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

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

where $\mu$ is the chemical potential, $z$ ionic valency, $F$ the Faraday number, $\varphi$ the metal potential, $\mu_0$ 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

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

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

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

It is not difficult to see that when $\tilde{a}$ is fixed, $\tilde{f}$ will not increase with increasing $\varphi$ 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 $\rightarrow$ 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

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

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

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

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 $\tilde{\lambda}$, $\Delta\mu_0$ denoting the difference between the corresponding standard chemical potentials. At the same time, from the condition of the thermodynamic equilibrium ($I = 0$, $\tilde{\lambda} = 0$) we obtain the equilibrium constant:

$$
K_p = \frac{k_1}{k_2} = e^{\frac{\Delta\mu_0}{zF}}.
$$

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

\[ i^0 = k_2 \tilde{a}_2 z F, \]  

we obtain

\[ I = i^0 \left( \frac{\tilde{A}}{z F} - 1 \right). \]  

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

\[ i_A = i^0 e^{\frac{\tilde{A}}{RT}} = i^0 e^{\frac{z F \eta}{RT}}, \]

where \( \tilde{A}/z F = \eta \) 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 \( c_0 \) in the bulk of the solution. In fact,

\[ \tilde{a}_2 = \tilde{f}_2 c_2 \exp \left( \frac{z F \phi_1}{RT} \right), \]

where \( \phi_1 \) is the average potential of ions in the dense part of the double layer. In accordance with the Boltzmann principle, however, the ionic interaction in the electrolyte is such that

\[ c_2 = c_0 \exp \left( - \frac{z F \phi_1}{RT} \right), \]

and, consequently,

\[ i^0 = k_2 z F \tilde{f}_2 c_0. \]

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 \( 1.4 \times 10^{-3} \) to \( 14.2 \times 10^{-3} \) and \( 119 \times 10^{-3} \) 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 \( 3.2 \times 10^{-3} \) and \( 1.6 \times 10^{-8} \) 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 stoichiometric coefficients \( v_i (i = 1, \ldots, n) \) participate in a given electrochemical reaction:

\[ \frac{I}{z F} = k_2 \prod_{i=m+1}^{n} \left( f_i c_i^0 \right)^{v_i} \left( \frac{\tilde{A}}{z F} \right)^{-1}, \]

where \( \tilde{A} = - \sum_{i=1}^{n} v_i \tilde{a}_i \); and \( 1, \ldots, m \) are the indices of the starting components, \( v_m \) appearing in \( \tilde{A} \) with the negative sign.

Correspondingly

\[ i_A = k_2 z F \prod_{i=m+1}^{n} \left( f_i c_i^0 \right)^{v_i} e^{\frac{\tilde{A}}{RT}}, \]

and

\[ i^0 = k_2 z F \sum_{i=m+1}^{n} \left( f_i c_i^0 \right)^{v_i}. \]

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