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THERMODYNAMICS OF THE MECHANICO-CHEMICAL EFFECT
II. The Range of Operation of Nonlinear Laws

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Phenomenological equations describing the mechanico-chemical effect in the range of operation of nonlinear laws were derived, and the validity of these equations was qualitatively proved by experiment.

A qualitative description of the mechanico-chemical effect by linear equations [1] is valid in the case of relatively small deviations of the system from an equilibrium state. When these deviations are substantial, however, chemical reactions are nonlinear processes.

It is therefore necessary to obtain and analyze kinetic relations for the principal fluxes and forces in the nonlinear range and then to verify the validity of the expression for entropy production [1] for the case of the operation of nonlinear laws so as to make it possible to calculate conjugate fluxes (i. e., mechanico-chemical and chemico-mechanical effects).

Using the well-known definition of the concept of activity a (or activity coefficient f), one may write for the electrochemical potential

$$\tilde{\mu} = \mu + zF\varphi = \mu_0 + RT\ln a + zF\varphi = \mu_0 + RT\ln\tilde{a}, \tag{1}$$

where μ is the chemical potential, z ionic valency, F the Faraday number, φ the metal potential, μ_0 the chemical potential of the substance in a certain standard state, a the activity, and $\tilde{a}$ will be called by analogy the "electrochemical activity" since

$$\tilde{a} = a\exp\frac{zF\varphi}{RT}. \tag{2}$$

Expressing Eq. (2) through the concentration $c = a/f$, we determine the electrochemical activity coefficient:

$$\tilde{f} = f\exp\frac{zF\varphi}{RT}. \tag{3}$$

It is not difficult to see that when $\tilde{a}$ is fixed, $\tilde{f}$ will not increase with increasing φ unless c decreases exponentially (with a negative component), which is in conformance with the Boltzman principle for a system of charged particles.

Let us derive a kinetic equation of a single anodic electrochemical reaction of metal ionization ($Me \rightleftarrows Me^{z+}$), using the law of mass action of chemical kinetics but, in contrast to the usual methods of the theory of retarded discharge, leaving aside the theory of the activation energy.

On the basis of the law of mass action the mass flux of the reaction product

$$\frac{I}{zF} = k_1\tilde{a}_1 - k_2\tilde{a}_2, \tag{4}$$

where I is the corrosion current, k_1 and k_2 are, respectively, metal ionization and reduction rate constants, and $\tilde{a}_1$ and $\tilde{a}_2$ denote chemical activities of the ion in the metal and in the solution, respectively.

Substituting $\tilde{a}$ from (1) in (4), we obtain

$$\frac{I}{zF} = k_2\tilde{a}_2\left[\frac{k_1}{k_2}\exp\left(\frac{\Delta\tilde{\mu} - \Delta\mu_0}{RT}\right) - 1\right] = k_2\tilde{a}_2\left(e^{\frac{A}{RT}} - 1\right), \tag{5}$$

where $\Delta\tilde{\mu}$ is the difference between the electrochemical potentials of ions in the metal and in the electrolyte, which here is equal to the electrochemical affinity of the reaction $\tilde{A}$, $\Delta\mu_0$ denoting the difference between the corresponding standard chemical potentials. At the same time, from the condition of the thermodynamic equilibrium ($I = 0$, $\tilde{A} = 0$) we obtain the equilibrium constant:

$$K_p \equiv \frac{k_1}{k_2} = e^{\frac{\Delta\mu_0}{RT}}. \tag{6}$$

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*Taking into account the fundamental relation of equilibrium electrochemistry $\Delta\mu_0 = -zF\varphi_0$, where φ_0 is the standard electrode potential, we conclude that Eq. (6) coincides with an analogous equation of equilibrium electrochemistry.

Denoting

$$i^0 = k_2 \tilde{a}_2 zF, \tag{7}$$

we obtain

$$I = i^0 (e^{\frac{\tilde{A}}{RT}} - 1). \tag{8}$$

Consequently, i^0 represents the "exchange current" so that for the anodic current we obtain a kinetic equation:

$$i_A = i^0 e^{\frac{\tilde{A}}{RT}} = i^0 e^{\frac{zF\eta}{RT}}, \tag{9}$$

where $\tilde{A}/zF = \eta$ is the overvoltage of the anodic reaction.

The magnitude of i^0 depends on the electrochemical activity $\tilde{a}_2$ of ions in the electrolyte, i.e., on their steady state concentration c_2^0 in the bulk of the solution. In fact,

$$\tilde{a}_2 = f_2 c_2 \exp \frac{zF\psi_1}{RT}, \tag{10}$$

where ψ_1 is the average potential of ions in the dense part of the double layer.* In accordance with the Boltzman principle, however, the ionic interaction in the electrolyte is such that

$$c_2 = c_2^0 \exp\left(-\frac{zF\psi_1}{RT}\right), \tag{11}$$

and, consequently,

$$i^0 = k_2 zF f_2 c_2^0. \tag{12}$$

Experimental data qualitatively agrees with the above dependence of i^0 on ion concentration [2]. Increasing the Bi ion concentration from 0.0023 to 0.023 and 0.23 M produced an increase in i^0 from 1.4×10^{-3} to 14.2×10^{-3} and 119×10^{-3} A/cm^2; even in the case of two different metals (of a normal group) Zn and Pb with ion concentrations of, respectively, 0.01 and 0.005 M, the exchange currents were 3.2×10^{-3} and 1.6×10^{-3} A/cm^2, in spite of different contents of zinc (0.983 at. %) and lead (0.587 at. %) in amalgam electrodes.

In the concepts of the theory of retarded discharge the result obtained should be qualified to imply the following values of the transfer coefficients of the direct and reverse reactions: $\alpha = 1$, $\beta = 0$.

In fact, it was shown by experiment that in the case of anodic dissolution of iron $\alpha = 1$ which, as was rightly pointed out by Antropov [3], cannot be explained in the framework of the theory of retarded discharge.

Finally, Bowden [4] showed in his derivation of the kinetic equation by a classical method using concepts of the activation energy that the activation energy for electrochemical reactions should be represented as a linear function of the overvoltage (not the potential) on the electrode; it was also shown by experiment [5] that the energy barriers of reversible electrodes with widely different equilibrium potentials are approximately the same. The foregoing proves the validity of the kinetic equation (9) together with Eq. (12).

The equations obtained can be easily extended by an analogous method to a case when m components with stoicheiometric coefficients ν_i (i = 1, ..., n) participate in a given electrochemical reaction:

$$\frac{I}{zF} = k_2 \prod_{i=m+1}^{n} (f_i c_i^0)^{\nu_i} (e^{\frac{\tilde{A}}{RT}} - 1), \tag{13}$$

where $\tilde{A} = -\sum_{i=1}^{n} \nu_i \tilde{\mu}_i$, and 1,...m are the indices of the starting components, ν_m appearing in $\tilde{A}$ with the negative sign.

Correspondingly

$$i_A = k_2 zF \prod_{i=m+1}^{n} (f_i c_i^0)^{\nu_i} e^{\frac{\tilde{A}}{RT}}, \tag{14}$$

and

$$i^0 = k_2 zF \sum_{i=m+1}^{n} (f_i c_i^0)^{\nu_i}. \tag{15}$$

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*In not too dilute solutions and in the absence of specific adsorption on the electrode $\psi = 0$.

Under conditions sufficiently removed from equilibrium $i_A \gg i^0$ and $I \simeq i_A$. Near the equilibrium ($A \ll RT$) we may expand the exponent in (14) into series; confining outselves to the linear approximation, we find

$$I = k_2 z \mathrm{F} \prod_{i=m+1}^{n} (f_i c_i^0)^{\nu_i} \frac{\tilde{A}}{RT}, \tag{16}$$

or, introducing the coefficient L_{22} of a linear phenomenological equation, we obtain

$$I = L_{22} \frac{\tilde{A}}{zF} = L_{22} \eta, \tag{17}$$

where

$$L_{22} = k_2 \frac{(z\mathrm{F})^2}{RT} \prod_{i=m+1}^{n} (f_i c_i^0)^{\nu_i} = \frac{k_2}{b} z\mathrm{F} \prod_{i=m+1}^{n} (f_i c_i^0)^{\nu_i}. \tag{18}$$

Here b = RT/zF is the full known coefficient in the Taffel formula which gives the slope of the polarization curve plotted in semilogarithmic coordinates.

If (15) is taken into account, (17) becomes

$$I = \frac{i^0}{b} \eta, \tag{19}$$

which formally coincides with an analogical relation in the theory of retarded discharge.* Expressing (13) through the phenomenological coefficient of the linear equation L_{22}, we find

$$I = bL_{22} (\mathrm{e}^{\frac{\eta}{b}} - 1). \tag{20}$$

Let us show that the above nonlinear kinetic equation does not invalidate the expression previously used [1] for entropy production in electrochemical fractions:*

$$\sigma^{II} = \frac{I\tilde{A}}{z\mathrm{F}T} = \frac{I\eta}{T}. \tag{21}$$

In the case of chemical reactions whose rate is sufficiently slow not to disturb the rate of distribution function of each of the system components, it is valid to use a general expression of the (21) type in which the entropy production is expressed through a product of fluxes and forces [7]. This condition is satisfied for those reactions which are described by a nonlinear dependence of I on the force A of this type

$$\frac{I}{z\mathrm{F}} = L (\mathrm{e}^{\frac{A}{RT}} - 1), \tag{22}$$

i. e., nonlinear relations of this type for chemical reactions are still within the limits of applicability of the nonequilibrium thermodynamics [8].

Since the kinetic equation (20) obtained for electrochemical reactions is of the same kind (the generalized force being represented by the electrochemical affinity $\tilde{A}$ instead of chemical affinity $\bar{A}$), it may be concluded that Eq. (21) is valid also in the range of nonlinear laws of the kinetics of electrochemical dissolution of metals.

It is now necessary to analyze mechanical processes conjugate with electrochemical phenomena.

As before [1] let us consider a uniform distribution of dislocations in an isothermic metal volume; the dislocations, whose density is N, move during plastic shear in coplanar series (limited slip) which is most characteristic in the case of corrosion under stress. This formulation of the problem makes it possible to regard the density of uniformly distributed dislocations and their chemical potential as scalar values.

Being free to chose the standard state [9], we may describe the chemical potential of dislocations by

$$\mu_D = RT \ln \frac{N_p}{N_0} + \mu_D^0, \tag{23}$$

where N_p is the dislocation density for a state with a chemical potential μ_D, N_0 denoting the dislocation density for a certain initial (equilibrium) state μ_D^0.

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*The results here obtained and showing that the exchange current is independent of the equilibrium potential (unlike results of the theory of retarded discharge) is in agreement with data of the quantum-mechanical theory of electron transitions [6].

**This expression was obtained without any assumptions regarding the character of the dependence of the flux on the generalized force.

Since the generalized force of the mechanical process is [1]:

$$A = \mu_D - \mu_D^0 = \frac{\Delta\tau}{\alpha}, \tag{24}$$

where Δt is the stress increment in the plastic strain range and α is a constant, taking into account (24) we obtain from (23)*

$$N_\text{p} = N_0 \, e^{\frac{\Delta\tau}{\alpha RT}}. \tag{25}$$

Then the density of new dislocations formed when the stress is increased by Δt is given by

$$N = N_0 \left(e^{\frac{\Delta\tau}{\alpha RT}} - 1\right). \tag{26}$$

The generalized flux was defined in [1] as the dislocation flux:

$$\dot{n} = \frac{\varepsilon_\text{p}}{b\Lambda}\Delta\varepsilon, \tag{27}$$

where ε_p is the plastic strain rate, b Burgers vector modulus, and Λ a constant characterizing the proportional decrease in the free dislocation path with increasing plastic strain $\Delta\varepsilon$ (this relation holding right until the specimen fracture [11]).

Taking into account the known relation $N = \alpha\Delta\varepsilon$ and correlating (26) and (27), we find

$$\dot{n} = \frac{\varepsilon_\text{p} N_0}{b\lambda\alpha}\left(e^{\frac{\Delta\tau}{\alpha RT}} - 1\right), \tag{28}$$

or, introducing the phenomenological equation coefficient L_{11},

$$\dot{n} = L_{11} RT \left(e^{\frac{\Delta\tau}{\alpha RT}} - 1\right). \tag{29}$$

It is easily seen that the nonlinear equation (29), demonstrating the dependence of the generalized flux on the generalized force of the reaction* of the formation and movement of dislocation, relates to the same type of nonlinear laws as Eq. (20) and (22). For this reason the previously obtained [1] expression for entropy production

$$\sigma^\text{I} = \frac{\dot{n}A}{\text{T}} \tag{30}$$

is valid also in the range of operation of the nonlinear law (29).

At small deviations from equilibrium, expanding the exponent of Eq. (29) into a series and using only the terms of up to and including the first power, we obtain a linear phenomenological equation [1]:

$$\dot{n} = L_{11} A. \tag{31}$$

Correlating (27) and (28), we obtain an expression for the stress dependence of plastic strain:

$$\Delta\varepsilon = \frac{N_0}{\alpha}\left(e^{\frac{\Delta\tau}{\alpha RT}} - 1\right). \tag{32}$$

In the initial portion of the strain/stress curve, Eq. (32) contains as an approximation (expanding the exponent into a series and taking the first and second power terms) a linear hardening stage and, following it, a parabolic hardening stage, which is in agreement with experiment.

Equation (32), having a general character for various portions of the stress/strain curve, points to the existence of "logarithmic hardening" under conditions sufficiently removed from equilibrium. Consequently, the stress/strain curve plotted in semilogarithmic coordinates should (in the strain-hardening range be represented by a straight line.

In the case when electrochemical and mechanical processes take place simultaneously, leaving unchanged the form of expressing the entropy production [1] (a sum of (21) and (30)), the system of phenomenological equations in the range of operation of nonlinear laws is represented by

$$\dot{n} = L_{11} RT \left(e^{\frac{A}{RT}} - 1\right) + L_{12}\eta, \tag{33}$$

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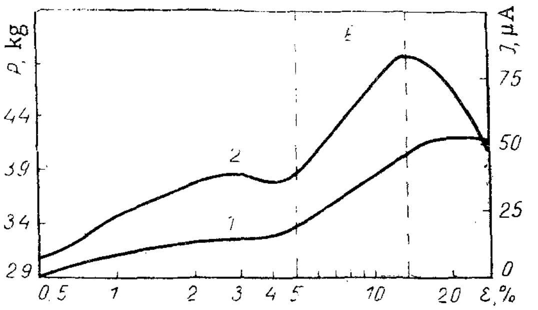
*An analogous expression was postulated in [10] but without making explicit the content of the coefficient in the exponential index.

**In view of the terminology used, it should be pointed out that in the dislocation theory of plastic deformation methods of the theory of absolute rates of reactions are used.

$$I = L_{21} A + L_{22} b (e^{\frac{\eta}{b}} - 1), \tag{34}$$

i. e., it is postulated that nonlinearity of the principal fluxes does not affect the linear character of the cross fluxes.



Tensile load P (curve 1) and corrosion current I (curve 2) plotted against strain ε.

The above hypothesis was verified by experiment. Using a method similar to that described in [12], we measured* the corrosion current between two vacuum-annealed (at 920° C) wire specimens of steel 08SV (of a composition approaching that of armco iron) in a 7N H_2SO_4 solution, one unstressed and the other deformed in tension at a constant strain rate of 34%/min.

The results obtained (see figure) show that, as was expected, there is a well defined linear correlation between the strain-hardening** curve and the curve representing the variation of the anodic current of self-dissolution of the metal (respectively, curves 1 and 2), i. e., $I = L_{21}A + \text{const}$. In the portion E of linear and parabolic hardening, the character of these curves is in accordance with Eq. (32) and (34), i. e., within the limits of the accuracy of the measurements the cross effects obey a linear law.

At the easy slip stages preceeding the hardening and fracture stages, the anodic current tends to decrease which is also in accordance with Eq. (34), since at these stages there is no hardening which increases the chemical potential of dislocations and, consequently, of the surrounding metal atoms reacting with the corrosive medium.

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