $\alpha'$  (Fig. 3). The external circuit may consist of a simple resistance or it may include one or several generators of current (Fig. 4). Our thermodynamic "closed" system is ( $\alpha''\alpha\beta\beta'\alpha'$ ), the external circuit being a portion of the surroundings. During the lapse of time  $dt$  we have  $dn_e$ - moles of electrons transported from terminal  $\alpha''$  to terminal  $\alpha'$ . The positive current  $I$  flows in the opposite direction and we have

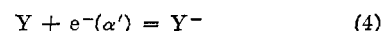
$$I = F \frac{dn_e}{dt} \quad (2)$$

in which  $F$  represents the Faraday. The layers of solution  $\beta$  and  $\beta'$  are taken at sufficient distances from  $\alpha$  and  $\alpha'$  to maintain from  $\beta$  to  $\beta'$  a composition identical with that before the passage of the current. The various phenomena resulting from the passage of the current (polarization, migration, diffusion) involve the layers between  $\alpha$  and  $\beta$  or  $\alpha'$  and  $\beta'$ .

If we consider  $dn_e$ - as positive we have at electrode  $\alpha$  the anodic reaction



and at electrode  $\alpha'$  the cathodic reaction

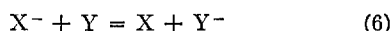


The symbols  $X$  and  $Y$  represent one or several species corresponding to the oxidized forms, the symbols  $X^-$  and  $Y^-$  one or several species corresponding to the reduced forms of the couples ( $X, X^-$ ) and ( $Y, Y^-$ ). It is convenient to write all electrochemical half-reactions in terms of one single electron. In addition to the electrode processes (3) and (4) we have the transfer of electrons from  $\alpha$  to  $\alpha''$



(9) E. Lange, "Elektrochemie des Phasengrenzen" in "Handbuch des Experimentalphysik," Vol. XII, Part 2; also, ref. 6, 1951, see pp. 317-343.

Adding processes (3), (4) and (5) we get the cell reaction



which, through addition on either side of ionic species not involved in the reaction, can always be written as a reaction between neutral species. This will of course be possible only if process (5) is added to (3) and (4). We have here one of the several reasons for making the terminals of the cell chemically identical. Another reason which will be immediately apparent is that in this manner there is no work of chemical extraction of the electrons to be considered in the total work done by the system.

**First Law of Thermodynamics for Electrochemical Systems.**—During the time  $dt$  the energy of the system is increased by  $dE$ , the heat received is  $dQ$ , the work done is  $dw$ . We have

$$dE = dQ - dw \quad (7)$$

The work against the external pressure is  $p dV$  and the work corresponding to the transfer of  $dn_{e^-}$  moles of electrons from  $\alpha''$  to  $\alpha'$  is

$$dw_{el} = F(\varphi^{\alpha'} - \varphi^{\alpha''})dn_{e^-} \quad (8)$$

The energy balance of our system is thus

$$dE = dQ - p dV - F(\varphi^{\alpha'} - \varphi^{\alpha''})dn_{e^-} \quad (9)$$

In the particular case of a short-circuit being established between the terminals, making  $\varphi^{\alpha''} = \varphi^{\alpha'}$ , we have the physical chemical change of state of the system remaining the same as in (9)

$$dE = dQ_s - p dV \quad (10)$$

in which the subscript  $s$  designates the condition of short-circuit. We have also

$$dQ_s = dQ - F(\varphi^{\alpha'} - \varphi^{\alpha''})dn_{e^-} \quad (11)$$

### Second Law of Thermodynamics for Electrochemical Systems

Introducing, in accordance with De Donder's method,<sup>2</sup> the uncompensated heat  $dQ'$ , the entropy increase  $dS$ , the affinity of the reaction  $A$  and its progress  $d\xi$  during the time  $dt$ , we have in the absence of electrical work, *i.e.*, for the condition of short-circuit in the case of our electrochemical system

$$dQ'_s = T dS - dQ_s = A d\xi \geq 0 \quad (12)$$

The affinity  $A$  is that of reaction (6) and is related to the free enthalpy  $G = E - TS + pV$  of the system by the relation<sup>3,10</sup>

$$\left(\frac{\partial G}{\partial \xi}\right)_{p,T} = -A \quad (13)$$

Here we have  $d\xi = dn_{e^-}$ . The ratio  $dQ'_s/dt$  has been called the power of irreversibility,<sup>3</sup> while the ratio of this quantity over the temperature  $T$  is the entropy production (see particularly Prigogine<sup>4</sup>). We have

$$P = \frac{dQ'_s}{dt} = A \frac{d\xi}{dt} = T \frac{diS}{dt} \geq 0 \quad (14)$$

The total change in entropy of the system is such that

$$\frac{dS}{dt} = \frac{deS}{dt} + \frac{diS}{dt} = \frac{1}{T} \times \frac{dQ_s}{dt} + \frac{diS}{dt} \quad (15)$$

(10) P. Van Rysselberghe, *Chem. Revs.*, **16**, 29, 37 (1935); *J. Chem. Educ.*, **16**, 476 (1939).

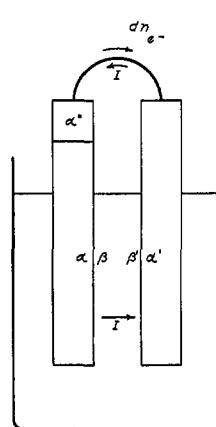


Fig. 1.

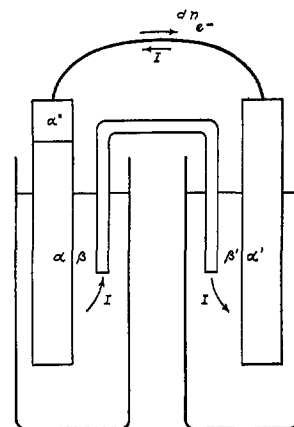


Fig. 2.

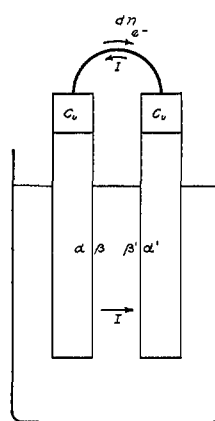


Fig. 3.

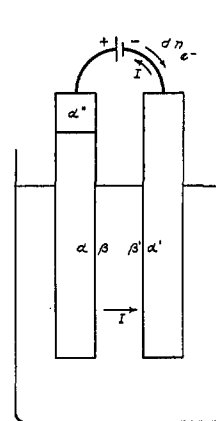


Fig. 4.

All this applies to the case of short-circuit. With performance of electrical work by the system the entropy production is decreased. The uncompensated heat, instead of being given by (12) is now given by (see (11) and (12))

$$dQ' = A d\xi - F(\varphi^{\alpha'} - \varphi^{\alpha''}) dn_{e^-} \geq 0 \quad (16)$$

or, in terms of the current defined in (2)

$$dQ' = [A/F - (\varphi^{\alpha'} - \varphi^{\alpha''})]I dt \geq 0 \quad (17)$$

Introducing the corresponding value of  $dQ$  in (9) we obtain

$$dE = T dS - p dV - dQ' - F(\varphi^{\alpha'} - \varphi^{\alpha''})dn_{e^-} \quad (18)$$

or also

$$dE = T dS - p dV - A d\xi \quad (19)$$

a formula which is identical with that holding in the absence of electrical work.<sup>3</sup> Our reasoning is thus seen to be equivalent to that of Prigogine<sup>4</sup> and of de Groot<sup>5</sup> which is based upon the hypothesis of the validity of Gibbs' fundamental formula for the differential of entropy outside of equilibrium. Introducing the electrical power produced by the system  $P_{el}$  we see that the power of irreversibility is given by the formula

$$P = Av - P_{el} \quad (20)$$

in which  $v$  is the reaction velocity  $d\xi/dt$  or  $dn_{e^-}/dt$ .

**Entropy Production Near Electrochemical Equilibrium and Entropy Production Due to the Joule Effect.**—The difference  $A - F(\varphi^{\alpha'} - \varphi^{\alpha''})$  being such that its product by the current is positive

can be regarded as the cause of this current and, in the range of small values of this difference, the current will be correspondingly small. The two quantities can then be regarded as proportional to each other. Representing the difference  $A - F(\varphi^{\alpha'} - \varphi^{\alpha''})$  by  $\bar{A}$  we have

$$v = L\bar{A} \text{ or } I = Fv = FL\bar{A} \quad (21)$$

in which  $L$  is the phenomenological coefficient<sup>2,5</sup> connecting reaction velocity and affinity. The power of irreversibility and the entropy production are then such that

$$P = T \frac{d_i S}{dt} = \frac{1}{F^2 L} \times I^2 \quad (22)$$

The quantity  $1/F^2 L$  can be considered as a generalized resistance  $r$  and we have

$$P = rI^2 \quad (23)$$

Let us now consider the case in which the only cause of irreversibility is the internal ohmic resistance of the cell. More precisely the only resistance to be taken into account is that between layers  $\beta$  and  $\beta'$ . We have then

$$\varphi^\beta - \varphi^{\beta'} = RI \text{ and } \varphi^{\alpha'} - \varphi^{\alpha''} = \frac{A}{F} - RI \quad (24)$$

and

$$P = T \frac{d_i S}{dt} = RI^2 \quad (25)$$

The net amount of heat received during the time  $dt$  is

$$dQ = T dS - RI^2 dt \quad (26)$$

while the uncompensated heat is

$$dQ' = RI^2 dt \quad (27)$$

**Decomposition of a Cell into Pairs of Phases in Contact Case of Reversible Electrodes.**—On the basis of formulas (24) we have

$$(\varphi^{\alpha'} - \varphi^{\beta'}) + (\varphi^\beta - \varphi^\alpha) + (\varphi^\alpha - \varphi^{\alpha''}) = A/F \quad (28)$$

when the only cause of irreversibility is the Joule effect. Decomposing  $A$  into a sum of three terms corresponding to the three processes (3), (4) and (5) and introducing the chemical potentials or sums of chemical potentials for the  $X$ ,  $X^-$ ,  $Y$ ,  $Y^-$  species and for the electrons, we find

$$\varphi^{\alpha'} - \varphi^{\beta'} = \frac{A_c}{F} = \frac{\mu_Y + \mu_e^{\alpha'} - \mu_{Y^-}}{F} \quad (29)$$

$$\varphi^\beta - \varphi^\alpha = \frac{A_a}{F} = \frac{\mu_X - \mu_X - \mu_e^\alpha}{F} \quad (30)$$

$$\varphi^\alpha - \varphi^{\alpha''} = \frac{A_s}{F} = \frac{\mu_e^\alpha - \mu_e^{\alpha''}}{F} \quad (31)$$

These equations are the equilibrium conditions for the corresponding processes. Let us introduce the electrochemical potentials by adding to each chemical potential of the product  $z_i F \varphi$  corresponding to the molar charge  $z_i F$  of reactant or product  $i$  and the electrical potential of the phase where this species  $i$  is reacting or produced. Let

$$\tilde{\mu}_i = \mu_i + z_i F \varphi \quad (32)$$

One easily finds that the equilibrium conditions (29) to (31) can then be written

$$\tilde{A}_c = \tilde{\mu}_Y + \tilde{\mu}_e^{\alpha'} - \tilde{\mu}_{Y^-} = 0 \quad (33)$$

$$\tilde{A}_a = \tilde{\mu}_X - \tilde{\mu}_X - \tilde{\mu}_e^\alpha = 0 \quad (34)$$

$$\tilde{A}_s = \tilde{\mu}_e^\alpha - \tilde{\mu}_e^{\alpha''} = 0 \quad (35)$$

in which  $\tilde{A}_c$ ,  $\tilde{A}_a$  and  $\tilde{A}_s$  are the electrochemical affinities of the three processes,  $\mu_X^-$ , etc., single electrochemical poten-

tials or sums of electrochemical potentials. Intermetallic contacts are known to be unpolarizable and therefore equation (35) will always hold. On the other hand the electrochemical affinities of the cathodic and anodic processes will be different from zero whenever there is polarization.

**Causes of Irreversibility Other than the Joule Effect—Polarization—Overvoltages.**—When the electrodes are polarized the power of irreversibility includes, besides the  $RI^2$  of formula (25), a term  $P_\pi$  which we shall call *power of polarization* and we have

$$P = \left[ \frac{A_c + A_a + A_s}{F} - (\varphi^{\alpha'} - \varphi^{\alpha''}) \right] I = RI^2 + P_\pi \quad (36)$$

From (24) and (31) we deduce

$$\left[ \frac{A_c + A_a}{F} - (\varphi^{\alpha'} - \varphi^{\beta'}) - (\varphi^\beta - \varphi^\alpha) \right] I = P_\pi \geq 0 \quad (37)$$

or, introducing separate cathodic and anodic powers of polarization

$$\varphi^{\alpha'} - \varphi^{\beta'} = \frac{A_c}{F} - \frac{P_{\pi c}}{I} \quad (38)$$

$$\varphi^\beta - \varphi^\alpha = \frac{A_a}{F} - \frac{P_{\pi a}}{I} \quad (39)$$

The ratios  $A_c/F$  and  $A_a/F$  also appear in formulas (29) and (30) which show them to be equal to the reversible values of the corresponding potential differences. Introducing again the electrochemical affinities one finds that formulas (38) and (39) can be written

$$\frac{P_{\pi c}}{I} = \frac{\tilde{A}_c}{F} = (\varphi^{\beta'} - \varphi^{\alpha'}) - (\varphi^{\beta'} - \varphi^{\alpha'})_{\text{rev}} = \eta_c > 0 \quad (40)$$

$$\frac{P_{\pi a}}{I} = \frac{\tilde{A}_a}{F} = (\varphi^\alpha - \varphi^\beta) - (\varphi^\alpha - \varphi^\beta)_{\text{rev}} = \eta_a > 0 \quad (41)$$

in which the familiar *overvoltages*  $\eta_c$  and  $\eta_a$  are related with the thermodynamic concepts of power of polarization and electrochemical affinity.

**Single Electrodes—Anodic and Cathodic Currents—Relative Electrical Potential Differences.**—The overvoltages defined in (40) and (41) are necessarily positive because thermodynamics requires the corresponding powers of polarization or uncompensated heats or entropy productions to be positive. It is, however, convenient, whenever one studies a single electrode whose operating potential difference from metal to solution is measured by means of the method of the Haber-Luggin capillary, *i.e.*, relatively to a standard reference electrode, to give a sign to the overvoltage and to the corresponding current. Calling  $\epsilon$  the metal and  $\delta$  the solution one would always write, whether the electrode functions as anode or cathode

$$\eta_\epsilon = (\varphi^\epsilon - \varphi^\delta) - (\varphi^\epsilon - \varphi^\delta)_{\text{rev}} \quad (42)$$

or

$$\eta_\epsilon = E_\epsilon' - E_\epsilon \quad (43)$$

in which  $E_\epsilon'$  designates the relative potential difference under current and  $E_\epsilon$  the reversible values of this relative difference. Both  $E_\epsilon'$  and  $E_\epsilon$  are so-called "reduction potentials." If one were to prefer to use "oxidation potentials"  $E_\delta'$  and  $E_\delta$  one would write

$$\eta_\epsilon = E_\delta - E_\delta' \quad (44)$$

with

$$E_\delta = -E_\epsilon \text{ and } E_\delta' = -E_\epsilon' \quad (45)$$

We have discussed elsewhere<sup>11</sup> the problem of nomenclature and conventions for these potentials. It appears preferable always to use potential differences from electrode to solution and to speak of reduction or of oxidation potentials according to whether the particular reaction under consideration occurs as a reduction or as an oxidation.

Since the second law requires that the power of polarization be positive we have

$$P_{\pi \epsilon} = \eta_\epsilon I_\epsilon \geq 0 \quad (46)$$

In the case of an anodic reaction both  $\eta_\epsilon$  and  $I_\epsilon$  are positive,

(11) P. Van Rysselberghe, ref. 6, 1951, see pp. 315-316; also, ref. 6, 1952, see pp. 409-415.

in the case of a cathodic reaction they are both negative. Introducing  $E_e'$  and  $E_e$  in (46) we obtain Pourbaix's formula<sup>6</sup>

$$(E_e' - E_e)I_e \geq 0 \quad (47)$$

Plots of  $E_e'$  against  $I_e$  are *polarization curves*. It is particularly convenient to use the following system of coordinates:  $E_e'$  is plotted vertically with the nobility, measured by increasing  $E_e'$  values, augmenting upwards; anodic currents are plotted horizontally toward the right and cathodic currents horizontally toward the left.

**Simultaneous Half-reactions at the Same Electrode.**—So far we have considered the case of a single half-reaction occurring in the anodic or in the cathodic direction at the electrode  $\epsilon$  or at each of the electrodes  $\alpha$  and  $\alpha'$  of the cells represented on Figs. 1 to 4. If several half-reactions

$$X_\rho^- = X_\rho + e^- \quad (\rho = 1, 2, \dots) \quad (48)$$

occur simultaneously at the same electrode (all in the same direction or some in the anodic direction and the others in the cathodic direction) the net current carried by the electrode will be

$$I_e = F \frac{dn_{e^-}}{dt} = F \sum \frac{d\xi_\rho}{dt} \quad (49)$$

The power of polarization is now given by

$$P_{\pi\epsilon} = \sum \eta_{\rho\epsilon} I_{\rho\epsilon} = E_e' I_e - \sum E_{\rho\epsilon} I_{\rho\epsilon} \geq 0 \quad (50)$$

in which  $\eta_{\rho\epsilon}$  is the overvoltage of reaction  $\rho$ ,  $I_{\rho\epsilon}$  the partial current of that reaction,  $E_e'$  the common reaction potential difference for all reactions and  $E_{\rho\epsilon}$  the reversible potential difference of reaction  $\rho$ . Interesting developments into which we shall not enter here involve the introduction of mixed overvoltages for the various anodic and cathodic reactions, of average reversible potential differences, etc. Let us consider only the simple case of one anodic and one cathodic reaction. Formula (50) becomes then

$$P_{\pi\epsilon} = E_e' I_e - (E_a I_a + E_c I_c) \quad (51)$$

with

$$I_e = I_a + I_c \quad (52)$$

$I_a$  being positive and  $I_c$  negative.

In the particular case of an isolated electrode carrying no net current we have  $I_c = -I_a$  and hence

$$P_{\pi\epsilon} = (E_c - E_a) I_a \quad (53)$$

The difference  $E_c - E_a$  is equal to the affinity of the resultant purely chemical reaction divided by  $F$  and we are thus led back to the non-electrochemical power of irreversibility

$$P = \frac{A}{F} \times I_a = A v \geq 0 \quad (54)$$

Further considerations of this type can be shown to bring a great deal of order in the electrochemical theory of corrosion phenomena.

**The Neighborhood of Equilibrium—Use of Onsager's Reciprocal Relations.**—Although the introduction in this thermodynamic theory of kinetic information such as that provided by Tafel's equation connecting overvoltage and current density is of very great interest we shall limit ourselves here to the neighborhood of equilibrium, *i.e.*, to the range of validity of the linear relations connecting reaction velocities and affinities. Let us consider two half-reactions 1 and 2 occurring in the same direction or in opposite directions at the same electrode. Their velocities will be linear functions of both electrochemical affinities provided the reversible potential differences of these reactions are sufficiently close to each other to allow the system to function in the close neighborhood of equilibrium. We then have

$$v_1 = L_1 \tilde{A}_1 + L_{12} \tilde{A}_2 \quad (55)$$

$$v_2 = L_{12} \tilde{A}_1 + L_2 \tilde{A}_2 \quad (56)$$

or, in terms of currents and overvoltages

$$I_1 = F^2(L_1 \eta_1 + L_{12} \eta_2) \quad (57)$$

$$I_2 = F^2(L_{12} \eta_1 + L_2 \eta_2) \quad (58)$$

formulas in which the Onsager reciprocal relation  $L_{12} = L_{21}$  has been taken into account. The power of polarization is then

$$P_{\pi\epsilon} = F^2[L_1(E' - E_1)^2 + L_2(E' - E_2)^2 + 2L_{12}(E' - E_1)(E' - E_2)] \quad (59)$$

or, in terms of the total current  $I$

$$P_{\pi\epsilon} = \frac{I^2}{F^2(L_1 + L_2 + 2L_{12})} + F^2 \frac{L_1 L_2 - L_{12}^2}{L_1 + L_2 + 2L_{12}} (E_1 - E_2)^2 \quad (60)$$

The existence of drag coefficients  $L_{12}$  different from zero would mean that polarization curves of single half-reactions are not additive when these reactions occur simultaneously at the same electrode. This additivity is often assumed in spite of considerable experimental evidence against its validity. Not only is the mutual influence corresponding to the  $L_{12}$  coefficients a theoretical possibility but its magnitude and direction might be such as to make one of the reactions occur in its otherwise non-spontaneous direction. In other words the *coupling* of an electrochemical half-reaction by one or several others is possible and should be looked for experimentally. Its existence could have consequences of very great practical interest.

**States of Minimum Entropy Production.**—A single electrode carrying a current  $I$  at a certain relative potential difference  $E'$  constitutes an open system in which several electrochemical affinities could be kept constant by means of suitable additions or removals of the various reactant and product species. Let us still consider the case of two simultaneous reactions and let us maintain the electrochemical affinity of reaction 1 constant by maintaining  $E'$  constant and the chemical affinity  $A_1$  constant. There will then be a possible state of the system for which the power of polarization or the entropy production will be a minimum. On the basis of Prigogine's theorem<sup>12</sup> on steady states of minimum entropy production, which we are here extending to electrochemical systems, the reasoning is as follows: we differentiate  $P_{\pi\epsilon}$  given by formula (59) with respect to  $E_2$  at  $E'$  and  $E_1 = A_1/F$  constant and obtain

$$\left( \frac{\partial P_{\pi\epsilon}}{\partial E_2} \right)_{E', E_1} = -2F^2[L_2(E' - E_2) + L_{12}(E' - E_1)] \quad (61)$$

Setting this derivative equal to zero we see that  $P_{\pi\epsilon}$  will be an extremum when

$$E_2 = \frac{E'(L_2 + L_{12}) + E_1 L_{12}}{L_2} \quad (62)$$

This extremum is a minimum since

$$\left( \frac{\partial^2 P_{\pi\epsilon}}{\partial E_2^2} \right)_{E', E_1} = 2F^2 L_2 > 0 \quad (63)$$

The value of the minimum is

$$P_{\pi\epsilon\text{min}} = F^2 \left( L_1 - \frac{L_{12}^2}{L_2} \right) (E' - E_1)^2 \quad (64)$$

For this particular state of the system the currents are

$$I_1 = F^2 \left( L_1 - \frac{L_{12}^2}{L_2} \right) (E' - E_1) \quad I_2 = 0 \quad (65)$$

During the transition of the system from its original state to that of minimum entropy production the electrochemical affinity of reaction 1 remains constant. That of reaction 2, however, will vary until the value

$$\tilde{A}_2 = F(E' - E_2) = -F \frac{L_{12}}{L_2} (E' - E_1) \quad (66)$$

is reached.

Prigogine's theorem is easily generalized to the case of several simultaneous reactions. If, out of a total of  $n$  reactions, the affinities (or here electrochemical affinities) of  $k$  reactions, are kept constant the system may reach in the course of time a state of minimum entropy production in which the velocities of the  $n-k$  reactions which are not controlled become equal to zero (see de Groot<sup>13</sup>). These stationary states of minimum entropy production can be shown to follow a principle analogous to that of Le Chatelier concerning the "moderation" of disturbances.

It would be highly interesting to explore experimentally the possible applications of these theoretical considerations in the field of electrochemistry. In corrosion, for instance, the establishment of stationary states of minimum entropy

(12) I. Prigogine, Ref. 3, pp. 55-59.

(13) S. R. de Groot, ref. 4, pp. 195-207.

production might lead to the blocking of destructive reactions through the device of maintaining other reactions at constant electrochemical affinities. It seems likely that new light could thus be thrown on the problem of corrosion inhibition. For example, the electrochemical mechanism which we have proposed with Pourbaix<sup>14</sup> for the inhibition

(14) M. Pourbaix and P. Van Rysselberghe, *Corrosion*, **6**, 313 (1950).

of the corrosion of iron by nitrites, chromates or even oxygen when present in sufficient amount lends itself to interesting further study on the basis of irreversible thermodynamics. Let us note in this connection that, through the approximate procedure of linearization of polarization curves, the practical range of usefulness of the above considerations can be considerably enlarged. We hope to return to this and other topics of theoretical and applied electrochemical thermodynamics in later communications.

## ANODIC POLARIZATION OF PASSIVE AND NON-PASSIVE CHROMIUM-IRON ALLOYS

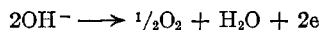
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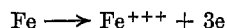
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Anodic polarization data for 0-16.7% Cr-Fe alloys in 3% Na<sub>2</sub>SO<sub>4</sub> are reported. Critical current densities for passivity accompanied by sudden reduction of anodic dissolution and a pronounced noble potential range from 150 ma./cm.<sup>2</sup> for iron to 0.05 ma./cm.<sup>2</sup> for 11.6% Cr. At 12% Cr and above, a critical current no longer exists; instead any small polarizing current produces a marked shift of potential in a noble direction. Small corrosion currents, therefore, can equipotentialize the surface and stifle the corrosion process in accord with the electrochemical mechanism of corrosion. Since 12% Cr and above mark the stable passive compositions (stainless steels) in solutions like Na<sub>2</sub>SO<sub>4</sub>, it appears that the property of so-called passive alloys to equipotentialize themselves is an important characteristic of passivity, and perhaps an essential condition to their remarkable resistance to corrosion. Coulometric measurements show that about 0.014 coulomb/cm.<sup>2</sup> or less is concerned with the passivation process for the 9.2-16.7% Cr alloys and probably for other compositions as well. This corresponds at most to a few monolayers of substance on the passive surface. Thick oxide films, therefore, cannot possibly be the primary cause of passivity.

When iron is polarized as anode at moderate current densities in dilute sodium sulfate or sulfuric acid, the major reaction is  $\text{Fe} \rightarrow \text{Fe}^{++} + 2e$ . As the current is increased, a critical value is reached at which the potential suddenly changes to a value more noble by about 2 v., and the anodic reaction changes to



accompanied by the reaction



Iron is said to become passive, both because it assumes a more noble potential and because oxygen evolving at its surface resembles the behavior of a noble metal electrode. Also, the dissolution rate is appreciably less than that of an active iron anode.

Soon after the polarizing current is stopped, the electrode again assumes the active state. If the current is gradually decreased, the active state is achieved at a current density somewhat lower than is necessary to achieve the passive state when applying progressively higher currents.

Conditions that apply for achieving anodic passivity of iron-chromium alloys substituted for iron have not yet been studied. Information of this kind should be of value to a better understanding of passivity, particularly since passivity is established in a more stable form when the chromium content reaches 12% or more. This composition establishes the basis for the modern stainless steels.

### Experimental Arrangement

Polarization data for the Cr-Fe alloys were obtained using the cell shown in Fig. 1. This was placed in an air thermostat maintained at  $25 \pm 1^\circ$ . Two circular platinum cathodes 3.1 cm. in diameter are located 1 cm. from either side of the alloy anode. The latter measures approximately 1 cm. square by 2 mm. thick. The electrolyte is 3% Na<sub>2</sub>SO<sub>4</sub>.

A tubulus, sealed at each end with asbestos fibers and filled with the same solution is mounted on one side of the anode close to the metal surface. The opposite end is immersed in a 0.1 N KCl solution into which an Ag-AgCl electrode also in 0.1 N KCl is immersed.

Potentials were measured using a vacuum tube potentiometer. No correction was made for liquid junction potentials, since these were assumed to be approximately constant throughout the measurements and, in any case, were small. Current was supplied usually by a high-voltage B battery through a high resistance, thereby maintaining constant current, actual values of which were read using a precision ( $\pm 1/4\%$ ) milliammeter and also, for very small currents, by the potential drop across a precision 100-ohm resistance.

For many measurements, the sodium sulfate solution was first freed of chlorides by adding silver sulfate and removing excess silver by electrolysis for several hours between platinum electrodes. Contaminating heavy metals were removed simultaneously. The pH was then adjusted to 7 by adding sodium hydroxide. This purification procedure did not appear to be critical, since values of potentials were the same within the experimental error whether or not pre-electrolysis was carried out.

Electrode materials consisted of electrolytic iron, and of laboratory melts of chromium-iron alloys. Alloys collected from three sources gave consistent results indicating that small differences in impurities are not important. Thermal history, however, was felt to be a significant factor, and, hence, all the alloys were heated in helium at 1000° and water quenched. Analyses are given in Table I.

Before measurements were made, the solutions were degassed about one hour by bubbling nitrogen through them. Nitrogen was previously purified by passing it over copper turnings maintained at 400°. The gas entered the cell through a sintered glass disc providing a fine dispersion of gas bubbles, but during measurements the gas was bypassed through a glass tube at the side of the cell, so that bubbles did not impinge on the anode. This was necessary because stirring had some effect on the critical current for passivity, greater current being necessary the higher the stirring rate.

**Preparation of Electrodes and Procedure.**—The anode was attached to a nickel wire by spot-welding and then sealed into a glass tube using de Khotinsky Cement to cover the exposed wire and the spot-welded area. The electrode