[1] Butler-Volmer Equation

The way in which an electric field can change the rate of an electrode reaction can be understood by the study of fig. (27). Let us suppose that a reactant ion M^{z+} has approached quite close to an electrode. Reaction will occur if electrons are transferred from electrode to ion,

$$M^{z+} + ze \rightarrow M.$$

We are going to apply the Eyring equation for the rate constant k_2 of a chemical reaction to this process, using the following form.

$$k_2 = (kT/hc^0) \exp(-\Delta G^{0*}/RT) \qquad \dots (3)$$

where ΔG^{0*} is the Gibbs free energy of activation. Figure (27) depects that the "reaction coordinate" in the Eyring formulation is normal to the electrode surface. The detailed mechanism of the reaction does not concern us here. (Like thermodynamics, the activated-complex theory of rate processes is not concerned with detailed molecular mechanisms). Thus, the curves in Fig. (27) represent reaction paths along the free energy surfaces between reactants and product species. The maxima of the curves locate activated complexes for the reaction, and the higher ΔG^* shows the free energy of activation for the thermal reaction.

The electrochemical reaction of electron transfer occurs in a region near the electrode that approxmiately coincides with the region of the electric double layer. The strength of the electric field in a double layer can be very high, for example, a potential difference of 1V across a typical double layer thickness of 1 nm is equivalent to a field strength of $10^9 \, V \, m^{-1}$. This is an enormous electric field, far greater than could be achieved over longer distances in laboratory apparatus. Such a high field can literally tear ions out of a solid metal and drag them into solution. If the potential difference across the double layer is changed by even a fraction of a volt, large effects on the rate of the electrode reaction can be expected.

The exact course of the potential Φ vs. distance x curve through the double layer is not known, but as an example a simple Helmholtz model can be assumed, with a linear dependence of Φ on x as shown in fig. (27). The reactant molecule can be located at x_0, the position of the outer Helmholtz plane.

For an electrochemical reaction with ionic reactants, the potential difference $\Delta\Phi$ across the double layer at the electrode surface assists the transfer of an ion through the double layer in one direction but inhibits its transfer in the opposite direction. When the activated complex is reached, only some fraction α of the electrical energy difference at the maximum in the free energy barrier, only some fraction α of the electrical energy difference $zF\,\Delta\Phi$ has been used This fraction α is called the *transfer coefficient*. Generally, α is in the neighborhood of 0.5.

As fig. (27) shows, a change from the equilibrium potential increases the current in one direction and decreases it in the other. By convention, a net cathodic current is taken as positive and a net anodic current as negative. Thus, α corresponds to the cathodic (reduction) process and $(1-\alpha)$ to the anodic (oxidation) process.

From the general equation (3) for a rate process, given by the transition state theory, we can write the anodic and cathodic current densities as follows :

$$\text{Anodic} : i_a = zFk_aC_{OR} \exp\left[\frac{-\Delta G_a^* - (1-\alpha)zF\,\Delta\Phi}{RT}\right]$$

$$\text{Cathodic} : i_c = zFk_cc_{OO} \exp\left(\frac{-\Delta G_c^* + \alpha zF\,\Delta\Phi}{RT}\right)$$

In these expressions, k_a and k_c are the pre-exponential parts of the rate constants for the forward (anodic) and reverse (cathodic) electron transfer, and c_{OR} and c_{OO} represent the surface

concentration of reduced product and oxidized reactant of the electrochemical reaction, $M^{z+} + ze \rightarrow M$. The ΔG_a^* and ΔG_c^* are the thermal Gibbs free energy barriers for the anodic and cathodic electrode reactions, respectively. In a regime in which diffusion is sufficiently rapid to eliminate concentration gradients, the ionic concentrations adjacent to the electrode can be taken as constant, independent of i and also of time (when the extent of reaction is small).

At equilibrium, we can .hus write for the exchange current per unit area,

$$i_0 = zFk_a c_{OR} \exp -\left[\frac{\Delta G_a^* + (1-\alpha)zF\,\Delta\Phi_{rev}}{RT} \right]$$

$$= zFk_c c_{OO} \exp -\left(\frac{-\Delta G_c^* - \alpha zF\,\Delta\Phi_{rev}}{RT} \right)$$

In terms of i_0 and $\eta_i = \Delta\Phi - \Delta\Phi_{rev}$ the activation overpoential,

$$i = i_c - i_a = i_0 \left[\exp\left(\frac{\alpha zF\eta_i}{RT} \right) - \exp\left(\frac{-(1-\alpha)zF\eta_i}{RT} \right) \right] \qquad \ldots (4)$$

Equation (4) is known as *Butler-Volmer equation.*

In fig. (28), the current density i is plotted against the overpotential in accord with equation (4). Two cases are shown. One, labelled A is a case in which there is rather high exchange current i_0 at both electrodes. (The individual electrode curves are labelled A' and A''. In this case, even a small change in potential from the equilibrium value, i.e., a small overpotential, will produce an appreciable current flow through the cell. The other case, labelled B, corresponds to a very low exchange current i_0. (The individual electrode curves are not drawn.) In this case, a large overpotential is required to cause appreciable current flow through the cell. We see that the governing factor that determines the activation overpotential, in accord with the Butler-Volmer equation, is the exchange-current density i_0. The transfer factor α influences the shape of the current density (i) vs. overpotential (η) curve. One way to measure α is to fit the experimental curve to the Butler-Volmer equation (4).
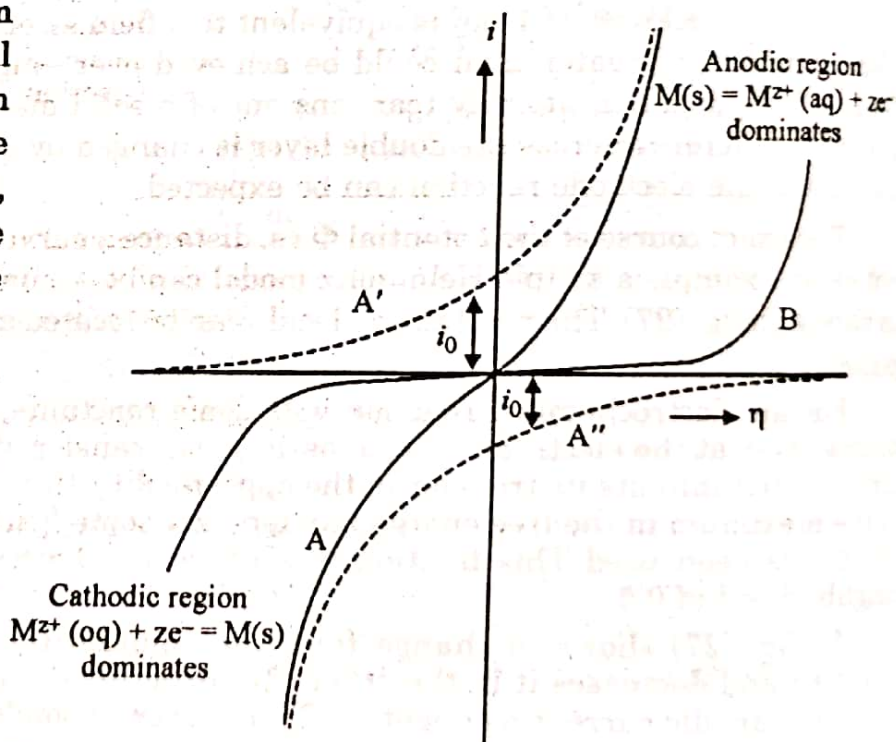

Fig. 28. Variation of current density with overpotential for activation polarization. These experimental curves closely follow the Butler-Volmer equation (4).

[III] Tafel Plot or Equations

If the overpotential has large positive or negative values, $|\eta| \gg RT/zF$, one of the partial currents becomes much greater than the other, which is then negligible. In this case, either.

$$\ln i_a = \ln i_0 - [(1-\alpha)zF/RT]\eta \qquad \ldots (5)$$

$$\ln i_c = \ln i_0 + (\alpha zF/RT)\eta \qquad \ldots (6)$$

This type of logarithmic dependence of i on η was found empirically in 1905 by Tafel. The slope of linear $\ln i$ vs. η plots gives the transfer coefficient α and the intercept gives the exchange current density i_0. [See fig. (29)]

Overpotentials can be caused by slow reactions in the solution adjacent to an electrode (reaction overpoential η_r) and in the process of deposition of a solid product on an electrode (crystallization overpotential η_c). In many cases, a diffusion overpotential (concentration polarization) occurs together with an activation over-potential, and methods are available for separating these factors. Thus, a great variety of interesting chemical kinetics can be studied by electronic techniques. Practical applications of this branch of kinetics are found in such fields as fuel cells, storage batteries for vehicle propulsion and electrochemical syntheses, where great selectivity can be achieved through the choice of electrodes and carefully controlled potentials.
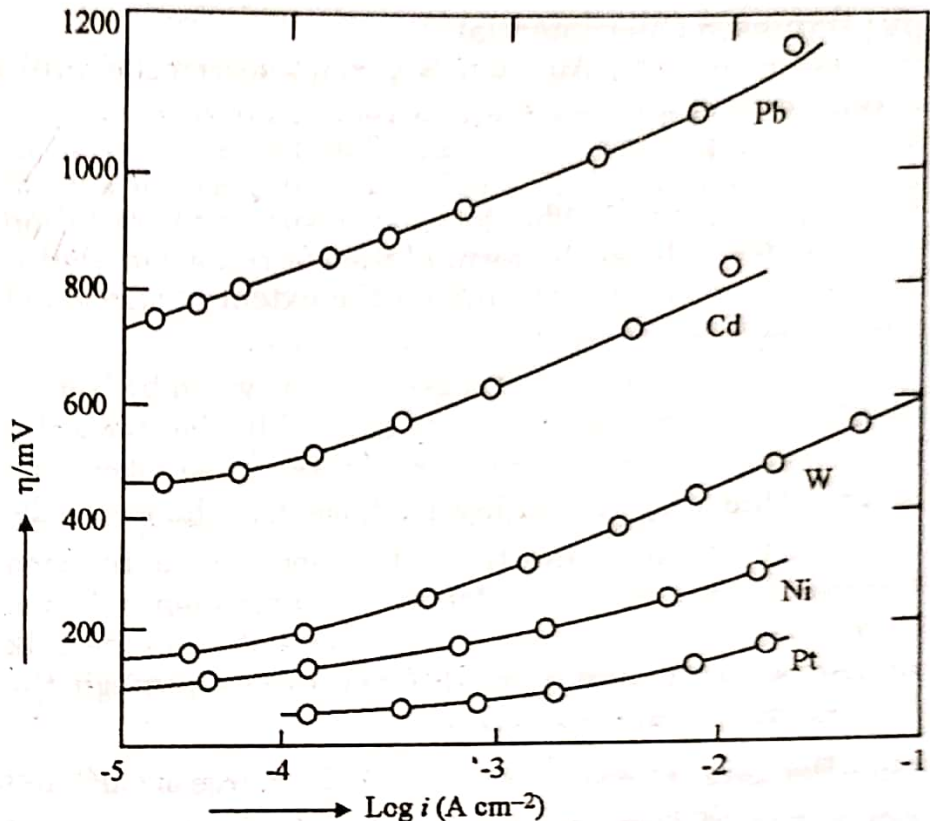

Fig. 29. Variation of overpotential for discharge of H^+ on various metals with current density. The linear portions of the curves are in accord with the Tafel equation (6)