MODULE III   ELECTRODE KINETICS

CHAPTER 1: SIGNIFICANCE OF OVERPOTENTIALS – ACTIVATION, OHMIC AND DIFFUSION OVERPOTENTIALS

LEARNING OBJECTIVES

After reading this chapter, you will be able to

(i) understand the importance of various overpotentials

(ii) estimate the magnitude of the concentration overpotential

and

(iii) comprehend the effect of migration on diffusion limited current

Types of Overpotential

The term overpotential refers to the potential ‘over and above’ the equilibrium potential (E_{eq}) applied to a system in order to perturb the equilibrium and bring about the net reaction. In chemical kinetics, the temperature is the usual control variable whereas in electrochemistry, the applied potential is the driving force in general and the net current (rate) of the reactions is measured as a function of the potential. The overpotential is defined as

$$\eta = (E - E_{rev}) = E - E_{eq}$$

It is customary to employ a three – electrode assembly in electrochemical techniques. This involves a working electrode (Pt, Ag, Au, glassy carbon etc), reference electrode (SCE, Ag|AgCl, SHE etc) and a counter electrode (Pt plate, Pt wire etc).

The Luggin capillary ensures the elimination of the 'iR' drop (ohmic overpotential). Fig 1 depicts the luggin capillary arrangement.In modern electrochemical workstations, the iR compensation can be made to the desired extent.

The principle of the three electrode-system for electrode potentials

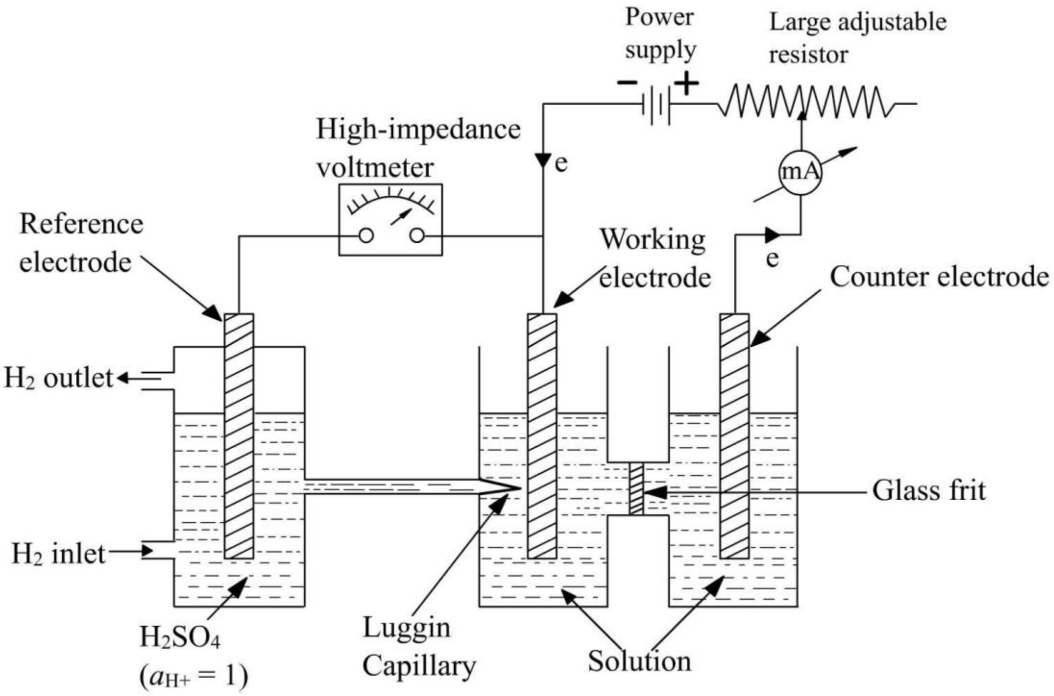


Fig 1: A schematic diagram of the three-electrode assembly illustrating the Luggin capillary

As mentioned earlier, the overpotential denotes the difference between the potential (E) pertaining to a net current, '*i*' and the equilibrium potential (E_{eq}). These changes in the potential need to be measured by coupling the working electrode with a reference electrode. A working electrode is combined with a counter electrode via a polarizing circuit. In a three electrode assembly the current is controlled by varying the potential of the working electrode. When a current 'i' passes through the circuit, the voltmeter reading gives the potential of the working electrode relative to that of the reference electrode.

Types of Overpotentials

There are different types of overpotentials in electrochemical systems and among them, the following are very common:

(i) Activation overpotentials or charge transfer overpotentials , η_{act} or η_{ct}
(ii) Resistance overpotentials or ohmic overpotentials, η_R or η_{ohmic}
(iii) Concentration overpotentials (or diffusion) overpotentials, η_{conc} or η_{diff}
(iv) Crystallization overpotentials or phase transition overpotentials η_{crys} or η_{phase}
(v) Decomposition overpotential η_{dec}

In any electrochemical experiment, the endeavor is to minimize each overvoltage in order to obtain maximum efficiency of the process, since these overpotentials lead to dissipated heat.

(i) Activation overpotential (η_{act})

The activation (or charge transfer) overpotential is the potential associated with climbing of the activation energy barrier in the potential energy diagram. Any net electrochemical reaction is an outcome of the applied potential over and above the equilibrium potential. At equilibrium, the net current is zero (i=0 at $\eta = 0$) the minimization of η_{act} requires a proper electrocatalyst and / or variation in reaction conditions. The activation overpotential will be discussed in the chapter on Butler – Volmer equation.

(ii) Resistance (ohmic)overpotential (η_R or η_{ohmic})

The ohmic overpotential η_R refers to the resistance offered by the medium and is given by Ohm's law. Obviously, for this contribution to be minimal, current should tend to zero or the conductance of the system must be infinity! In practice, the ohmic overpotential includes the resistances arising from the bulk electrolyte, electrode and the surface films.

The resistance overpotential is minimum if aqueous electrolytes are employed since the conductivity of the latter is high. On the other hand, modern electrochemical instruments have an in – built arrangement for the minimisation of η_{ohmic} ('iR compensation'). The older instruments employed the Luggin capillary arrangement depicted in Figure 1.

(iii) Concentration overpotentials, η_C

The concept of concentration overpotential can be understood with the help of the Nernst diffusion layer approximation whereby a linear variation of concentration with distance is assumed, as shown in the Fig. below:

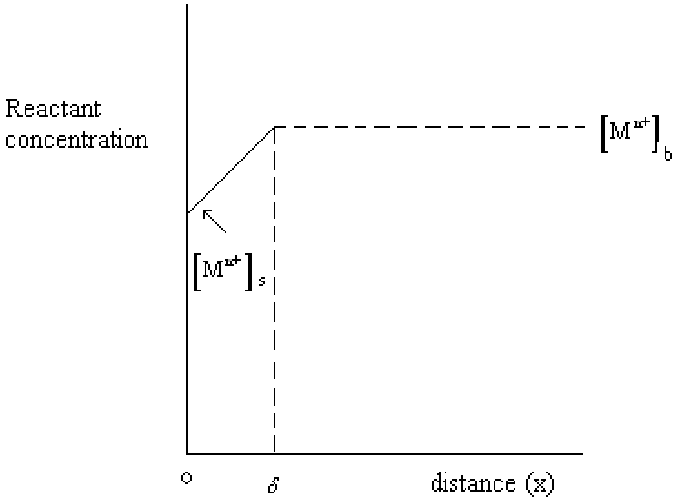


Fig 2: Nernst Diffusion Layer approximation

Consider the electron transfer process $M^{n+} + n\bar{e} \rightarrow M$

According to the Fick's first law of diffusion, the flux is given by

$$J_{diff} = -D\left[\frac{\partial C}{\partial x}\right]_{x=0} = D\frac{[C_b - C_s]}{\delta - 0} \qquad (1)$$

where C_s refers to the concentration of $\left[M^{n+}\right]$at the electrode surface and C_b denotes the concentration of $\left[M^{n+}\right]$ at the bulk. Hence

$$J_{M^{n+}} = D_{M^{n+}}\left\{\frac{\left[M^{n+}\right]_b - \left[M^{n+}\right]_s}{\delta}\right\} \qquad (2)$$

However, the diffusion current density $j = nFJ_{M^{n+}}$ which is experimentally measurable.

$$i = nFJ_{M^{n+}} = nFD_{M^{n+}}\frac{\left[M^{n+}\right]_b - \left[M^{n+}\right]_s}{\delta} \qquad (3)$$

For maximum current density to be reached , the surface concentration of the reactant $\left[M^{n+}\right]_s \to 0$ and hence the limiting current density is

$$i_{\lim} = \frac{nFD\left[M^{n+}\right]_b}{\delta} \qquad (4)$$

However, the concentration overpotential η_{conc} is given by

$$\eta_{conc} = \frac{RT}{nF}\ln\left(\frac{\left[M^{n+}\right]_b}{\left[M^{n+}\right]_s}\right) \qquad (5)$$

indicating that the ratio of concentration at the electrolyte solution and electrode surface dictates the overpotential.

Using equations (3) and (4), the concentration overpotential becomes

$$\eta_{conc} = -\frac{RT}{nF}\ln\left(1-\frac{i}{i_{\lim}}\right) \qquad (6)$$

The above equation provides a method of estimating the concentration overpotential by the measurement of current in potential step experiments. We emphasize that, for all practical application in electrochemistry, the overpotentials should be minimized.

For any electrochemical process, the transport of ions can occur by (i) diffusion (ii) migration and (iii) convection. The convection is often eliminated by keeping the electrode stationary. while the migration can be avoided by the use of excess supporting electrolyte. When the reactant concentration at the electrode surface is different from that in the bulk, concentration overpotential arises. Fig 3 describes the variation of the concentration overpotential with current.

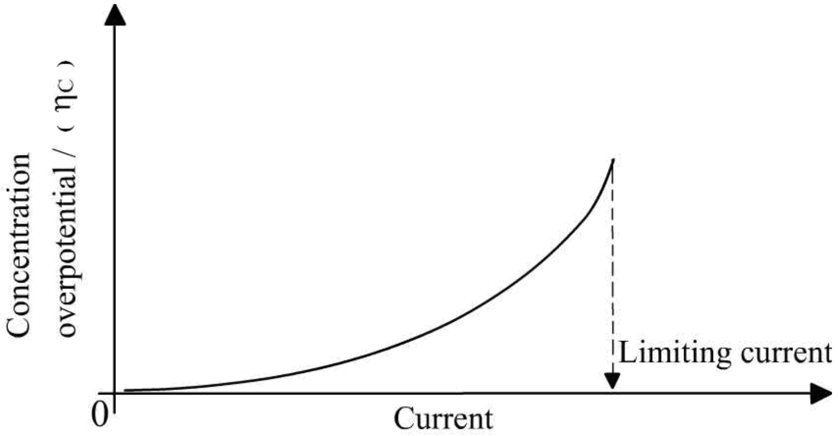


Fig 3: Dependence of the concentration overpotential on current

When the current density, *i* is lower than to the limiting value, i_{lim}, the above equation can be expanded and a linear relation between η_C and *i* is obtained which is ohm's law. Further, when $i \rightarrow i_{\lim}$ as i approaches i_l, the ratio $\left(\frac{i_{\lim}}{i_{\lim}-i}\right)$ becomes very large, and η_C increases rapidly with change in '*i*'. This can be seen in the figure given above.

The limiting current is related to the rate of diffusion of ions which in turn depends upon the nature and bulk concentration of the ions. The limiting current density, i_{lim} is given by the expression

$$i_{\lim} = \frac{nFD_i c_b}{\delta} \qquad (7)$$

where D_i is the diffusion coefficient of the ion whose concentration is c_b, and 'δ' is the thickness of the diffusion layer .

The above equation assumes that the transport number of the ions arriving at the surface is nearly unity. There exist various methods of estimating 'δ' viz.

(i) Potential step; (ii) Potential sweep; and (iii) Hydrodynamic experiments

Fig 4 depicts the region where each overpotential appears in the experimental polarization curves.

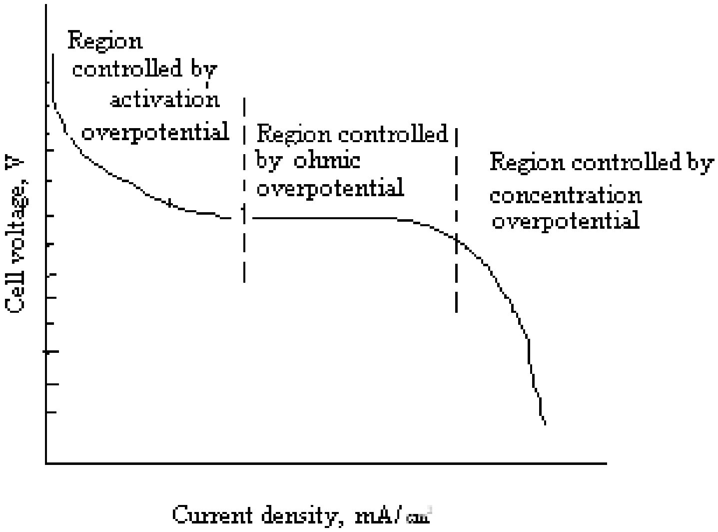


Fig 4: Typical polarization curve depicting various overpotentials

Coupling between diffusion and migration: Dependence of the diffusion layer thickness on transport number of reactants

The Nernst Planck equation for the cation flux is

$$J_+ = -D_+ v_+ \frac{\partial c}{\partial x} - z_+ u_+ F c_+ \frac{\partial \phi}{\partial x} \qquad (8)$$

where v_+ denotes the stoichiometric number of the cations and x is the distance from the electrode surface. The first term on the r.h.s is the diffusion part while the second is the migration contribution. The current is due to the flux of all ions, but at the electrode surface the cations contribute to the current and eqn ( ) becomes

$$i = -z_+ F J_+ \qquad (9)$$

Since anions do not undergo any reaction, their flux at the electrode surface is zero.

$$J_- = -z_- u_- F v_- c \frac{\partial \phi}{\partial x} - D_- v_- \frac{\partial c}{\partial x} = 0 \qquad (10)$$

Combining eqns (8) and (10) and eliminating the potential gradient, the current follows as

$$\frac{i}{z_+ v_+ F} = \left(\frac{z_- u_- D_+ - z_+ u_+ D_-}{z_- u_-} \right) \frac{\partial c}{\partial x} \qquad (11)$$

Note that the mobility is associated with the potential gradient while the concentration gradient appears separately.The transference number of cations is

$$t_+ = \frac{z_+^2 u_+ c_+}{z_+^2 u_+ c_+ + z_-^2 u_- c_-} = \frac{z_+ u_+}{z_+ u_+ + z_- u_-}$$

The diffusion coefficient of the electrolyte is defined as

$$D = \frac{z_+ u_+ D_- - z_- u_- D_+}{z_+ u_+ - z_- u_-} \qquad (12)$$

where D_+ and D_- denotes respectively the cationic and anionic diffusion coefficient. Hence

$$\frac{i}{z_+ v_+ F} = \frac{D}{1 - t_+} \frac{\partial c}{\partial x} \qquad (13)$$

If we consider the reduction process, $M^{n+} + ne^{-} = M$, the product $z_+ v_+$ is nothing but number of the electron transferred ‘n’. Hence

$$i = \frac{nFD}{1-t_+}\frac{\partial c}{\partial x} \qquad (14)$$

If the Nernst diffusion layer approximation is made, viz

$$i = nFD\frac{\partial c}{\partial x}$$

then

$$\frac{\partial c}{\partial x} \simeq \frac{c_\infty}{\delta} \qquad (15)$$

where c_∞ is the bulk (15) concentration, for maximum limiting current to be reached

Hence,

$$\mathrm{i}_{\lim} = \frac{nFDc_\infty}{\delta(1-t_+)} \qquad (16)$$

The above equation indicates how the limiting current is dependent on the transport number of ions also.

WORKED OUT EXAMPLES

1. During the deposition of Ni from $NiSO_4$ solution at 20 °C, the cell current is 98% of the limiting current. (i) If the concentration of $NiSO_4$ electrolyte is doubled, what is its influence on the concentration overpotential? (ii) what is the effect of increasing the temperature from 20ºC to 70ºC?

Using equation (6),

$$\eta_{Conc} = 0.029\log\frac{i_{\lim}}{i_l - 0.98 i_{\lim}} = 0.029\log 50 = 0.049\text{V}$$

Assuming D_i, δ and t_i are constant, the new value of the concentration overpotential is given by

$$\eta_{Conc} = 0.029 \log \left[\frac{2i_l}{2i_l - 0.98 i_l} \right]$$

$$\eta_{Conc} = 0.029 \log 1.96 = 0.008\text{V}$$

The concentration overpotential has decreased by 84%.

At 20 °C, the concentration overpotential is 0.049 V.At 70 °C the concentration

overpotential is

$$\eta_{Conc} = \frac{0.06808}{2} \log \left[\frac{2i_l}{2i_l - 0.98 i_l} \right] = 0.01 \text{ V.}$$

2. In the electrolysis of water using a cathode of 10 cm^2 area, estimate the limiting current. The diffusion coefficient and the transport number of H^+ ions are respectively

9.3×10^{-5} cm^2/sec and 0.64 at 25 °C? The diffusion layer thickness is 0.5 cm.

Consider $2H_2O \rightarrow 2H_2 + O_2$

$D_i = 9.3 \times 10^{-5}$ cm^2/sec; n = 2;

F = 9.65×10^4 C mol^{-1}; $a_i = 10^{-7}$ M; δ = 0.05 cm

$$i_{lim} = \frac{nFDc_\infty}{\delta(1-t_+)} = 10^{-7} \text{ A/cm}^2$$

For a cathode of area 10 cm^2, the limiting current is therefore 10 μA.

EXERCISES

1. Explain the concept of overpotential. What are the various types of overpotentials encountered in electrode processes? Indicate strategies by which each overpotential can be minimized.

2. Assuming that D = 1.0 $\times 10^{-5}$ cm^2/s, estimate the diffusion layer thickness after 73 seconds, if diffusion – limited kinetics is obeyed.

3. Using the Nernst diffusion layer approximation, derive the expression for the current density of an electrochemical reaction.

4. Derive the expression for the concentration overpotential in terms of the limiting current density.

5. If the diffusion coefficient of an analyte is $0.5*10^{-5}$ cm^2 sec^{-1} , provide an approximate estimate of the time taken by it to travel a distance of 0.01 cm.

6. Write the expression for the diffusion layer thickness in the case of the following: (a) Chronoamperometry;(b) cyclic voltammetry and (c) Hydrodynamic voltammetry.

7. Write the expression for the experimental current in terms of the diffusion-controlled and activation-controlled currents.

SUMMARY

The various types of overpotentials has been outlined. The importance of the concentration overpotential has been discussed.

CHAPTER 2– KINETICS OF ELECTRODE REACTIONS: BUTLER – VOLMER EQUATION AND MARCUS THEORY

LEARNING OBJECTIVES

After reading this chapter, you will be able to

(iv) comprehend the principles of electrode kinetics

(v) derive the Butler – Volmer equation and its special cases

and

(vi) deduce the Marcus cross – exchange relation for electron transfer processes

Consider a simple electron transfer process represented by

Ox+ n e- = Red (1)

where Ox denotes the oxidized form of the species under consideration and Red indicates its reduced form. It is of interest to enquire the current-potential relation for the above simple scheme. The formulation pertaining to eqn (1) arose from the works of Erdey-Gruz, Butler and Volmer . It is customary to denote the resulting equation as the Butler-Volmer equation. The detailed derivation is as follows:

The net rate of the above surface reaction (mol cm $^{-2}$ sec $^{-1}$) is given by

$$\mathrm{v} = \mathrm{v}_{Ox} - \mathrm{v}_{\mathrm{Red}} \qquad (2)$$

The individual reaction rates are given by

$$\mathrm{v}_{Ox} = k_f\,[Ox] \qquad (3)$$

$$\mathrm{v}_{\mathrm{red}} = k_{\mathrm{b}}\,[\mathrm{Red}] \qquad (4)$$

where k_f and k_{b} denote the forward and backward electron transfer frequencies

(sec^{-1}) and [Ox] and [Red] denote respectively the surface concentrations (mol cm $^{-2}$) of the oxidized and reduced forms. The velocities have the unit moles cm $^{-2}$ sec $^{-1}$ and have the interpretation that it represents the number of moles at the reaction zone per unit area per unit time. The current density follows as

$$i = nF\left(\mathrm{v}_{Ox} \ - \mathrm{v}_{\mathrm{Red}}\right)$$

The forward and backward rate constants can be written employing the absolute reaction rate theory of Eyring as

$$k_{\mathrm{Ox}} = \left(k_B T/h\right) e^{-\Delta G^{\#}_{\mathrm{Ox}}/RT} \qquad (5)$$

$$k_{\mathrm{Red}} = \left(k_B T/h\right) e^{-\Delta G^{\#}_{\mathrm{Red}}/RT} \qquad (6)$$

where k_B denotes the Boltzmann constant, h being the Planck constant. The Gibbs free energies of activation for forward and backward reactions are denoted as $\Delta G^{\#}_{Ox}$ and $\Delta G^{\#}_{\mathrm{Re}d}$. At this stage, a model for the dependence of the Gibbs free energy of activation on the electrode potential is needed. It is postulated that

$$\Delta G^{\neq}_{\mathrm{Ox}}\left(E\right) = \Delta G^{\neq}_{\mathrm{Ox}}\left(E_e\right) + \alpha nFE \qquad (7)$$

$$\Delta G^{\neq}_{\mathrm{Re}d}\left(E\right) = \Delta G^{\neq}_{\mathrm{Re}d}\left(E_e\right) - \left(1-\alpha\right)nFE \qquad (8)$$

where α is designated as the symmetry factor or transfer coefficient. It is a measure of the symmetry of the activation energy barrier, whose value is in general 0.5. Fig1 depicts the influence of the applied potential on the free energy of activation for the forward and backward reactions. Since the heterogeneous rate constant is exponentially related to the Gibbs free energy of activation, we may rewrite the rate constants as

$$k_f = \frac{k_{\mathrm{B}}T}{h}\ \exp\left(-\Delta G_f^{\neq}\left(E_e\right)/RT\right)\exp\left(-\alpha nFE/RT\right) \tag{9}$$

$$k_{\mathrm{b}} = \frac{k_{\mathrm{B}}T}{h}\ \exp\left(-\Delta G_{\mathrm{b}}^{\neq}\left(E_e\right)/RT\right)\ \exp\left[\left(1-\alpha\right)nFE/RT\right] \tag{10}$$

The rate constants at the equilibrium potential are known as the standard rate constants as

$$k_{f,O} = \frac{k_{\mathrm{B}}T}{h}\ \exp\left[-\Delta G_f^{\neq}\left(E_e\right)/RT\right] \tag{11}$$

$$k_{\mathrm{b},O} = \frac{k_{\mathrm{B}}T}{h}\ \exp\left[-\Delta G_{\mathrm{b}}^{\neq}\left(E_e\right)/RT\right] \tag{12}$$

The velocities now become

$$\mathrm{v}_f = k_{f,0}\left[O\mathrm{x}\right]\ e^{-\left(\alpha nFE/RT\right)} \tag{13}$$

$$\mathrm{v}_{\mathrm{b}} = k_{b,0}\left[\mathrm{Red}\right]\ e^{\left(1-\alpha\right)nFE/RT} \tag{14}$$

Hence the net current density follows as

$$i = n\ F\ \left\{k_f\left[O\mathrm{x}\right]e^{-\alpha nFE/RT} - k_{\mathrm{b}}\left[\mathrm{Red}\right]e^{\left(1-\alpha\right)nFE/RT}\right\} \tag{15}$$

The current density at the equilibrium potential is referred to as the exchange current density defined as

$$i_0 = nF\ k_{f,0}\left[O\mathrm{x}\right]\ e^{-\left(\alpha nFEe/RT\right)} \tag{16}$$

$$= nF\ k_{\mathrm{b},0}\left[\mathrm{Red}\right]e^{\left(1-\alpha\right)nFEe/RT} \tag{17}$$

From equations (16) and (17)

$$nF\ k_{f,0}\left[O\mathrm{x}\right] = i_0\ e^{+\left(\alpha nFEe/RT\right)} \tag{18}$$

$$nF\ k_{\mathrm{b},0}\left[\mathrm{Red}\right] = i_0\ e^{-\left(1-\alpha\right)nFEe/RT} \tag{19}$$

Substituting the above equations in eqn (1), the simplified Butler-Volmer equation follows as

$$i = i_0\left[e^{-\alpha nF\eta/RT} - e^{(1-\alpha)nF\eta/RT}\right] \qquad (20)$$

where η is the activation overpotential given by

$$\eta = \left(E - E_e\right)$$

Nernst equation is given by

$$E_e = E^o - \frac{RT}{nF}\ln\frac{[\mathrm{Red}]}{[Ox]}$$

$$i_o = nFk_{f,o}[Ox]e^{-\alpha nFE_e/RT}$$

$$= nFk_{f,o}[Ox]e^{-\frac{\alpha nF}{RT}\left(E^o - \frac{RT}{nF}ln\frac{[\mathrm{Red}]}{[Ox]}\right)}$$

$$= nFk_{f,o}[Ox]e^{-\frac{\alpha nFE^o}{RT}}\left(\frac{[\mathrm{Red}]}{[Ox]}\right)^{\alpha}$$

$$i_o = nFk_{f,o}[Ox]^{1-\alpha}[\mathrm{Red}]^{\alpha}e^{-\frac{\alpha nFE^o}{RT}} \qquad (21)$$

The standard heterogeneous rate constant k_0^0 is

$$k_o^o = k_{f,0}\ \exp\left[-\alpha nFE^{'0}/RT\right] = k_{\mathrm{b},0}\ \exp\left[\left(1-\alpha\right)nFE^{'0}/RT\right] \qquad (22)$$

Hence the standard exchange current density is

$$i_0 = nFk_o^o\left[ox\right]^{1-\alpha}\left[\mathrm{Red}\right]^{\alpha} \qquad (23)$$

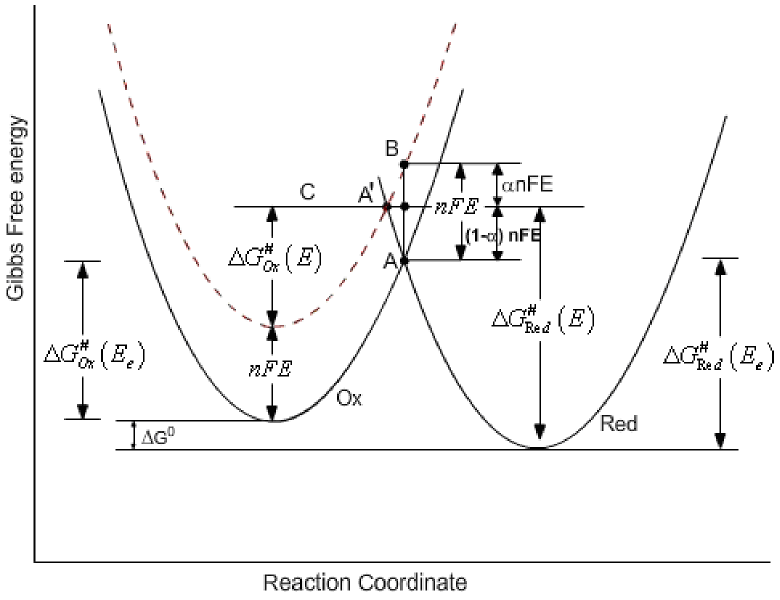


Fig 1: Effect of applied potential on the activation energies for the reaction $\mathbf{Ox + ne^- \rightleftarrows Red}$ when the overpotential is negative

At equilibrium, $[ox]_{eq} = [Red]_{eq}$ and hence eqn (23) becomes

$i_o = nFk_o^o[ox]$ (24)

Note that with rate constant in cm sec^{-1}, Faraday in C mol^{-1} and concentration in mol lit^{-1}, the unit of i_o turns out to be A cm^{-2}.

Sign convention: In the above derivation of the Butler Volmer equation, the cathodic current has been assumed to be positive while the anodic current has been assumed to be negative. If the cathodic process dominates, the net current is positive. On the other hand, an alternate convention (recommended by IUPAC) is that the anodic current be positive. Thus, the net current may be written as

$i = i_a - i_c$

and in this convention, if a cathodic process dominates, the net current is negative. It is essential that one is familiar with both conventions.

Ohm's Law

If the exponential terms are linearized in equation (20), it follows that

$$\frac{i}{i_o} = \left[1 - \frac{\alpha nF\eta}{RT}\right] - \left[1 + (1-\alpha)\frac{nF\eta}{RT}\right]$$

$$= \frac{nF\eta}{RT}$$

Hence $i = i_o \frac{nF\eta}{RT}$ (25)

which is the linear relation between current and potential viz Ohm's law.

It is of interest to note that eqn (21) rewritten as

$$\eta = \frac{RTi}{nFi_o}$$

is reminiscent of Ohm's law and hence the quantity $\frac{RT}{nFi_o}$ is a 'resistance', customarily denoted as R_{ct} where $R_{ct} = \frac{RT}{nFi_o}$,

the subscript ct denoting charge transfer.

TAFEL EQUATIONS

For large negative overpotentials, $\eta \ll 0$, the anodic reactions can be neglected and hence equation (20) becomes the cathodic Tafel equation viz

$$i_c = i_o e^{-\alpha nF\eta_c/RT}$$

or

$$\eta_c = \frac{2.303RT}{\alpha nF}\log i_o - \frac{2.303RT}{\alpha nF}\log i_o$$

$$= a + b \log i \qquad (26)$$

where a and b are known as the cathodic Tafel constants.

Analogously, for large positive overpotentials η>>0, the cathodic reaction can be neglected and hence equation (20) becomes

$$i_a = i_o(-1)e^{(1-\alpha)nF\eta_a/RT}$$

or

$$\eta_a = \frac{RT}{(1-\alpha)nF}\left[-\ln i + \ln i_o\right] = \frac{2.303RT}{(1-\alpha)nF}\log i_o - \frac{2.303RT}{(1-\alpha)nF}\log i \qquad (27)$$

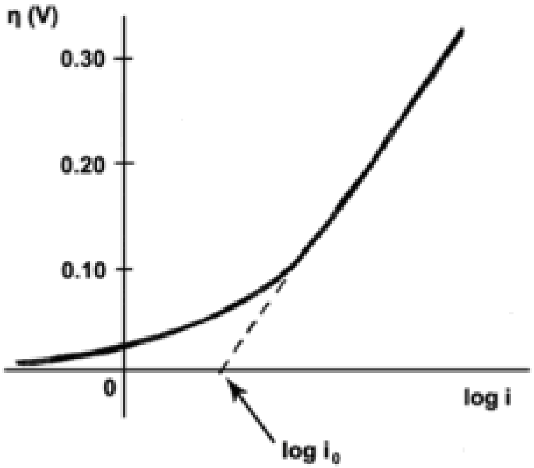


Fig 2 : Tafel Equation for oxidation

Nernst Equation

It is customary to deduce the Nernst equation using the Gibbs free energy changes in terms of the reaction quotient. Alternately, Nernst equation can also be derived from the Butler – Volmer equation as shown below. Consider equation (15)

$$i = nFA\left[k_f\,[\mathrm{ox}]\,e^{-\alpha nF\eta/RT} - k_b\,[Red]\,e^{(1-\alpha)nF\eta/RT}\right]$$

At, equilibrium, the net current is zero and hence

$$k_f\,[\mathrm{ox}]\,e^{-\alpha nF\eta/RT} = k_b\,[Red]\,e^{(1-\alpha)nF\eta/RT}$$

$$\ln\left(\frac{k_f}{k_b}\right) + \ln\frac{[\mathrm{ox}]}{[Red]} = nFE_{eq}\,/\,RT$$

$$\therefore E_{eq} = \frac{RT}{nF}\ln\left(\frac{k_f}{k_b}\right) + \frac{RT}{nF}\ln\left(\frac{[\mathrm{ox}]}{[Red]}\right) = E^\circ - \frac{RT}{nF}\ln\frac{[\mathrm{Red}]}{[\mathrm{ox}]}$$

which is the familiar Nernst equation usually derived using the chemical potentials or Gibbs free energies.

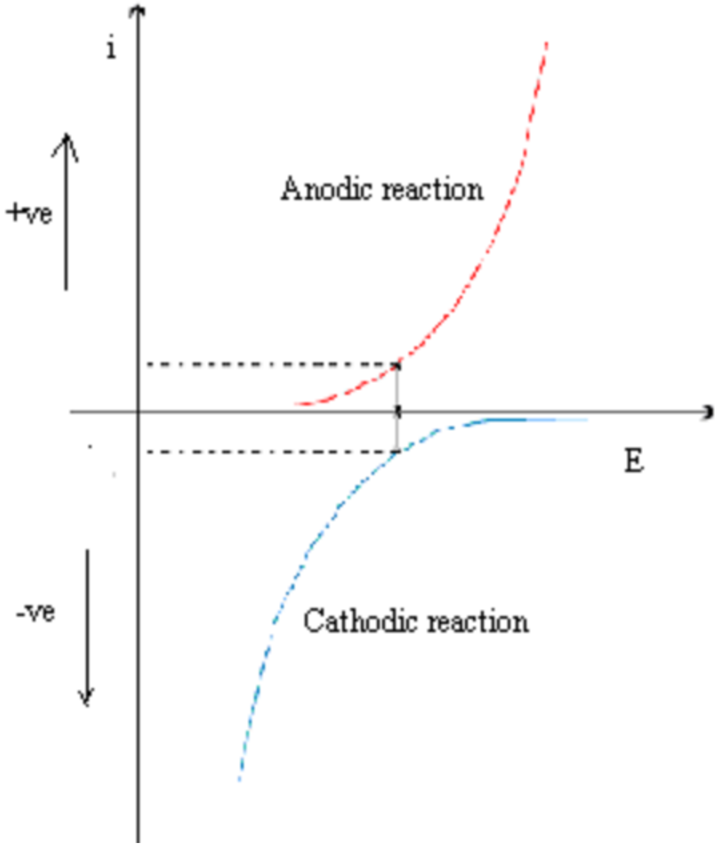


Fig 3: Tafel equations depicting anodic and cathodic currents. The intercept on the y-axis indicates the exchange current density while the value in the abscissa denotes the equilibrium potential.

Table 1: Heterogeneous standard rate constants at 20°C on Hg electrodes for a few reactions

System	**Heterogeneous standard rate constant (in cm sec^{-1})**
$Pb^{2+} + 2e \rightleftarrows Pb$	2.0
$Ti^{4+} + e \rightleftarrows Ti^{3+}$	0.009
$T1^{+} + e \rightleftarrows T1$	1.8
$V^{III} + e \rightleftarrows V^{II}$	0.0032
$Zn^{2+} + 2e \rightleftarrows Zn$	0.003

At this stage, it is imperative to emphasize that the rate of entropy production can be estimated using the rate constants and it has been shown that the Onsager's phenomenological coefficient is indeed constant and is independent of the driving force.

MARCUS THEORY

The seminal contributions of R.A.Marcus spans a variety of diverse topics and among them, mention may be made of the following (i) RRKM theory of unimolecular reactions;(ii) mechanism of electron transfer, proton transfer and group transfer reactions;(iii)prediction of rate constants for cross-exchange electron transfer reactions;(iv) correlation between homogeneous and heterogeneous rate constants and (v) prediction of solvent influence in reactions.

A simple derivation of the Marcus cross-exchange relation

The rate constant k for any reaction can be written in terms of the Gibbs free energy of activation $\Delta G^{\#}$ as

$$k = Ze^{-\Delta G^{\#}/RT} \tag{1}$$

where Z denotes the corresponding frequency factor. For a typical self exchange electron transfer reaction such as

$Fe^{2+} + Fe^{*3+} \rightarrow Fe^{3+} + Fe^{*2+}$,

the rate constant k_{11} now becomes

$$k_{11} = Z_{11}e^{-\Delta G^{\#}/RT} \tag{2}$$

where Z_{11} represents the frequency factor for the self exchange reaction. In the above chemical reaction, the star indicates the isotopically labelled constituent.

As has been demonstrated by Marcus, the Gibbs free energy of activation for the cross-exchange reaction is given by a quadratic dependence on the driving force as shown below for general scheme. The Gibbs free energy of the reactant in terms of the reaction coordinate x is given by

$$G_R = kx^2$$

Since the free energy of the product takes into account the intrinsic Gibbs free energy change (ΔG^o), the Gibbs free energy of the product G_p is

$$G_P = k\left(x - x_1\right)^2 + \Delta G^0$$

At the transition state, we can equate the Gibbs free energies so as to obtain

$$kx^{*2} = k\left(x - x_1\right)^2 + \Delta G^0$$

But, $x^2 = \left(x - x_1\right)^2 = x_1^2 + x^2 - 2x_1x$

where x$_1$ denotes the equilibrium distance

Hence $\left(x - x_1\right)^2 = x_1^2 - 2x_1x + x^2$

$$kx_1^2 - 2kx_1x^* + \Delta G^0 = 0$$

$$x^* = \frac{kx_1^2 + \Delta G^0}{2kx_1}$$

But $G = kx_1^2 = \lambda$

$$\therefore x^* = \frac{\left(\lambda + \Delta G^0\right)}{2kx_1}$$

$$\Delta G^{\#} = kx^{*2} = k\frac{\left(\lambda + \Delta G^0\right)^2}{4k^2x_1^2} = \frac{\left(\lambda + \Delta G^0\right)^2}{4\lambda}$$

$$\Delta G_{12}^{\#} = \frac{\lambda_{12}}{4}\left(1 + \frac{\Delta G^0}{\lambda_{12}}\right)^2$$

$$\Delta G_{12}^{\#} = \frac{\lambda_{12}}{4}\left(1 + \frac{\left(\Delta G^0\right)^2}{\lambda_{12}^2} + \frac{2\Delta G^0}{\lambda_{12}}\right)$$

The above equation is the central feature of the Marcus theory in so far as it predicts a quadratic dependence of the Gibbs free energy of activation on the driving force.

Furthermore, according to Marcus theory, $\Delta G_{11}^{\#} = \frac{\lambda_{11}}{4}$ for the self exchange reaction, if the work terms are neglected. Thus

$$k_{11} = Z_{11}e^{-\lambda_{11}/4RT} \qquad (3)$$

Hence

$$\ln k_{11} = \ln Z_{11} - \frac{\lambda_{11}}{4RT} \qquad (4)$$

Analogously, for another self-exchange reaction such as $Ce^{3+} + Ce^{*4+} \rightarrow Ce^{4+} + Ce^{*3+}$

whose rate constant is k_{22}, we obtain

$$\ln k_{22} = \ln Z_{22} - \frac{\lambda_{22}}{4RT} \qquad (5)$$

The overall cross-exchange electron transfer reaction consisting of the two self-exchange reactions is

$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$

The frequency factor for the above is Z_{12} and the rate constant is k_{12}. Thus,

$$k_{12} = Z_{12} e^{-\Delta G_{12}^{\#}/RT} \qquad (6)$$

Neglecting the ΔG_0^2 term and assuming λ_{12} to be the arithmetic mean of λ_{11} and λ_{22} viz. $\lambda_{12} = \frac{\lambda_{11} + \lambda_{12}}{2}$

(7)

$$\Delta G_{12}^{\#} \cong \frac{\lambda_{12}}{4} + \frac{\Delta G^0}{2} \cong \left(\frac{\lambda_{11} + \lambda_{12}}{2}\right)\frac{1}{4} + \frac{\Delta G^0}{2} \qquad (8)$$

$$e^{-\Delta G_{12}^{\#}/RT} = e^{-\frac{1}{8RT}(\lambda_{11} + \lambda_{22})} e^{-\frac{\Delta G^0}{2RT}} \qquad (9)$$

But $e^{-\lambda_{11}/4RT} = \frac{k_{11}}{Z_{11}}$ and $e^{-\lambda_{22}/4RT} = \frac{k_{22}}{Z_{22}}$

Substituting the above equations in (6) and making use of equations (4) and (5)

$$\frac{k_{12}}{Z_{12}} = \left(\frac{k_{11}}{Z_{11}}\right)^{1/2} \left(\frac{k_{22}}{Z_{22}}\right)^{1/2} (K_{12})^{1/2}$$

Assuming $Z_{12} = (Z_{11} Z_{22})^{1/2}$, we obtain

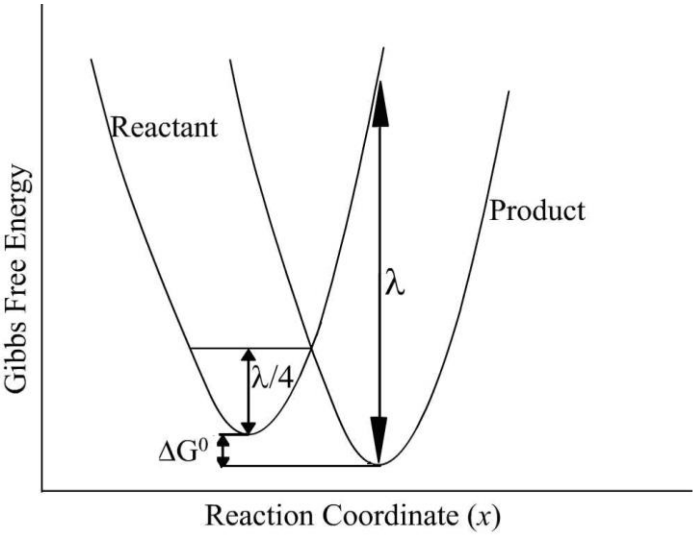
$$k_{12} = \left(k_{11}k_{22}K_{12}\right)^{1/2}$$

(10)

In deducing the above simple Marcus correlation, all the work terms have been neglected and the quadratic term (ΔG_0^2) has been omitted whereas including these terms will yield a correction factor f, thereby leading to

where f = $k_{12} = \left(k_{11}k_{22}K_{12}\mathrm{f}\right)^{1/2}$.

In general, f is nearly unity thus implying that the above equation (10) is adequate for all practical purposes.



Schematic representation of the solvent re-organisation energy

Equation (10) is the well – known Marcus cross – exchange relation valid for a variety of reactions whose rate constants span 10 orders of magnitude.

The quadratic dependence of the Gibbs free energy of activation enunciated by Marcus is valid also for proton transfer, atom transfer and radical transfer reactions. In fact, the Marcus formalism is valid for electrochemical reactions involving cleavage of bonds.

WORKED OUT EXAMPLES

1. The exchange current of $Fe^{3+} + e^{-} = Fe^{2+}$ reaction is 150 μA at an electrode of area 0.1 cm^2. If the concentrations of the reduced and oxidized forms are 0.1M, estimate the standard heterogeneous rate constant.

   From eqn (24)

   $$i_o = nFk_o^o\left[ox\right]$$

   i_o = 150 μA cm^{-2}

   150×10^{-6} Amp cm^{-2} = 1×96500 C $mol^{-1} \times k_o^o \times 0.01$ mol x $(1000\ cm^3)^{-1}$

   $$k_o^o = \frac{150 \times 10^{-6}\ C\ sec^{-1}\ cm^{-2} \times 1000\ cm^3}{96500\ C \times 0.1}$$

   $$= 1.55 \times 10^{-5}\ cm\ sec^{-1}$$

2. In the reaction $Fe^{2+} + 2e \rightarrow Fe$, the symmetry factor is 0.5. Estimate the activation overvoltage required to increase the current density by one order of magnitude.

   Since the reaction is a reduction process,

   $$i = i_o e^{-\alpha nF\eta/RT}$$

   $$i_1 = i_o e^{-(0.5) \times 2\,F\eta_1/RT}$$

   $$i_2 = 2i_1 = i_o e^{-(0.5)\,(2)\,F\eta_2/RT}$$

   Dividing eqn (1) by eqn (2), and rearranging,

   $$\frac{RT}{F}\ln 0.5 = \eta_2 - \eta_1$$

Since $\frac{RT}{F}$ = 26.5 mV at 298K, the increase in the overpotential required is 18.37 mV in the negative direction ie. Overpotential should be made more negative.

3. Estimate the charge transfer resistance at 298K for the reaction $M^+ + e^- \rightarrow M$ from a solution of 0.01 mol L^{-1} at an electrode of area 1 cm^2 if the exchange current density is 2.5 x 10^{-15} A cm^{-2}.

   The charge transfer (or polarization) resistance is given by

$$R_{ct} = \frac{RT}{nFi_o}$$

$$= \frac{26.5 \times 10^{-3} V}{2.5 \times 10^{-15} A\ cm^{-2}}$$

$$= 1.06 \times 10^{13}\ \Omega cm^{-2}$$

4. Show that the rate constant of an electrochemical reaction has the unit of cm sec^{-1}

   For an electron transfer process such as

   $ox + ne^- \rightarrow Red$

   we can write the rate equation as

$$\frac{-dN_{ox}}{dt} = A\ k_{het} C_{ox}$$

   where N_{ox} denotes the number of moles of ox, A is the area of the electrode and C_{ox} is the bulk concentration of ox. Hence, it follows that

   mol sec^{-1} = cm^2 k_{het} moles cm^{-3}

Thus k_{het} has the dimension cm sec^{-1} Analogous consideration holds good for the oxidation process.

5. The exchange current density for the reaction $½H_2$ □ $H^+ + e^-$ on Au is 0.001 A/cm^2. Calculate the number of H^+ ions produced per cm^2 per sec.

Number of equivalents produced per cm^2 $= \dfrac{0.001 \text{ A cm}^{-2}}{1 \text{ x } 96500 \text{ C}}$

$$= 1.04 \text{ x } 10^{-6}$$

1 equivalent yields $6.023 \text{ x } 10^{23}$ H^+ ions

$\therefore$ $1.04 \text{ x } 10^{-6}$ equivalent yields $6.24 \text{ x } 10^{17}$ H^+ ions

6. In a hydrogen-oxygen fuel cell, hydrogen is supplied at a rate of 10 cm^3 per minute at STP. Assuming Faraday's law to be valid, estimate the current.

Assuming that hydrogen behaves as an ideal gas, the rate of supply of H_2 is given by

$$\frac{dN}{dt} = \frac{P}{RT}\frac{dV}{dt}$$

At STP, $\dfrac{dN}{dt}$ $= 4.10 \text{ x } 10^{-4}$ mol H_2/min

Since $2H^+ + 2e^- = H_2$

$$i = nF\frac{dN}{dt} = \frac{2\times96500\times4.10\times10^{-4}}{60}$$

$$= 1.32 \text{ Amperes}$$

7. For the reductive clearage of C – Cl bonds, the current density is 600 μA cm^{-2} with a overpotential of -0.2 V. Assuming α = 0.5, estimate the charge transfer resistance of the reduction.

For the reductive clearage of C – Cl bond n = 2.

$$i = i_0 e^{-\alpha nF\eta/RT}$$

or

$$i_0 = ie^{+\alpha nF\eta/RT}$$

$$= 600\times10^{-6}\times e^{-0.5\times2\times96500\times0.2/8.314\times298}$$

$$= 6\times10^{-4}\times4.18\times10^{-4} = 25.08\times10^{-8}\ \text{Amp cm}^{-2}$$

$$\text{R}_{CT} = \frac{RT}{nFi_0}$$

$$= \frac{8.314\times298\times10^{7}}{2\times96500\times2.5}$$

$$= 5.134\times10^{-3}\times10^{7}\ \text{ohm} = 5.134\times10^{4}\ \text{ohm} = 51340\ \text{ohm}$$

8. Calculate the approximate value of cross exchange rate constant for the reaction

$$\left[Co\left(NH_3\right)_6\right]^{3+} + V\left(PiC\right)_3^{-} \rightleftharpoons \left[Co\left(NH_3\right)_6\right]^{2+} + \left[V\left(PiC\right)_3\right]$$

The self exchange rate constants for the reactions

$$\left[Co\left(NH_3\right)_6\right]^{3+} + \left[Co\left(NH_3\right)_6\right]^{2+} \rightleftharpoons \left[Co\left(NH_3\right)_6\right]^{2+} + \left[Co\left(NH_3\right)_6\right]^{3+}$$

and

$$\left[V^*\left(PiC\right)_3\right]^{-} + \left[V\left(PiC\right)_3\right] \rightleftharpoons \left[V^*\left(PiC\right)_3\right] + \left[V\left(PiC\right)_3\right]^{-}$$

are 1 x 10^{-7} M^{-1} S^{-1} and 2.7 x 10^{6} M^{-1} S^{-1} respectively. The standard reduction potential

values for these two systems are

$Co^{3+} + e \rightleftharpoons Co^{2+}$ $\quad$ $\text{E}^0 = 0.06\ \text{V}$

$V^{3+} + e \rightleftharpoons V^{2+}$ $\quad$ $\text{E}^0 = 0.41\ \text{V}$

$$E^0_{cell} = E_R - E_L = 0.06 - (-0.41)$$
$$= 0.47 \text{ V}$$

Since

$$nFE^\circ_{cell} = RT \ln K_{12},$$

$K_{12} = 8.9 \times 10^7$

for the cross – exchange electron transfer process. From the Marcus cross – exchange equation,

$$K_{12} = (k_{11}k_{22}K_{12})$$
$$= \left(1\times10^{-7}\times2.7\times10^6\times8.9\times10^7\right)^{1/2}$$
$$= 5\times10^3 \text{ M}^{-1}s^{-1}$$

EXERCISES

1. Derive the Butler-Volmer equation and explain the various terms involved in it. Deduce the following as special cases: (i) Nernst equation; (ii) Tafel equations and (iii) Ohm's law.

2. Illustrate using a graphical procedure, the method of obtaining the exchange current density and the transfer coefficients.

3. An electrode reaction for which the exchange current density is 5.0 $\times10^{-7}$ A cm^{-2} is proceeding at an overpotential of -0.20V. What is the current density if the transfer coefficient of the reaction is 0.48?

4. The rate constant (k_f) for the reduction of of Zn^{2+} ions in aqueous 0.1M KCl at potential -0.86V and -1.00V Vs SHE are 5.2×10^{-3} and 6.4×10^{-2} cm.sec^{-1} respectively If the standard reversible potential of Zn^{2+} /Zn system is -0.76V vs SHE, what is the cathodic transfer coefficient for the reduction of Zn^{2+} ion discharge reaction? Calculate the standard rate constant for the reduction.

5. Distinguish between exchange current density and standard exchange current density.

6. The following results were obtained for the chlorine evolution reaction at metals A and B. Deduce which is the better electrocatayst among A and B

Electrode	Overpotential η /V at a fixed current density	$d\eta/d(\log i)$/V
A	-0.43	-0.12
B	-0.34	-0.11

7. By passing a current through a cadmium sulfate solution for 210 seconds, $15 cm^3$ of O_2 at STP is liberated at the anode and the equivalent quantity of Cd^{2+} ions is reduced to Cd. If the anode area is $3.0\ cm^2$ and the cathode area is $1.2\ cm^2$, what are the rates of the anodic and cathodic reactions in A/cm^2?

8. By how much amount, does the Gibbs free energy of activation change from its equilibrium value if an over- potential of +0.10V is applied for an oxidation reaction? Assume $\alpha = 0.4$ and $T = 35^0C$.

9. Gold is deposited from Au^{3+} solution when $[Au^{3+}] = 0.10$ mol /L at 20^0C. If $\alpha = 0.74$ and $i_0 = 45 A/cm^2$, calculate the potential at the current density of $1\ A/cm^2$.

10. Estimate the charge transfer resistance at 298K for the reduction of hydrogen ions from solution of 0.0100 mol lit^{-1} on a nickel electrode with an area of $1.50\ cm^2$ if the exchange current density is 2.5×10^{-15} $A\ cm^{-2}$.

11. If $i_0 = 2.5\times10^{-5}$ A/m^2 and $\alpha = 0.5$ for the $Cu^{2+} + 2e^- = Cu$ reaction, calculate the overpotential required to deposit Cu(s) from 1 M Cu^{2+} solution at $i = 5\times10^{-3}$ A/m$^{2.}$

12. According to the IUPAC convention, the sign of the anodic current is considered to be ----------and that of the cathodic current is -----------.

13. The current – potential data for the redox reaction involving Fe^{2+}/Fe^{3+} at platinum electrodes (area 1.5 cm^2) is given below :

η (V)	$\lvert i \rvert$ in (mA)
0.02	3.20
0.05	9.9
0.06	17.0
0.10	35.2
0.12	55.9
0.15	110.8
0.20	343.7

Estimate the symmetry factor and exchange current density.

14. The transfer coefficient of a reaction involving M^{4+} / M^{3+} is 0.42, at 298K. At η = 105 mV, current equals 17.0 mA cm^{-2}. What is the overvoltage required when the current density becomes 72.8 mA cm^{-2}?

15. The activation overpotentials for the reduction of H^+ ions at a constant current density and at identical concentrations H^+ ions for 4 different metals are as follows: (A) 0.035 V; (B) 0.56 V; (C) 0.76 V and (D) 1.10 V. The best electrocatalyst for the hydrogen evolution reaction among the above is ------------.

16. The transfer coefficient of the Cd^{2+}/Cd redox reaction is 0.48 at 298K. When the activation overpotential is 105mV, the net current density is 17.0mA cm^{-2}. What is the activation overpotential when the current density increases to 73. 5 mA cm^{2}?

17. The transfer coefficient of a reaction is 0.5 and the number of electrons transferred is 2. Estimate the activation overvoltage required to increase the reduction current density by one order of magnitude at 300 K.

18. For the hydrogen evolution reaction at Ni electrodes, the following data was obtained:

η(V)	I(A cm^{-2})
0.27	1×10^{-3}
0.49	1×10^{-2}
0.57	1.5×10^{-2}
0.62	1×10^{-1}

Estimate the following quantities approximately:

(a) Exchange current density; (b) transfer coefficient; (c) standard heterogeneous rate constant and (d) polarization resistance.

FREQUENTLY ASKED QUESTIONS

1. What is the special feature of the Butler – Volmer equation, justifying its validity for all types of electrochemical reactions?
2. Where does the dependence of rate constant on the nature of the metals and solvent dipoles occur in the Butler – Volmer equation?
3. What is the difference between the exchange current density and standard exchange current density?

SUMMARY

The basic principles of electrode kinetics have been illustrated with the derivation of the Butler – Volmer equation which provides the current - potential response. The Tafel equations and Nernst equation are derived as special cases. The Marcus cross – exchange relation is derived.

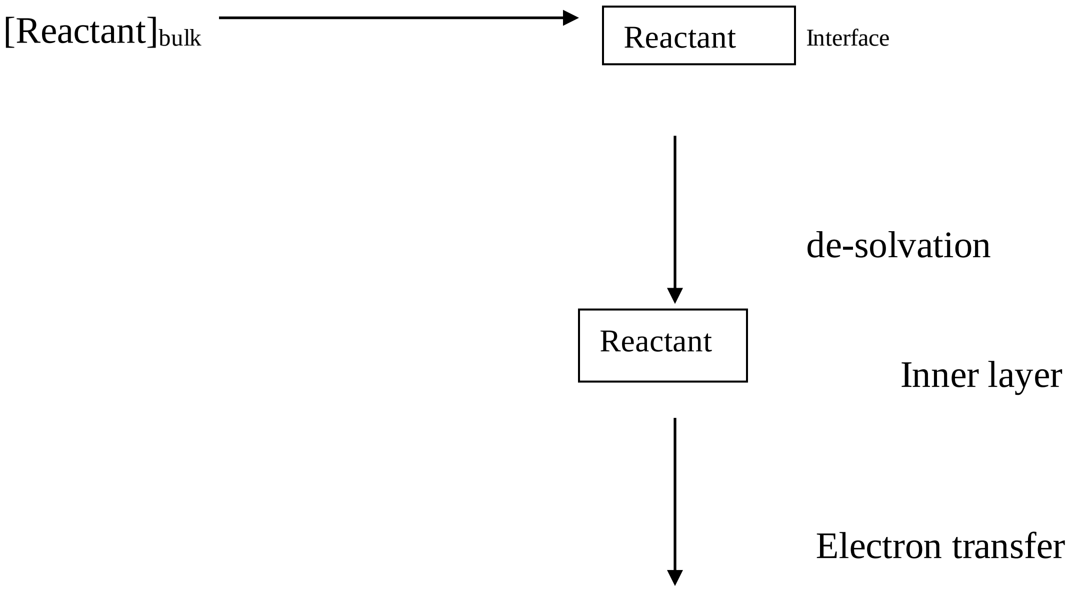
CHAPTER 3: EXPERIMENTAL METHODS OF ESTIMATING RATE CONSTANTS – COULOMETERY AND HYDRODYNAMIC VOLTAMMETRY

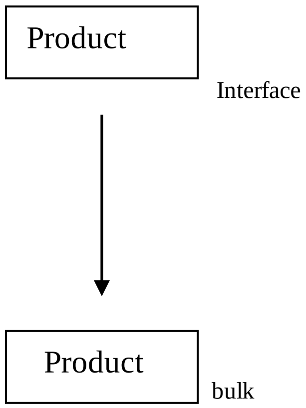
Learning objectives

After reading this chapter, it will be possible to

(i) comprehend the rate constants arising in the bulk electrolysis
(ii) obtain preliminary ideas about rotating disk electrodes
and
(iii) analyze the influence of mass transfer and electron transfer processes in the observed current.

The scheme shown below provides the possible transport processes occurring at electrode/electrolyte interfaces





Schematic Visualization of electron transfer

Techniques for the measurement of rate constants

Coulometric Analysis for estimating the 'rate constant'

For the reduction process, Ox+ n e^- → Red, the cathodic current is given by

$$i(t) = -nF\frac{dn_{ox}}{dt}$$

where n_{ox} is the number of moles of ox. Since the molar concentration is given by $C_{ox} = \frac{n_{ox}}{V}$

$$i(t) = -nFV\frac{dC_{ox}}{dt} \qquad (1)$$

If the observed current is solely due to diffusion, the limiting current is given by

$$i_{\mathbf{lim}}(t) = \frac{nFAD_{ox}}{\delta}C_{ox} \qquad (2)$$

Combining equations (1) and (2) , we obtain

$$\frac{dC_{ox}}{dt} = -\frac{AD_{ox}C_{ox}}{V\delta} = -k_{first}C_{ox}$$

$$\therefore C_{ox}(t) = C_{ox}(0)e^{-k_{first}t}$$

$$\therefore i_{\mathbf{lim}}(t) = \frac{nFD_{ox}}{\delta}C_{ox}(0)e^{-k_{first}t}$$

Hence a plot of ln (i) vs t yields the ‘first order rate constant’. Note that the so-called rate constant is a peculiar combination of the area of the electrode, diffusion coefficient of Ox and volume of the solution etc.

The practical utility of the above equation consists in estimating the current efficiency of a reaction by measuring the time taken for the reactant to decrease to a specific amount.

ROTATING DISC ELECTORDE

The rotating disk electrode is a commonly used system in the study of electrode kinetics. In view of its simplicity in controlling the mass transfer towards the electrode by means of rotating the electrode immersed in the electrolyte under consideration. In hydrodynamic experiments, the flow can be either laminar or turbulent

There are dimensionless numbers introduced so as to simplify the analysis. The commonly known one is the Sherwood number (Sh) which itself is an explicit function of Reynolds number (Re) and Schmidt number (Sc).

In the analysis of Levich for rotating disk electrodes, Sherwood number (Sh) is given by

$$Sh = 0.62L^{1/2}\upsilon^{1/2}v^{-1/6}D^{-1/3}$$

where L is the characteristic length of the problem, υ being the velocity of the fluid. v denotes the kinetic viscosity of the medium and D is the diffusion coefficient of the reactant. Since Sherwood number is related to the diffusion layer thickness as

$$Sh = \frac{L}{\delta}$$

It follows that the diffusion layer thickness is given by

$$\delta = \frac{L}{Sh} = \frac{\left(L \big/ \upsilon \right)^{1/2} v^{1/6} D^{1/3}}{0.62}$$

$$\delta = 1.61 \left(L \big/ \upsilon \right)^{1/2} v^{1/6} D^{1/3}$$

Note that the dimension of r.h.s is length as shown below:

$$\begin{aligned} \text{r.h.s} &= 1.61 \left(\text{cm} \big/ \text{cm}\,\text{sec}^{-1} \right)^{1/2} \left(\text{cm}^2\ \text{sec}^{-1} \right)^{1/6} \left(\text{cm}^2\ \text{sec}^{-1} \right)^{1/3} \\ &= \text{sec}^{1/2}\,\text{sec}^{-1/6}\,\text{sec}^{-1/3}\,\text{cm}^{1/3}\text{cm}^{2/3} \\ &= \text{cm} \end{aligned}$$

The actual analysis of the current for r.d.s can be obtained by solving the diffusion – convection equation at steady state as shown below:

Diffusion convection equation

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \upsilon_x \frac{\partial c}{\partial x}$$

At steady state, $\frac{\partial c}{\partial t} = 0$

Hence, $D \frac{\partial^2 c}{\partial x^2} = \upsilon_x \frac{\partial c}{\partial x}$

The above equation needs to be solved subject to the conditions:

(i) As $\text{x} \to 0, c \to c_s$

(ii) As $\text{x} \to \infty, c \to c_\infty$

While the general expression for the velocity is cumbersome, we can approximate the same as

$$v_x \simeq -c_{hyd}x^2$$

where

$$c_{hyd} = 0.51\omega^{3/2}\nu^{-1/2}$$

The steady state diffusion – convection equation now becomes

$$D\frac{\partial^2 c}{\partial x^2} = -c_{hyd}x^2\frac{\partial c}{\partial x}$$

If X is defined as

$$X = xc_{hyd}^{1/3}D^{-1/3}$$

$$\frac{\partial^2 c}{\partial X^2} = -X^2\frac{\partial c}{\partial X}$$

Multiplying both sides of the above equations by $e^{-X^3/3}$

$$\frac{\partial c}{\partial X} = \left(\frac{\partial c}{\partial X}\right)_{X=0}\exp\left(-\frac{1}{3}X^3\right)$$

On integrating the above

$$c = c_s + \left(\frac{\partial c}{\partial X}\right)_{X=0}\int_0^X \exp\left(-\frac{1}{3}X^3\right)d\lambda$$

Since our aim is to obtain the relation between c_∞ and c_s, we rewrite the above as

$$c_\infty = c_s + \left(\frac{\partial c}{\partial X}\right)_{X=0}\int_0^\infty \exp\left(-\frac{1}{3}\lambda^3\right)d\lambda$$

$$\int_0^\infty e^{-\frac{\lambda}{3}}d\lambda = ?$$

Substituting $\frac{\lambda^3}{3} = \mathrm{y}$, $\lambda^2 d\lambda = dy$

$$\therefore d\lambda = \frac{dy}{3^{2/3}y^{2/3}}$$

$$\therefore \int_0^\infty e^{-\frac{\lambda}{3}} d\lambda = \int_0^\infty \frac{e^{-y}dy}{3^{2/3}y^{2/3}} d\lambda = \frac{1}{3^{2/3}} \int_0^\infty e^{-y} y^{-2/3} dy$$

$$= \frac{1}{3^{2/3}} \Gamma^{\left(\frac{1}{3}\right)} = \frac{1 \times 3\Gamma^{\left(\frac{4}{3}\right)}}{3^{2/3}} = 3^{1/3}\Gamma^{\left(\frac{4}{3}\right)} = 1.288$$

The gamma function is defined as

$$\Gamma(z) = \int_0^\infty t^{z-1} e^{-t} dt$$

$$1.288 \left(\frac{\partial c}{\partial X}\right)_{X=0} = c_\infty - c_s$$

$$\left(\frac{\partial c}{\partial X}\right)_{X=0} = \frac{c_\infty - c_s}{1.288}$$

$$ie. \left(\frac{\partial c}{\partial x}\right)_{x=0} \frac{1}{c_{hyd}^{1/3} D^{-1/3}} = \frac{c_\infty - c_s}{1.288}$$

we also know that

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} = \frac{c_\infty - c_s}{\delta}$$

$$\therefore \delta = \frac{1.288}{c_{hyd}^{1/3} D^{-1/3}}$$

$$\text{But} \quad \mathrm{c}_{hyd} = 0.51 \mathrm{W}^{3/2} v^{-1/2}$$

$$\therefore \delta = \frac{1.288}{(0.51)^{1/3}\, \mathrm{W}^{1/2} \upsilon^{-1/6} D^{-1/3}}$$

$$= 1.61\ \mathrm{W}^{-1/2} \upsilon^{1/6} D^{1/3}$$

where W is the angular frequency in radians/sec and δ is the “diffusion layer thickness”

υ = kinematic viscosity (m^2 sec^{-1})

At this stage, it is imperative to separate the current due to electron transfer and mass transfer in a simple manner as shown below.

D = Diffusion coefficient (m^2 sec^{-1})

Let us define a mass transfer rate constant k_D as

Mass transfer rate constant $k_D = \frac{D}{\delta}$ (cm sec^{-1})

Analogously, the electron transfer rate constant is k_{het} (cm sec^{-1})

Flux due to mass transfer $J_{diff} = \frac{D}{\delta}\left(c_\infty - c_s\right)$ (1)

Flux due to electron transfer $J_{obs} = k_{het} c_s$ (2)

In the steady state, the electron flux equals the mass transfer flux. Hence

$$\frac{D}{\delta}\left(c_\infty - c_s\right) = k_{het} c_s$$

$$c_s\left[k_{het} + \frac{D}{\delta}\right] = \frac{Dc_\infty}{\delta}$$

$$c_s = \frac{c_\infty\left(D/\delta\right)}{\left[k_{het} + \frac{D}{\delta}\right]}$$

$$= \frac{c_\infty}{\left(1 + \frac{k_{het}\delta}{D}\right)}$$

From eqn (2), $c_s = \frac{J_{obs}}{k_{het}}$

Since $J_{diff} = J_{obs}$ at steady state,

$$J_{obs} = \frac{Dc_\infty}{\delta} - \frac{D}{\delta}\frac{J_{obs}}{k_{het}}$$

$$\therefore J_{obs}\left[1 + \frac{D}{\delta k_{het}}\right] = \frac{Dc_\infty}{\delta}$$

$$J_{obs} = \frac{\left(Dc_\infty/\delta\right)}{\left(1 + D/k_{het}\delta\right)}$$

$$\frac{1}{J_{obs}} = \frac{1+\dfrac{D}{\mathrm{k_{het}}\delta}}{\dfrac{Dc_\infty}{\delta}} = \frac{1}{\left(Dc_\infty / \delta\right)} + \frac{1}{\mathrm{k_{het}}c_\infty}$$

$$\frac{1}{J_{obs}} = \frac{1}{\dfrac{Dc_\infty}{\delta}} + \frac{1}{\mathrm{k_{het}}c_\infty}$$

$$\frac{1}{J_{obs}} = \frac{1}{J_{diff}} + \frac{1}{J_{act}}$$

If diffusion is the rate determining step, $J_{obs} = J_{diff}$

If electron transfer is the rate determining step, $J_{obs} = J_{act}$

$\therefore$ kinetic control vs mass transfer control can be elucidated.

Current, $i = nF J_{obs}$

$$\therefore \frac{1}{i_{obs}} = \frac{1}{i_{diff}} + \frac{1}{i_{act}}$$

WORKED OUT EXAMPLES

1. A rotating ring disc electrode (2500 rpm) yields a disk current of 15.3 µA for oxidation of 3×10^{-3} M Potassium ferrocyanide solution. Calculate the reduction current observed at the surrounding ring using a 9×10^{-3} M Potassium ferrocyanide and rotation speedof 1600 rpm (N=0.66).

   The relation between the disk current and ring current is given by

$$\frac{i_D}{15.3} = \frac{K\left(9\times10^{-3}\right)\left(1600\right)^{1/2}}{K\left(3\times10^{-3}\right)\left(2500\right)^{1/2}} = 2.4$$

$$i_D = 36.72\ \mu\text{A}$$

However, $N = -\frac{i_R}{i_D}$; Hence the ring current follows as

$$i_R = -Ni_D = -0.66\times36.72$$

$$i_R = 24.235\ \mu\text{A}$$

2. A rotating Hg film electrode of 2 mm diameter yields a stripping peak current of 4.4 μA for a 2 x 10^{-8} M Cu (II) solution following a 6 minutes deposition at -1.0 V with a 3000 rpm. Calculate peak current for 5 x 10^{-8} of Cu(II) solution followed by 3 min deposition with 1500 rpm.

   From the Levich eqn,

$$\frac{\left(I_p\right)_1}{\left(I_p\right)_2} = \frac{c_1 t_1 \omega_1^{1/2}}{c_2 t_2 \omega_2^{1/2}} = \frac{4.4}{\left(I_p\right)_2}$$

Hence $\left(I_p\right)_2 = 3.88\ \mu\text{A}$

3. Calculate the diffusion coefficient of the Pb^{2+} is whose limiting current in r.d.e is 5 μA at a rotation of 2500 rpm. The area of the electrode is 0.2826 cm^2. The kinematic viscosity of the medium is 1 cm^2 sec^{-1} while the concentration of Pb^{2+} is 5 x 10^{-3} M.

$$i_L = 0.62\ \text{nFAD}^{2/3}\omega^{1/2}v^{-1/6}c$$

$$5\times10^{-6}\,A = 0.62(2)(96500)(0.2826)\text{D}^{2/3}(2500)^{1/2}\left(1\right)^{-1/6}\,5\times10^{-3}$$

$$D = 2.47\times10^{-5}\,\text{cm}^2/\text{s}$$

4. Estimate the diffusion layer thickness for the process ox + e- → Red studied at a rotating disk electrode. The diffusion coefficient, kinematic viscosity and the rotation speed are respectively 1 x 10^{-9} m^2 s^{-1}, v=10^{-12} m^2 s^{-1} and 2500 rpm.

The diffusion layer thickness is given as

$$
\begin{aligned}
\delta &= 1.61\mathrm{D}^{1/3}\omega^{-1/2}v^{1/6} \\
&= 1.61(10^{-9})(2500)^{-1/2}\left(10^{-12}\right)^{1/6} \\
&= 1.61(10^{-3})\left(10^{-2}\right)(2500)^{-1/2} \\
&= 3.22\times10^{-7}\,\mathrm{m}^2\mathrm{s}^{-1}
\end{aligned}
$$

EXERCISE

1. A rotating mercury film electrode (of 2 mm diameter) yielded a stripping peak current of 2.2 µA for a 1 x 10^{-8} M Cd^{2+} solution following a 3 minutes deposition with an 1800 rpm rotation. Calculate the peak current for 2.5 x 10^{-8} M Cd^{2+} solution following a 2 minutes deposition with a 2900 rpm rotation.

2. An electrolyte containing both M^+ and M^{2+} ions was electrolyzed for 240 minutes. If 10% of the total current is dissipated and the two reduction processes consume equal amount of electricity, estimate the amount required to deposit 40 grams of M on the cathode? Atomic weight of M = 63.54 g/mol.

CHAPTER 4: HYDROGEN EVOLUTION REACTION

LEARNING OBJECTIVES

After reading this chapter, you will be able to

(i) understand the intricacies involved in the hydrogen evolution reaction

(ii)study the influence of the electrode on the exchange current density

and

(iii)comprehend the role of the adsorption isotherms in altering the exchange current densities.

The Hydrogen Evolution Reaction (H.E.R) is customarily represented as the reduction of hydronium ions viz.

$$2H_3O^+ + 2e^- \rightarrow H_2 + 2H_2O$$

This reaction has been studied on a variety of metals and the exchange current densities vary from 10^{-12} A cm^{-2} for Pb to 10^{-3} A cm^{-2} for Pt. This wide variation has been interpreted using three classical mechanisms viz Volmer, Tafel, Heyrovsky assuming that the rate–determining step (r.d.s) is different for different types of metals. However, in each of the mechanism, the preliminary step is the formation of the adsorbed hydrogen atoms. The support for each mechanism originates from the experimental Tafel slopes in conjunction with theoretical calculation of the surface coverages using simple adsorption isotherms for hydrogen atoms. The other essential insights for HER come from the (i) correlations with the work function of metals (Fig 1); (ii) Volcano plot (Fig 2) and (iii) extent of % d-character of metals.
The mechanisms are briefly discussed below:
The Volmer mechanism postulates the following step for the formation of adsorbed hydrogen atoms.

$$H_3O^+ + e^- \rightarrow H_{ads} + H_2O(r.d.s)$$

The formation of H_2 from the adsorbed hydrogen atoms can then occur via either

Heyrovsky mechanism

$H_{ads} + H_3O^+ + e^- \rightarrow H_2 + H_2O(r.d.s)$ (desorption of adsorbed hydrogen atoms)

or

Tafel mechanism viz.

$H_{ads} + H_{ads} \rightarrow H_2 (r.d.s)$ (re – combination of adsorbed hydrogen atoms)

Since each mechanism invokes the formation of the adsorbed hydrogen atoms, the influence of the metal surface becomes crucial. There are three essential parameters which aid in elucidating the reaction mechanism of HER. These are (i) exchange current density (i_0) (ii) symmetry factor (α) and (iii) cathodic Tafel slope (b_c). Among them, the exchange current density has been extensively analyzed in order to decipher the influence of the electrode surface. There are other quantities such as heat of adsorption, surface coverage and reaction orders that are also essential for a complete interpretation.

(i) Correlation of the exchange current density

In view of the availability of the magnitude of i_0 for nearly 50 electrodes, it is but imperative to look for empirical correlations. There have been nearly ten correlations of i_0 with the tabulated parameters. The two most important correlations that have survived till now are the correlation with (A) the work function of the metal and (B) Metal – Hydrogen bond energies.

(A) Correlation with the work function

Dependence of log i_0 on Work Function

The experimental data suggest a linear correlation of log i_0 with ϕ_M. In particular, two straight lines with *identical slopes* but different intercepts have been deduced from the experimental data. The two different intercepts pertain to metals Hg, Pb, T1, etc. (lower ϕ_M) and Pt, Pd, Fe, Co, Ni, Cu, Au, Ag, etc. (higher ϕ_M). The approximate linear regression equations are

log i_0 = 5.97 ϕ_M - 33.09

$$\log i_0 = 5.97\ \phi_M - 34.09$$

for the two different series of metals. Interestingly the slope is 5.97 eV^{-1}. The slope and intercept however vary to nearly 15%.. The values of i_0 vary with the electrolyte,work functions and method of measurement.

There have been attempts to explain the origin of the above two equations in terms of the hydration energies of H^+ ions, dipole potential, desorption energies of water dipoles as well as density functional theories.

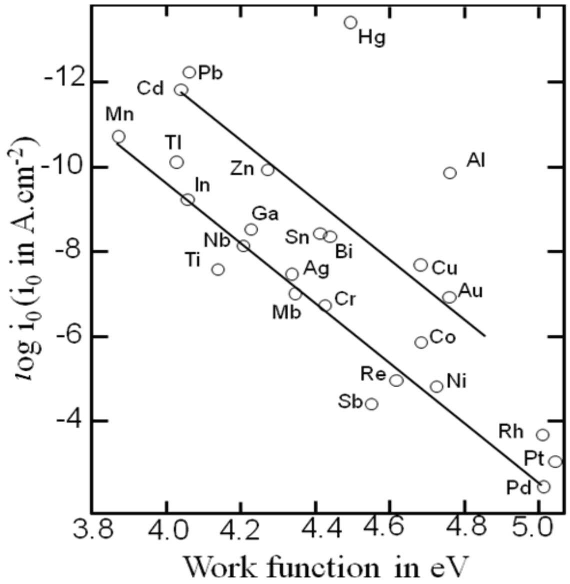


Fig 1 Dependence of the exchange currrent density of the Hydrogen Evolution Reaction on the work function of the metals

(B) Correlation with metal –Hydrogen bond energy

Another important correlation that is anticipated and verified is the variation of i_0 with metal – hydrogen bond energies. The latter is a tabulated quantity and hence is valuable in truly asserting its influence on the exchange current density. Interestingly, a so-called volcano plot arises if $\log(i_0)$ vs ΔG_{M-H} variation is constructed as shown in Fig 2.

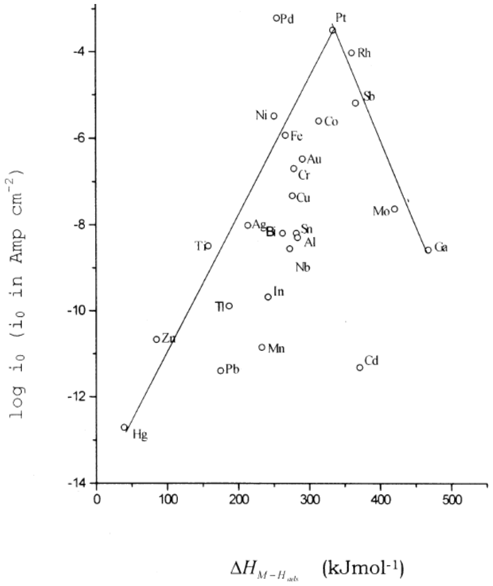


Fig 2: The 'volcano plot' depicting the variation of the log (exchange current density) with metal-hydrogen bond energy. The points denote the experimental data while the line is drawn as a guide to the eye.

The salient feature of the above correlation is that Pt groups of metals are the most suitable electrocatalysts. It is not clear why the decreasing portion of the volcano plot arises despite the work functions of those metals being high.

(ii) Analysis of Tafel slopes

The method based on the estimation of the symmetry factor *vis a vis* transfer coefficient is more powerful since it can provide not only a clue to the reaction mechanism but also yield the number of electrons involved in the rate determining step (r.d.s). However, the theoretical justification for the experimentally observed parameters crucially depends upon the nature of the adsorption isotherm employed for hydrogen atoms, the extent of surface coverage and the influence of the electrical double layer on the derived rate constants.

Mechanism	Diagnostic Criteria	Metals following the mechanism
Tafel	Tafel slope of -30 mV; transfer coefficient varies with pH; current is independent of pH.	Hg, Pt
Heyrovsky	Tafel slope of -40 mV and transfer coefficient =0.5; log[current] varies by one unit when pH decreases by one unit.	Ag, NiO, Pd, Co, Cr, Boron-doped diamond

It is also possible for Tafel mechanism to change to Heyrovsky mechanism for the same metal, when experimental conditions are altered.

Tafel Mechanism

The adsorbed hydrogen atoms yield H_2 via the following process viz.

$2H_{ads} \rightarrow H_2$ (rds)

Although the rate determining step does not involve electrons, there is a current with the previous Volmer step wherein two electrons have been transferred while leading to the adsorbed hydrogen atoms. Thus, the above desorption step alone is the rate determining step. A notable feature of this mechanism is that there is a current associated with the r.d.s in this case in contrast to Tafel mechanism which is a recombination of the adsorbed hydrogen atom.

The Tafel slope can be invoked as a diagnostic criterion for the mechanism. As a typical verification for the Tafel mechanism given above, let us write a generic adsorption isotherm for hydrogen atoms viz.

$$\frac{\theta}{1-\theta} = \beta a_{H+} \exp(-EF/RT)$$

In the above eqn, θ denotes the surface coverage while β denotes the standard adsorption equilibrium constant, E being the electrode potential and a_{H+} is the activity H^+ ions. The current associated with the adsorption step (rate-determining step in the Tafel mechanism), may be written as follows:

i_{rds} is proportional to $Fk_2\theta^2$

For small values of surface coverage, (1 – θ) tends to unity and hence

i_{rds} is proportional to $\beta^2 k_2 \exp(-2EF/RT) a^2{}_{H^+}$

$(\partial \log i_{rds} / \partial \log a_{H^+})_E = -(\partial \log i / \partial_{pH})_E = 2$

The above equation serves as a criterion to infer the validity of Tafel mechanism. Furthermore $\ln i_{ads} \alpha \frac{-2EF}{RT}$ for a given activity of H^+. Hence it follows that the Tafel plot between η and log i has a slope of $-2.303\frac{RT}{2F}$ and this value is the cathodic transfer coefficient. Thus a value of $\alpha_c = 2$ is indicative of the validity of the Tafel mechanism. Further, the cathodic Tafel slope (b $_c$)

$b_c = -2.303\left(\frac{RT}{nF}\right) = -2.303\left(\frac{RT}{2F}\right) \simeq -30 \text{ mV}$

Thus (i) a cathodic Tafel slope of -30 mV and (ii) the slope of $(\partial \, log \, i \, / \partial p^H) = -2$ are diagnostic criteria for the validity of the Tafel mechanism.

Heyrovsky Mechanism: If the Heyrovsky mechanism is valid and the surface coverage is nearly unity, one anticipates a slope of ~ 120 mV (2.3 x 2RT/F), assuming α_c = 0.5, as shown below:

$$\eta_c = b_c \log \frac{i}{i_\circ}$$

$$\eta_c = a_c + b_c \log |i|$$

where η_c is the cathodic overvoltage and b_c is the cathodic Tafel slope

$$b_c = \frac{dE}{d \log |i|} = -\frac{2.303RT}{\alpha_c}$$

and a_c is

$$a_c = \frac{2.303RT}{\alpha_c nF} \log i_\circ$$

If n=1 and α_c = 0.5 , the cathodic Tafel slope becomes nearly equal to -120 mV at 300K. However, many intriguing questions arise regarding (i) the rate determining step; (ii) number of electrons transferred in the r.d.s; (iii) symmetry factor and (iv) mechanism of formation of H_2 from the adsorbed hydrogen atoms.

Role of Adsorption Isotherms

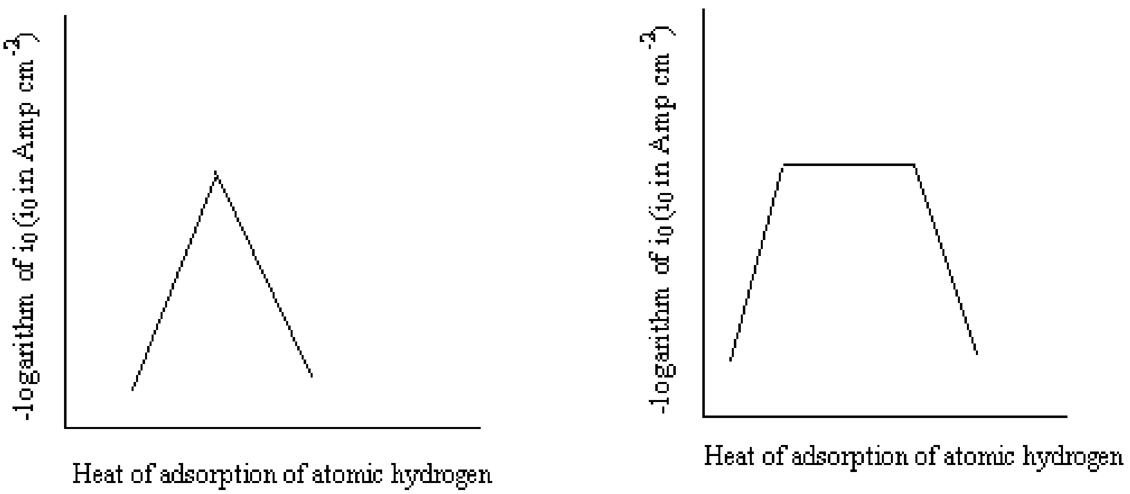
In the case of Volmer mechanism, i_0 given as

$$\left(i_\circ\right)_{volmer} = e\left(\frac{kT}{h}\right) a_{H^+}^{1-\alpha} \left(\theta\right)^{\alpha} \left(1-\theta\right)^{1-\alpha} \exp\left(-\frac{\left(\left(1-\alpha\right)\overrightarrow{\Delta} G_1^\circ\right) + \left(\alpha\right)\overleftarrow{\Delta} G_1^\circ}{RT}\right)$$

Analogously, i_0 for Tafel and Heyrovsky steps can be formulated. e is electronic charge while a_{H^+} denotes the activity of H^+. The dependence of i_0 on surface coverages and heat of adsorption of atomic hydrogen is analyzed to explain the volcano plot. In an analogous manner, Temkin isotherm may also be employed yielding

$$\theta = \frac{1}{f} ln\, p_{H_2} - \frac{\Delta G^{\circ}}{fkT} + \frac{1}{2}$$

where the dimensional quantity f incorporates the difference between the heat of adsorption of molecular hydrogen and atomic hydrogen.



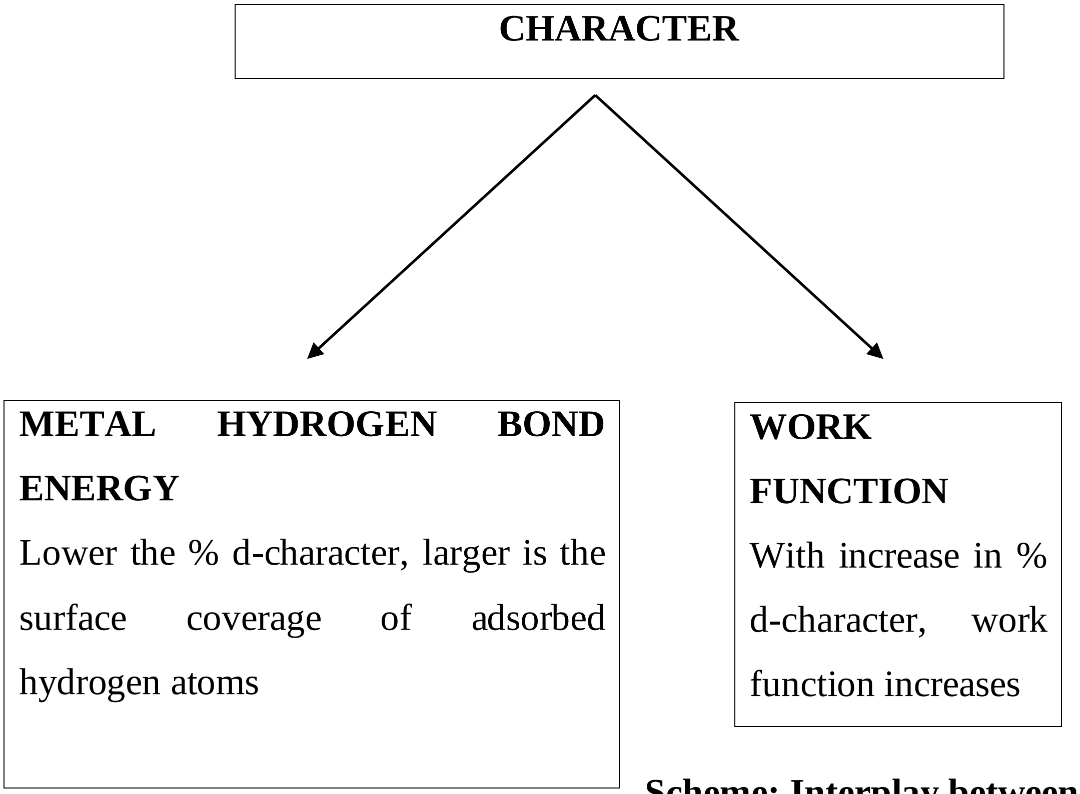
(a) (b)

Fig 3: Schematic variation of the exchange current density with the enthalpy of adsorption of atomic hydrogen on the electrode for (a) Langmuir isotherm and (b) Temkin isotherm

Hydrogen Evolution Reaction and % d character of Metals:

The percentage d- character of a metal represents the number of unpaired electrons in its d band and is a measure of the energy required to extract an electron from it. It has been noted using experimental data on a large number of metals that log i_0 increases with the % d character.

INFLUENCE OF PERCENTAGE d -



CHARACTER

METAL HYDROGEN BOND ENERGY

Lower the % d-character, larger is the surface coverage of adsorbed hydrogen atoms

WORK FUNCTION

With increase in % d-character, work function increases

Scheme: Interplay between metal – hydrogen bond energies, work function and % d – character

TABLE: Exchange Current Densities for Hydrogen Evolution Reaction at 298K

Metals	ϕ_M **in eV**	**Electrolyte**	**-log i_0** **(i_0 in A cm^{-2})**
Ag	4.30	0.1M H_2SO_4	7.90
Au	4.79	0.5M H_2SO_4	6.50
Cd	4.12	1M H_2SO_4	11.60
Cr	4.40	0.5 M H_2SO_4	7.00
Cu	4.70	0.5 M H_2SO_4	7.80
Mn	3.90	0.05 M H_2SO_4	10.90
Ni	4.73	0.5 M H_2SO_4	5.25

Pt	5.03	1M H_2SO_4	3.00
Ti	4.10	H_2SO_4	8.30
Zn	4.30	1M H_2SO_4	10.50
Fe	4.65	0.5 M H_2SO_4	5.60
Co	4.70	0.5 M H_2SO_4	5.30
Hg	4.50	7.5M $HClO_4$	12.30
Mo	4.30	0.1M HCl	7.30
Nb	4.20	0.5 M H_2SO_4	8.40
Pd	5.01	1M H_2SO_4	3.10
Rh	4.99	0.5 M H_2SO_4	3.50
Bi	4.36	1M H_2SO_4	7.80
Al	4.78	1M H_2SO_4	8.00
Ga	4.25	1M H_2SO_4	8.40
In	4.08	0.1M H_2SO_4	9.50
Pb	4.18	1M HCl	11.40
Sb	4.56	1M H_2SO_4	5.10
Sn	4.35	1M H_2SO_4	7.80
T1	4.02	0.1M $HClO_4$	9.60

In order to estimate the activation energy of HER, one requires the exchange current density at a range of temperatures. This has been achieved by employing temperatures ranging from 200K to 380K and the activation energy is $\simeq 30\ \mathrm{kJ/mol}$

QUANTUM MECHANICAL FORMULATIONS OF HER

The description of HER using electronic density of states of substrates has been extensively discussed during the past decade in terms of the coupling between the reactant and electronic density of states. The major factors such as work function, metal-hydrogen bond formation, etc is introduced and the exchange current densities at various metal electrodes are estimated using the time-dependent perturbation theory. The free electron gas model for the electronic structure of the metal and the distribution functions arising from Gerischer's formalism yields equilibrium free energy of activation as

$$\Delta G_{eq} = E_a^{\circ} - \gamma E_{M-H_{ads}} + eE_e$$

where E_a° represents the energy level of the unoccupied state of the electron acceptor; γ is the solvent shielding factor; $E_{M-H_{ads}}$ denotes the enthalpy of formation of M-H bond E_e is the equilibrium potential of the H^+/H^2 reaction. The metals can also be classified on the basis of their interaction with the electrode surface. While the exchange current densities deduced from this approach confirm the linear dependence of the activation energy on the metal – hydrogen bond energies, the volcano plot could not be nationalized.

Kinetic Isotope Effect

The influence of D_2O upon the rate of HER is very interesting. By comparing the rate of HER in H_2O and D_2O, it was concluded that the overpotential influences the magnitude of the kinetic isotope Effect. This was interpreted in terms of the crossing of potential energy curves. The rate constants of hydrogen evolution reaction in H_2O (k_H) and D_2O (k_D) is affected by following factors; (i) difference of the equilibrium energies of the isotopes, (ii) double layer structure and (iii) solvent reorganization energies. The difference in equilibrium energies determines the relative vertical shift of the potential energy curves. The difference in the diffuse layer potentials between H_2O and D_2O is approximately -1.7 mV on Hg, whereas on Ga electrode this difference is nearly 20 mV and hence a large kinetic isotope effect is noticed for Ga. Further, the solvent reorganization energy for D_2O on Ga is larger than that of H_2O on Ga.

It is of interest to mention that several recent studies indicate the efficacy of MoS_2 as well as BCN surfaces which exhibit comparable HER activity with that of noble metals.

WORKED OUT EXAMPLES

1. Deduce the stoichiometric numbers, if rate determining steps for the reaction $2H^+ + 2\,e^- \rightarrow H_2$ are as follows

   (a) $H_3O^+ + e^- \rightarrow H_2O$ r.d.s

   (b) $H_3O^+ + H + e^- \rightarrow H_2O$ r.d.s

   (c) $H + H \rightarrow H_2$ r.d.s

   The stoichiometric number represents the number of times the r.d.s occurs for yielding

   the desired product. Hence the stoichiometric numbers are (a) 2; (b) 1and

   (c) 1

2. The Tafel slope for Hydrogen Evolution reaction at a metal is estimated as 120.7 millivolts at 413K and the surface coverage by the adsorbed hydrogen atoms was much less than unity. Estimate the symmetry factor if the number of electrons transferred is unity.

$$b_c = \frac{2.303RT}{n\alpha_c F}$$

Substituting the values,

$$\alpha_c = \frac{2.303 \times 8.314 \times 413}{120.7 \times 10^{-3} \times 96500} \simeq 0.49$$

3. The hydrogen evolution reaction was studied on a metal with a large work function. The Tafel mechanism was found to be valid at 300K. Deduce the (a) Tafel constant and (b) stoichiometric number.

(a) As per the Tafel mechanism,

$$b_c = \frac{-2.303RT}{2F} = \frac{-2.303\times 8.314\times 300}{2\times 96500} = -30\ \text{mV}$$

(b) The stoichiometric number is 1.

4. The variation of log i_0 with work function of the metals Tl, Tn, Pt, Pd etc follow a linear regression equation given by

$$\log i_0 = 5.97\phi_M - 28.09$$

where ϕ_M is the work function of the metal (in eV) and i_0 is in A cm^{-2}. Predict the exchange current density for Ni using the same eqn.

The work function of Ni = 4.2 eV

$$\log i_0 = -3.016$$

Substituting the work function of Ni as 4.2 eV in the given equation, i_0 follows as 9.63×10^{-4} A cm^{-2}.

PRACTICE PROBLEMS

1. A Tafel slope of 120 mV per decade was deduced for the Hydrogen Evolution Reaction when Pt (100) was the surface, the electrolyte being H_2SO_4. Which mechanism is consistent with this Tafel slope?
2. Metals that adsorb hydrogen strongly should in principle be the best electrocatalysts for Hydrogen Evolution Reaction. However, Mo, W

and Ta are found to be unsuitable for HER. What is the plausible interpretation?

FREQUENTLY ASKED QUESTIONS

1. Can there be a single mechanism valid for all metals?
2. What are the differences between the work function of the bare electrode and solvated electrode?
3. Why the exchange current densities decrease with increase in work function for some metals?

SUMMARY

The Tafel, Volmer, Heyrovsky mechanism for HER has been briefly indicated. The diagnostic criteria for various mechanisms have been provided.