

## □ EXCHANGE CURRENT DENSITY

A metal electrode acts as a catalytic surface that facilitates transfer of electrons to and from chemical reactant molecules and ions. Thus, an electrode reaction can be viewed as a succession of steps similar to those in heterogeneous catalysis.

- (i) Diffusion of reactants to electrode
- (ii) Adsorption of reactants on electrode
- (iii) Transfer of electrons to or from adsorbed reactant species
- (iv) Desorption of products from electrode
- (v) Diffusion of products away from electrode

In an electrode reaction, the energy of an electric field acts on charged species, such as ions and electrons, so as to help them surmount an activation energy barrier. Since electrochemical reactions are always studied at some temperature  $T > 0$ , there will also be a thermal contribution to the energy of activation; consequently, electrochemical kinetics is based upon a combination of thermal and electrical activation.

At equilibrium, for each ionic species, the rate of electron transfer across an electrode in the cathodic direction is exactly balanced by an equal rate of electron transfer in the anodic direction, so that the *current density*,  $i$  (current per unit area) is

$$i_c = i_a = i_0 \quad \dots (1)$$

The equilibrium difference in electric potential  $\Delta\Phi_c$  is determined by this condition. As in any chemical reaction, the condition of equilibrium is not the cessation of all exchange, but the equality of forward and backward reaction rates. *The current density at equilibrium,  $i_0$  is called the exchange current density.* Values of  $i_0$  for some electrode reactions are given in table-4. We see that these exchange reaction rates vary over many orders of magnitude.

**Table-4**  
Exchange current densities  $i_0$  at 25°C for some electrode reactions

Metal	System	Medium	Log $i_0$ (A cm <sup>-2</sup> )
Mercury	Ce <sup>4+</sup> /Ce <sup>3+</sup>	KCl	- 6.0
Platinum	Ce <sup>4+</sup> /Ce <sup>3+</sup>	H <sub>2</sub> SO <sub>4</sub>	- 4.4
Platinum	Fe <sup>3+</sup> /Fe <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	- 2.6
Palladium	Fe <sup>3+</sup> /Fe <sup>2+</sup>	H <sub>2</sub> SO <sub>4</sub>	- 2.2
Gold	H <sup>+</sup> /H <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	- 3.6
Platinum	H <sup>+</sup> /H <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	- 3.1
Mercury	H <sup>+</sup> /H <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	- 12.1
Nickel	H <sup>+</sup> /H <sub>2</sub>	H <sub>2</sub> SO <sub>4</sub>	- 5.2

The rate  $v$  of a chemical reaction at a surface is usually expressed in units of mol m<sup>-2</sup>s<sup>-1</sup>. The rate  $i$  of charge transfer at an electrode is expressed in units of A m<sup>-2</sup> if the charge number of the ionic species involved is  $|z|$ ,  $v = i/|z| F$ , where  $F$  is the faraday, i.e., 96,500 C mol<sup>-1</sup>. Thus, in

electrochemical reactions a high current density means a high reaction rate. A typical rate would be  $100 \text{ A m}^{-2}$ , equivalent to about  $10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$  for ions of unit charge.

Electrodes that have a high exchange-current density for a given reaction are said to be *non-polarizable*. If the applied potential difference across such an electrode is increased, there is an increased flow of charge between electrode and solution, but the potential difference across the double layer does not change. In other words, charge moves rapidly to and from the electrode and does not build up a charge density in the surface layers. An example of such an electrode is the calomel electrode.

Electrodes that have a low exchange current density for a given reaction are said to be *polarizable*. If the applied potential difference across such an electrode is increased, there is little flow of charge into the solution. The charges remain in the double layer and increase the potential difference across it. An example is a mercury electrode in a solution of KCl.

### [I] Polarization

When an electrochemical cell is operating under non-equilibrium conditions,  $i_c \neq i_a$  and there is a net current density  $i = i_c - i_a$ , the electric potential difference between the terminals of the cell departs from the equilibrium value  $\Delta\Phi = E$ , the emf. If the cell is converting chemical free energy into electric energy,  $\Delta\Phi < E$ . If the cell is using an external source of electric energy to carry out a chemical reaction,  $\Delta\Phi > E$ . The actual value of  $\Delta\Phi$  depends on the current density  $i$  at the electrodes. The difference,

$$\Delta\Phi(i) - \Delta\Phi(0) = \eta$$

is called the polarization or, probably more commonly now, the *overpotential* of the cell. The value of  $\eta$  is determined in part by the potential difference ( $IR$ ) necessary to overcome the resistance  $R$  in the electrolyte and leads. The corresponding electrical energy  $I^2Rt$  is dissipated as heat, being analogous to frictional losses in irreversible mechanical processes. The remaining part of  $\eta$ , which is the part of theoretical interest, is due to rate-limiting processes at the electrodes; the corresponding electrical energy is being used to provide part of the free energy of activation in one or more of the steps in the electrode reaction.

In electrochemical kinetics, we usually have to study reactions at a particular electrode. We measure the potential at this electrode by introducing into the cell an auxiliary reference electrode with a lead into the electrolyte very close to the experimental electrode. Such an arrangement is shown in fig. (26).

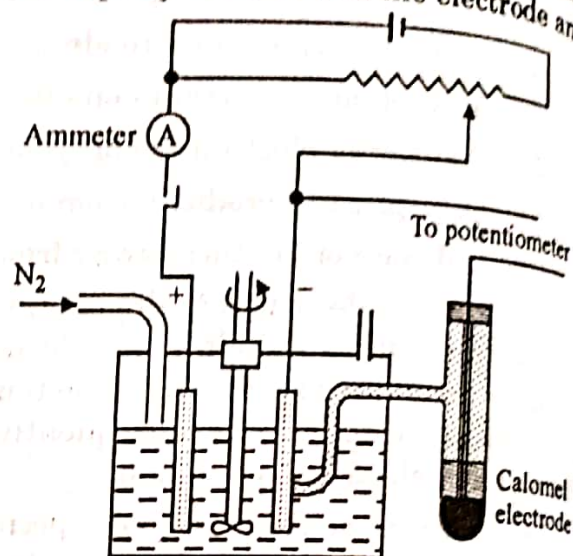


Fig. 26. Apparatus for measuring the potential of an electrode relative to that of a reference electrode. The potential is measured as a function of the current density at the electrode under study.

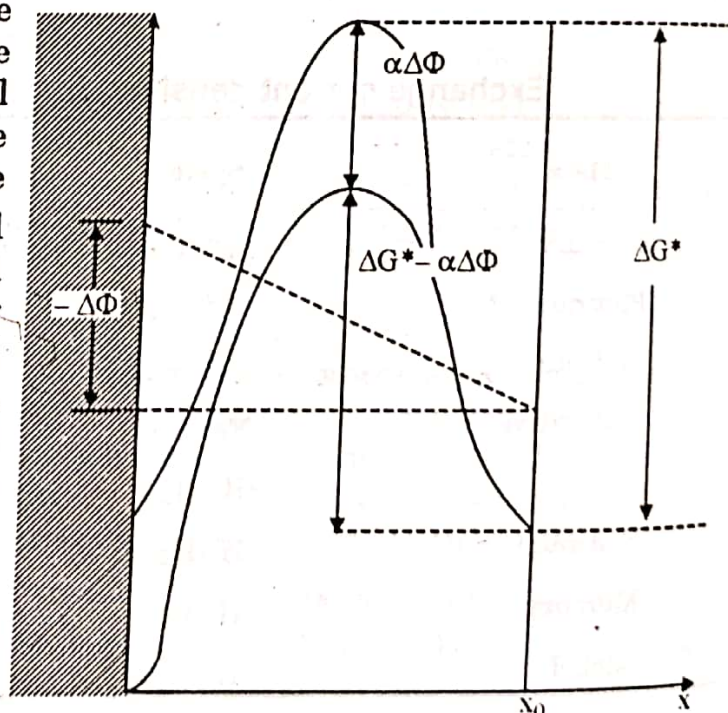


Fig. 27 Schematic Gibbs free-energy curves for the electrode reaction  $M^{2+} + ze \rightarrow M$  in the neighbourhood of the electrode surface, showing how the electric potential  $\Delta\Phi$  lowers the free energy of activation  $\Delta G^*$  by an amount  $\alpha z F \Delta\Phi$ .