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ELECTROCHEMICAL KINETICS
INTRODUCTORY REPORT

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THIS report presents an explanation of the principle of a method that permits the predetermination, on the basis of results obtained at low temperatures, of the rate and other conditions under which electrochemical reactions proceed at elevated temperatures[1]. We may recall here that it is possible to catalyse electrochemically certain chemical reactions in the presence of aqueous solutions, and to predict such catalysis[2].

Several chemical reactions in which aqueous solutions participate result, in fact, from the superimposition of two electrochemical reactions, one of which is an oxidation (with liberation of negative electric charge) and the other a reduction (with fixation of negative electric charge). Six examples of such reactions follow:

(a) the corrosion of iron in acids:

$$\begin{aligned} Fe &\rightarrow Fe^{2+} + 2e^- && \text{(oxidation)} \\ 2H^+ + 2e^- &\rightarrow H_2 && \text{(reduction)} \\ \hline Fe + 2H^+ &\rightarrow Fe^{2+} + H_2 \end{aligned}$$

(b) the synthesis of water:

$$\begin{aligned} 2H_2 &\rightarrow 4H^+ + 4e^- && \text{(oxidation)} \\ O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O && \text{(reduction)} \\ \hline 2H_2 + O_2 &\rightarrow 2H_2O \end{aligned}$$

(c) the decomposition of hydrogen peroxide:

$$\begin{aligned} H_2O_2 &\rightarrow O_2 + 2H^+ + 2e^- && \text{(oxidation)} \\ H_2O_2 + 2H^+ + 2e^- &\rightarrow 2H_2O && \text{(reduction)} \\ \hline 2H_2O_2 &\rightarrow O_2 + 2H_2O \end{aligned}$$

(d) the oxidation of sulphites by oxygen:

$$\begin{aligned} 2SO_3^{2-} + 2H_2O &\rightarrow 2SO_4^{2-} + 4H^+ + 4e^- && \text{(oxidation)} \\ O_2 + 4H^+ + 4e^- &\rightarrow 2H_2O && \text{(reduction)} \\ \hline 2SO_3^{2-} + O_2 &\rightarrow 2SO_4^{2-} \end{aligned}$$

(e) the oxidation of arsenious anhydride to arsenic anhydride by oxygen:

$$As_2O_3 + 2H_2O \rightarrow As_2O_5 + 4H^+ + 4e^- \quad \text{(oxidation)}$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$
$$As_2O_3 + O_2 \rightarrow As_2O_5$$

(f) the formation of copper sulphate by the action of oxygen on copper in sulphuric acid solution:

$$2Cu \rightarrow 2Cu^{2+} + 4e^- \quad \text{(oxidation)}$$
$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \quad \text{(reduction)}$$
$$2Cu + O_2 + 4H^+ \rightarrow 2Cu^{2+} + 2H_2O$$

We have elsewhere explained, using the reaction (b) of the synthesis of water as an example, how the derivation of polarization curves permits the

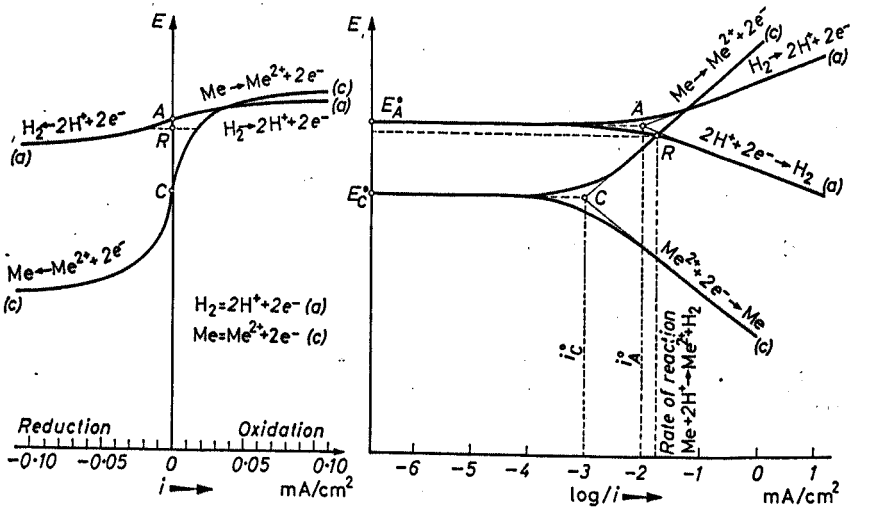

Figure 1. Polarization curves of 'substantially reversible' reactions

determination of the rate of such chemical reactions and the determination of catalysts for the reactions[2]*.

The rate of the over-all chemical reaction obtained on an electrically isolated metallic surface is the same as the rates of the two component electrochemical reactions, which are determined by the respective polarization curves, and are equal and of opposite sign. These circumstances are indicated on the left-hand side of *Figures 1* and *2*, in the case of substantially reversible reactions and in the case of distinctly irreversible reactions, respectively[2]†. In the right-hand diagrams of these figures, polarization curves are given as log (current density) versus potential, and in the left-hand

* Unpublished discussions between J. WEYDEMA, W. A. BURGERS and M. POURBAIX (1949).

† The numerical values indicated in all the figures in this paragraph are purely fictitious; they are given in order to fix ideas.

as current-density versus potential. The logarithmic curves are often rectilinear, according to Tafel's classical law, when neither concentration polarization nor any modification of the surface of the electrode need be considered; the two rectilinear Tafel lines relating to oxidation and reduction senses of any particular reaction intersect at a point which HOAR[3] has shown (for the oxygen electrode) corresponds to thermodynamic equilibrium of the reaction. BOWDEN and AGAR[4] express this as follows: the current-density corresponding to this dynamic equilibrium—the 'exchange current'—is a measure of the *catalytic activity of the electrode* for the electrochemical reaction considered. As Audubert showed, the effect of the electrode potential on the *electrolysis current i* (the algebraic sum of the two *reaction currents* of the reaction considered) is represented by two curves that tend

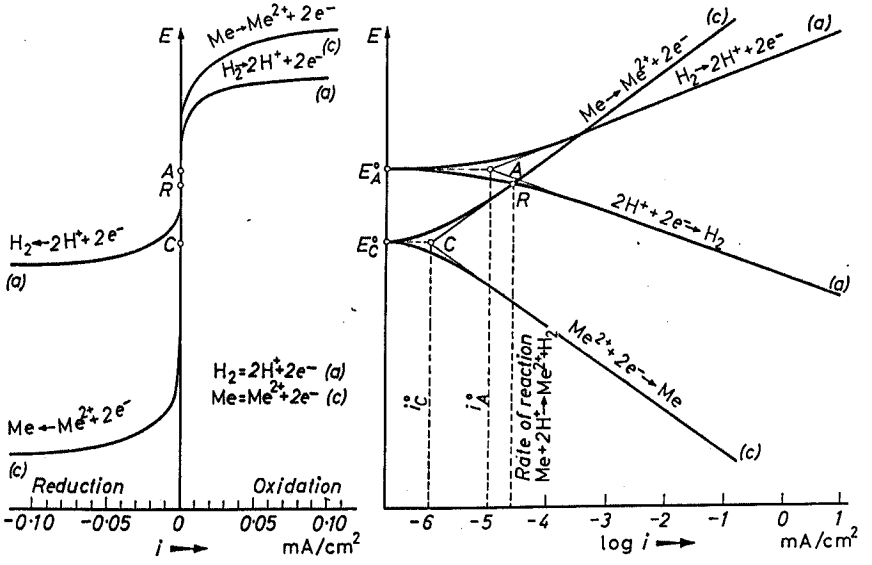

Figure 2. Polarization curves of 'distinctly irreversible' reactions

asymptotically together with $\log i \to -\infty$ (corresponding to a zero net rate for the reaction) when the electrode potential is the equilibrium potential E° of the reaction. In this method of representation, the conditions of electrode potential E and of rate i at which the over-all reaction is attained on an electrically isolated metallic surface can be calculated, respectively, from the ordinate and abscissa values of the point of intersection R. A current of 1 mA (or $\log i = 0$) corresponds to a reaction rate of 0·037 mg-equiv./hr., for example, the corrosion (or electrodeposition) of 1·04 mg/hr. of iron and the liberation (or oxidation) of 0·037 mg/hr. of hydrogen.

In the case of substantially reversible electrochemical reactions, represented in *Figure 1*, the over-all corrosion reaction $Me + 2H^+ \to Me^{2+} + H_2$ proceeds at $10^{-1\cdot75}$ or 0·018 mA/cm², corresponding to 0·00067 mg/cm² hr. of hydrogen and in the case of iron corrosion, for example, to the dissolution

of 0·018 mg/cm² hr. of iron, i.e. 160 mg/cm² year, or a diminution in thickness of 0·21 mm/year.

In the case of distinctly irreversible electrochemical reactions represented in *Figure 2*, the rate is only $10^{-4\cdot60}$ or 0·000025 mA/cm², 720 times smaller than in the preceding case; such a rate is zero for many practical purposes.

During preliminary experiments for a particular case, we have studied the effect of temperature on the equilibrium characteristics and rate of certain electrochemical reactions*:

(a) The equilibrium potential E° of an electrochemical reaction varies inversely with the absolute temperature T. It can be written as $E^\circ = (A/T) + B$, where A and B are constants.

(b) The logarithm of the exchange current i° of an electrochemical

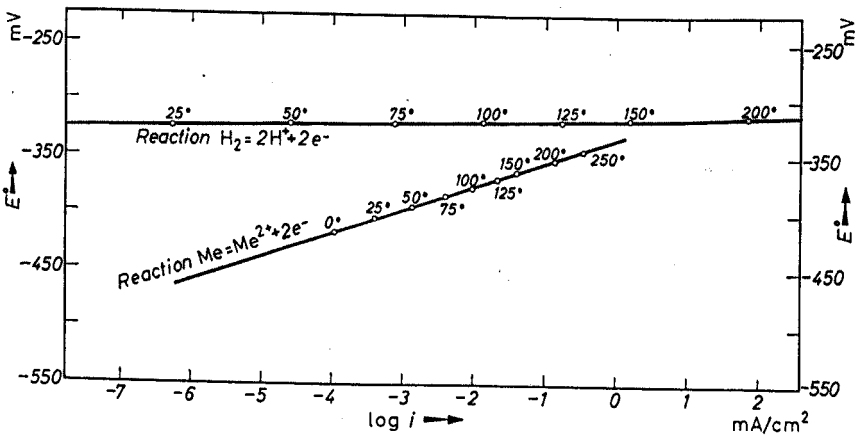

Figure 3. Effect of temperature on the equilibrium potentials and on the exchange currents of the reactions $Me = Me^{2+} + 2e^-$ *and* $H_2 = 2H^+ + 2e^-$

reaction also varies inversely with absolute temperature. It can be written as $\log i^\circ = (a/T) + b$, where a and b are constants.

(c) The two relationships above lead to

$$E^\circ = A/a \log i^\circ - [(bA/a) - B]$$

which indicates a linear relationship between the equilibrium potential E° and the logarithm of the exchange current $\log i^\circ$.

Such a relationship is represented graphically in *Figure 3* for the reactions $H_2 = 2H^+ + 2e^-$ and $Me = Me^{2+} + 2e^-$. Two straight lines are obtained, for the temperatures as indicated between from 0 to 200°C.

Diagrams such as *Figure 3* could include the polarization curves of the type shown in *Figures 1* and *2* for different temperatures for each of the two reactions; in *Figure 4* such curves are drawn, for the reduction $2H^+ + 2e^- \rightarrow H_2$

* These experiments have not been the object of a systematic study and are reported with all reserve.

and for the oxidation $Me \rightarrow Me^{2+} + 2e^-$. The slope of the Tafel lines for the reactions has been taken as being proportional to absolute temperature T. For each temperature, the rate and electrode potential for the over-all reaction $Me + 2H^+ \rightarrow Me^{2+} + H_2$ of electrically isolated metal are indicated, as in *Figures 1* and *2*, by the ordinate and abscissa values of the points of

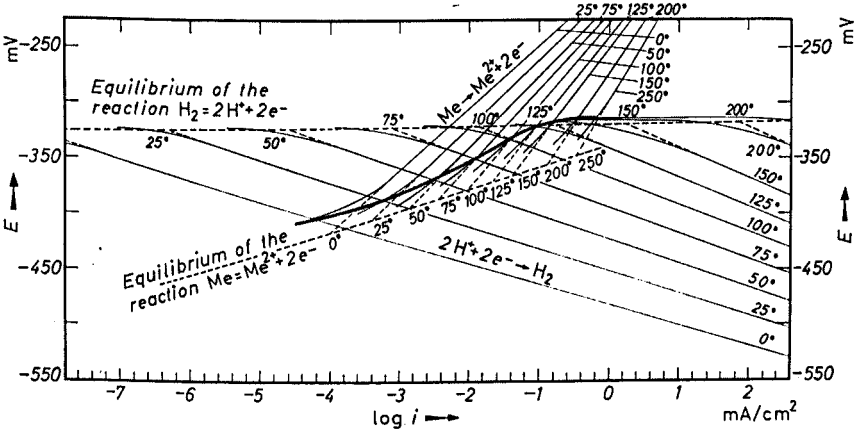

Figure 4. Prediction of the characteristics of the reaction $Me + 2H^+ \rightarrow Me^{2+} + H_2$ *at different temperatures*

intersection of the two polarization curves relating to this temperature. The full line in *Figure 4* joining these points of intersection thus indicates the rate of the corrosion reaction $Me + 2H^+ \rightarrow Me^{2+} + H_2$ and also the electrode potential of the corroding metal temperatures between 0 and 250°. *Table I* gives these values.

Table I

Temperature (°C)	*Electrode potentials* E (mV)	*Reaction rate*	
		log i (mA/cm²)	i (mA/cm²)
0°	−503	−4·24	0·00006
25°	−487	−3·22	0·0006
50°	−467	−2·52	0·0033
75°	−450	−1·94	0·012
100°	−433	−1·44	0·036
125°	−420	−1·04	0·091
150°	−417	−0·80	0·16
200°	−415	−0·50	0·32
250°	−415	−0·20	0·63

The above remarks on the determination of reactions at high temperatures are based on several insufficiently checked hypotheses. This method of study could, with advantage, be made the object of systematic research for confirmation.

The new Commission on Electrochemical Kinetics should undertake such systematic investigations. A start would be the assembly of bibliographical details concerning:

(1) Exchange currents of electrochemical reactions.

(2) The slopes of the Tafel lines of these reactions in the oxidation and in the reduction senses.

(3) The influence of temperature on equilibrium potentials, exchange currents and the Tafel line slopes.

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[2] POURBAIX, *Rapport Technique RT.1 Cebelcor* (1952)
[3] HOAR, *Proc. Roy Soc.* A 142 (1933) 642
[4] BOWDEN and AGAR, *Ann. Rep. Chem. Soc.* 35 (1938) 90–113

DISCUSSION

T. P. HOAR: The contribution Dr. Pourbaix has made is, I think, sufficient to indicate that a Commission on Electrochemical Kinetics might make considerable progress in co-ordinating research in the field.

I was partly responsible, in some work on the oxygen electrode*, for introducing the method of extrapolation of the logarithmic parts of the cathodic and anodic polarization curves to obtain reversible potentials and exchange currents, although J. A. V. Butler† and others had earlier indicated the principle. I should therefore like to emphasize that many cases exist where the simple method cannot be applied: for example, when the exchange current is relatively high and current limitation by diffusion and/or migration processes in the electrolyte sets in at relatively low current values, there may be no logarithmic parts of the experimental V/i curve. Even so, an extension of the analysis of the V/i curve can in suitable cases give significant information: I shall develop this matter in a paper for the proposed Commission.

M. POURBAIX: I agree with Dr. Hoar on the fact that the method of linear extrapolation of polarization curves has a limited field of application. I have considered, for clarity, a simple case where polarization 'curves' are straight lines; the method I have briefly described is then rather easily applicable, but a similar method might also be used when polarization curves have another shape. The main purpose of my paper is to emphasize the usefulness of more systematic work on polarization curves, considering preferably first reactions with linear logarithmic polarization curves; it would be useful to have, for several reactions of this kind, more data for exchange currents, Tafel coefficients and equilibrium potentials at different temperatures.

G. VALENSI: Cependant, outre le cas qui signale Hoar, où le courant d'échange pourrait être limité par la migration au lieu de la réaction d'électrode, je voudrais attirer l'attention sur celui, plus fréquent qu'on ne le pense généralement, où la réaction cathodique et la réaction anodique que traduisent respectivement les deux courbes expérimentales de polarisation, ne sont pas les mêmes, au sens près. Ainsi, comme l'a montré Coursier à la Réunion de Berne (*C. R. de la 3e Réunion du C.I.T.C.E.*

* HOAR, *Proc. Roy. Soc.* A 142 (1933) 628.
† BUTLER, *Trans. Faraday Soc.* 19 (1924) 734.

1951 Milan (1952) 235) si on polarise positivement une électrode de platine plongeant dans un mélange de thiosulfate et de tétrathionate, il y a oxydation anodique du thiosulfate en tétrathionate, mais si on la polarise négativement, il y a réduction des ions H^+ de l'eau, à des potentiels plus élevés que ceux où il y aurait réduction du tétrathionate en thiosulfate, réaction complètement masquée expérimentalement. La valeur de la tension réversible de l'électrode $Pt|S_2O_3^{2-}, S_4O_6^{2-}$ serait donc erronée si on la déduisait de l'extrapolation des courbes de polarisation. Une remarque du même genre a d'ailleurs déjà été faite par Lange dans la discussion du mémoire 4.3. de Van Rysselberghe, pour la partie relative à l'emploi des nouveaux termes 'potentiel d'oxydation' et 'potentiel de réduction'.

Je voudrais d'autre part faire remarquer que la relation $E^\circ = \frac{A}{T} + B$ n'est pas thermodynamiquement correcte, car c'est le logarithme de la constante d'équilibre k, et non $E^\circ = \frac{RT}{nF} \log k$, qui varie ainsi.

R. DEFAY: Il y a lieu de ne pas perdre de vue, si l'on parle de l'irréversibilité d'une électrode, que le mot 'irréversibilité' n'a pas alors la même signification qu'on thermodynamique. L'irréversibilité thermodynamique peut se mesurer par la chaleur non compensée au sens de Clausius dQ', ou par la création d'entropie dQ'/T qui accompage la transformation. Pour une réaction de cellule galvanique, on a

$$dQ' = [A + \zeta F(\psi^1 - \psi^{1'})]d\xi$$

où A est l'affinité chimique, ζF la charge transportée de 1 en 1′ par unité d'avancement et ξ l'avancement de la réaction.

Une électrode dite '*réversible*', lorsqu'elle est le siège d'une réaction électrochimique qui s'effectue avec une vitesse non nulle participe donc à un phénomène *irréversible*.

Il est extrêmement regrettable que le mot 'irréversible' soit employé simultanément avec deux significations aussi différentes. Je crois qu'il serait utile que notre Commission de Nomenclature étudie ce problème, trouve le moyen de réserver au mot irréversible sa signification thermodynamique et propose une appellation plus heureuse pour désigner les électrodes qui ne peuvent atteindre l'équilibre thermodynamique en un temps fini.

M. POURBAIX: I agree with Defay that the concepts of reversibility and irreversibility should always have their thermodynamic significance. One should not speak of reversible electrodes but only of reversible (or irreversible) processes.

I wish to point out that reversible reactions do not exist; reactions are always irreversible. It is of practical interest, however, to make distinction between electrochemical reactions which are very irreversible (e.g. the reaction $H_2 = 2H^+ + 2e^-$ on lead or mercury or the reaction $Ni = Ni^{2+} + 2e^-$) and electrochemical reactions the irreversibility of which is very small (e.g. the reaction $H_2 = 2H^+ + 2e^-$ on a platinum electrode, or the reaction $Pb = Pb^{2+} + 2e^-$). In my paper, I have made this distinction by speaking of 'substantially reversible reactions' (*Figure 1*) and of 'distinctly irreversible reactions' (*Figure 2*). I have arbitrarily considered that a reaction may be considered as 'substantially reversible' or as 'distinctly irreversible' when the value of the exchange current is respectively greater or less than 10^{-3} mA/cm^2.

M. BALKANSKI: Il est certainement interessant de réunir des données concernant des grandeurs telles que le courant d'échange pour un système donné et le potentiel d'équilibre, mais ceux qui sont appelés à s'occuper de cinétique électrochimique sont intéressés en premier lieu par les théories de la surtension; par les renseignements que l'on peut tirer des courbes de polarisation au sujet du mécanisme de l'électrodéposition; par les calculs des énergies d'activation, etc. Ne pourrait-on pas envisager une mise au point historique générale concernant la littérature qui a trait aux théories de la surtension et le mécanisme de l'électrolyse? Il serait d'autre

part souhaitable qu'une discussion approfondie soit consacrée à l'opportunité de calculer l'énergie d'activation de la décharge. On sait que cette valeur est essentiellement relative car elle ne peut être évaluée que par rapport à un système de référence donné (le potentiel par rapport à l'électrode de référence adopté entrant dans le calcul). Pour que le calcul soit possible, il faut en outre supposer que l'énergie d'activation ne varie pas avec la température. Il faut tout d'abord éclaircir si cette condition est accomplie dans les conditions dans lesquelles se place l'électrochimiste. Une Commission de Cinétique Électrochimique pourrait se saisir de tous ces problèmes.

Following the discussion, the Committee decided to undertake systematic research work in electrochemical kinetics. A general survey of present knowledge on this subject, including data on exchange currents, activation energies, etc., would be welcome.

Members of the Committee who are willing to collaborate in this work were requested to approach the Secretary-General, and to make proposals concerning the general programme and their own contributions.