Chapter 4 – Electrochemical Kinetics: the Effects of Electrical Current

There are two major effects in an Electrochemical cell taken away from equilibrium when current is passed, we have:
i) Ohmic voltage drop (iR_E) and
ii) change in voltage, η, at current, i, due to reaction resistance, R_i.

These 2 resistances, R, created by passing current, *i*, *are*:

1. R_E resistance of the electrolyte - independent of the voltage
2. R_i reaction resistance - dependent on the voltage
   - $R_i = E_i / i$ where E_i is the half cell reaction potential
   - R_i is increasing polarization of electrodes with increasing current

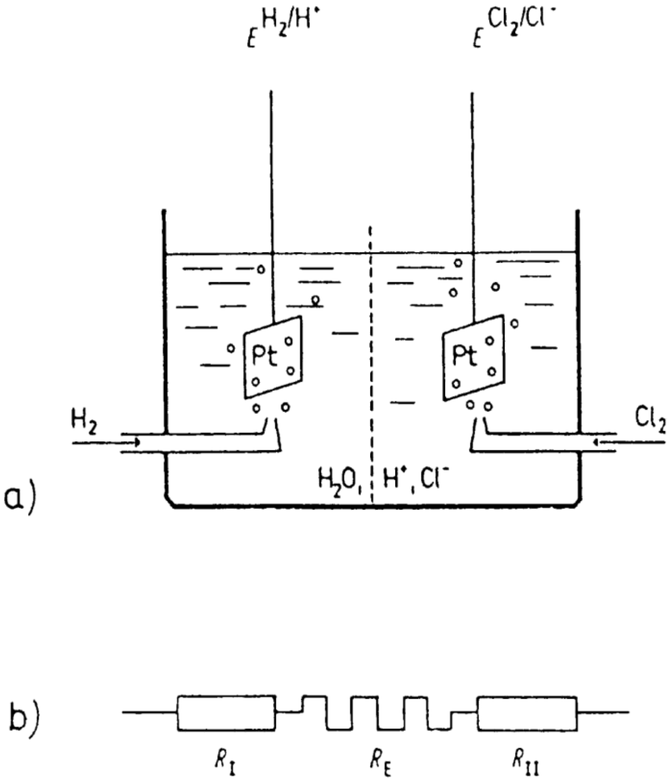


Fig. 4.1
a) Example of an electrochemical cell
b) Equivalent circuit of this cell.

1. Potentials at equilibrium (zero current)

The cell in figure 4.1 a) has Pt catalyzed hydrogen anode and Pt catalyzed chlorine cathode in hydrochloric acid establishing an *emf*.

At unit activity of electrolyte concentrations with the cell at rest (zero current), the EMF of the cell is the standard cell voltage, V^0_{cell} :

$$V^0_{cell} = E^{0,\,Cl_2|Cl^-} - E^{0,\,H^+|H_2} = +1.37\ V$$

and the corresponding standard Gibbs free energy, ΔG^0, of the reaction is:

$$\Delta_r G^0 = -\,n\,F\,E^0$$

2. Potential changes with passing of current

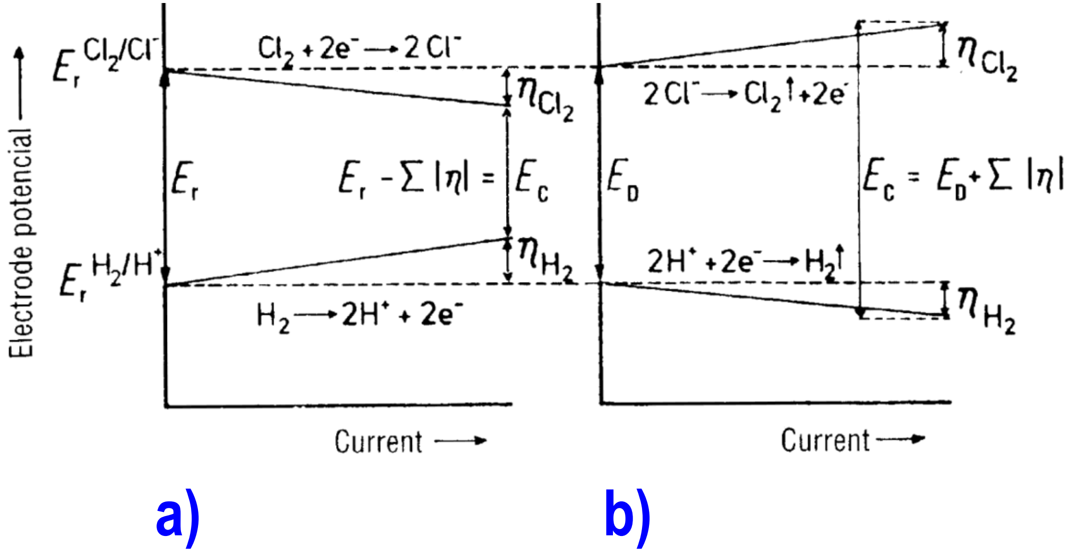


Fig. 4.2 Schematic representation of the variation of cell voltage with current for the case of :

- **a) a galvanic (or "fuel ") cell based on the Cl_2/H_2, reactions,**
- **b) an electrolysis cell using hydrochloric acid solution as an electrolyte.**

a) If the cell passes current by operating as a power source by joining the two electrodes through a resistor, then the spontaneous *cell voltage decreases more and more* as more and more current is passed.

The potential of the hydrogen electrode will shift in the positive direction for the oxidation reaction

$\mathrm{H_2 \rightarrow 2\,H^+ + 2\,e^-}$ Transfer of electrons from the solution species - anode

while the potential of the chlorine electrode will be reduced (shifts negative) as Cl_2 is electrochemically reduced to Cl^-.

$\mathrm{Cl_2 + 2\,e^- \rightarrow 2\,Cl^-}$ Transfer of electrons into the solution species - cathode

b) If the cell is operated in electrolysis mode (by imposing a voltage that is larger than the equilibrium EMF), then *the cell voltage increases more and more as more and more non-spontaneous current is being passed*. The two cell reactions are increasingly driven in opposite potential directions with increasing current :

$\mathrm{2\,Cl^- \rightarrow Cl_2 + 2\,e^-}$ Transfer of electrons from the solution - anode

$\mathrm{2\,H^+ + 2\,e^- \rightarrow H_2}$ Transfer of electrons into the solution - cathode

The Concept of Overpotential (η)

Definition: The magnitude of the deviation of the electrode potential, E, at an anode or cathode from the equilibrium value of potential (also called rest or reversible value), E_r, is termed the overpotential (η), defined as:

$$\eta = E - E_r$$

Different types of overpotential:

- *At low current densities*, the rate of change of electrode potential with current is associated with the limiting rate of electron transfer across the phase boundary between the electronically conducting electrode and the ionically conducting solution, and is termed the *electron transfer overpotential*.

- *At higher current densities*, the electron transfer process is usually no longer rate limiting:
  - i) instead, limitations arise through slow transport of reactants from solution to the electrode surface or conversely the slow transport of product away from the electrode (*diffusion overpotential*)

    or
  - ii) through the inability of chemical reactions coupled to the electron transfer step to keep pace (*reaction overpotential*) . For example, fast H^+ -reduction is rate limited by slow H^+ dissociation from a weak acid, HA.

The Measurement of Overpotential:

the Current-Potential Curve for a Single Electrode

The *rest* (*equilibrium*) potential, E_r, of a chlorine electrode versus a hydrogen electrode is directly measured using a high impedance voltmeter in a 2 electrode configuration.

The measurement of the *potential E of the chlorine electrode when a current is flowing* is more tricky. The measured cell voltage will include contributions from the cell resistance, iR_e, and overpotential of the chlorine electrode. To minimize contribution from iR_e, a 3 electrode configuration is used, where current is passed between the working chlorine electrode and the hydrogen (counter) electrode, and potential of the working chlorine electrode is measured to a third reference electrode using a zero current high-impedance voltmeter (see Fig. 4.3).

Three electrode electrochemical cell:

- W - working electrode
- R - reference electrode
- C - counter electrode

The 3 electrode configuration virtually allows observation of the overpotential at the working electrode only.

Potentiostatic control in electrochemistry - control working electrode *E* versus R, and measure resulting *i* between W and C . *Galvanostatic* control in electrochemistry - control *i* and measure resulting W (working electrode) *E* versus R potential.

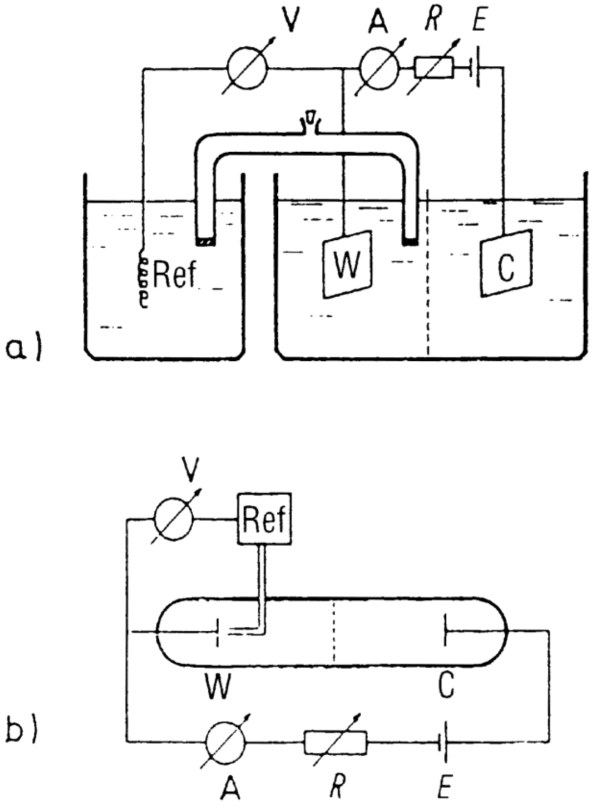


Fig. 4.3
(a) The experimental arrangement for measurement of the electrode potential upon passing a finite current:
(b) a simple circuit representation.

Current Potential Characteristic of the Electrode

The variation of current with potential measured as above is termed the current-potential characteristic of the electrode, and such a characteristic, as measured for the chlorine electrode above, is shown in the Figure4.4. Clearly the linear drop potential with current shown in Fig 4.2 is NOT valid for potential greater than a few mV from E_r

- At low overpotentials, the relationship between I and E is approximately linear.
- For potentials more than a few mV from the rest potential, the current potential dependence is more complicated.

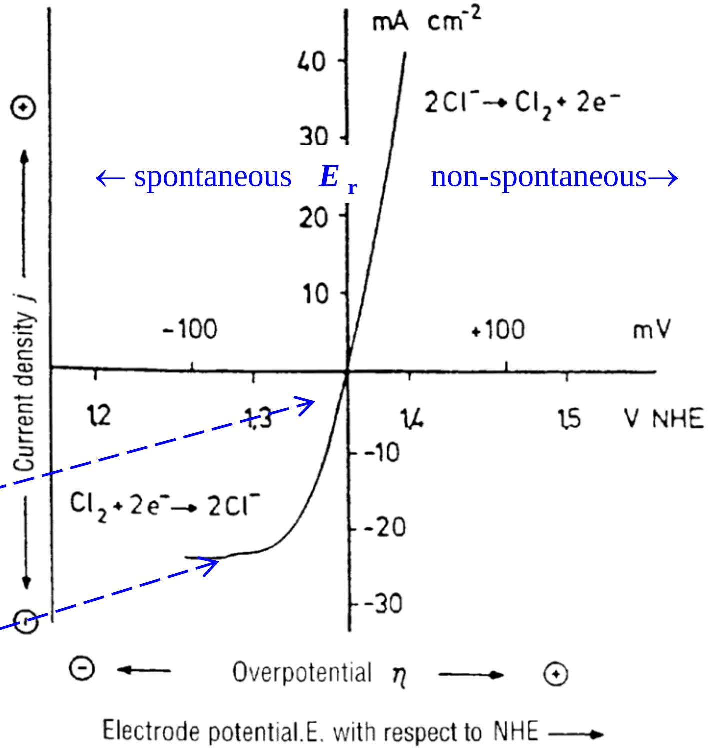


Fig 4.4 The current-potential characteristic for a chlorine-sparged platinum electrode of 1 cm^2 area in aqueous HC1. p_{Cl2} = 1 atm; a_{HCl} = 1

The *Electron-Transfer* Region of the Current-Potential (*i* / V) Curve

Consider a general process:

$$Ox + ne^- \leftrightarrow Red$$

- At equilibrium, the forward (cathodic) and the reverse (anodic) processes must be taking place at the same rate.
- As a result, a there is no net chemical conversion process taking place at the electrode, and the net current is zero.

- If an reducing overpotential is now applied to the electrode, then the cathodic reaction rate (current) will be increased and the anodic reaction rate slowed down … or vice versa.
- The result is that a net chemical conversion process takes place at the electrode, corresponding to a net current flows through the external circuit.

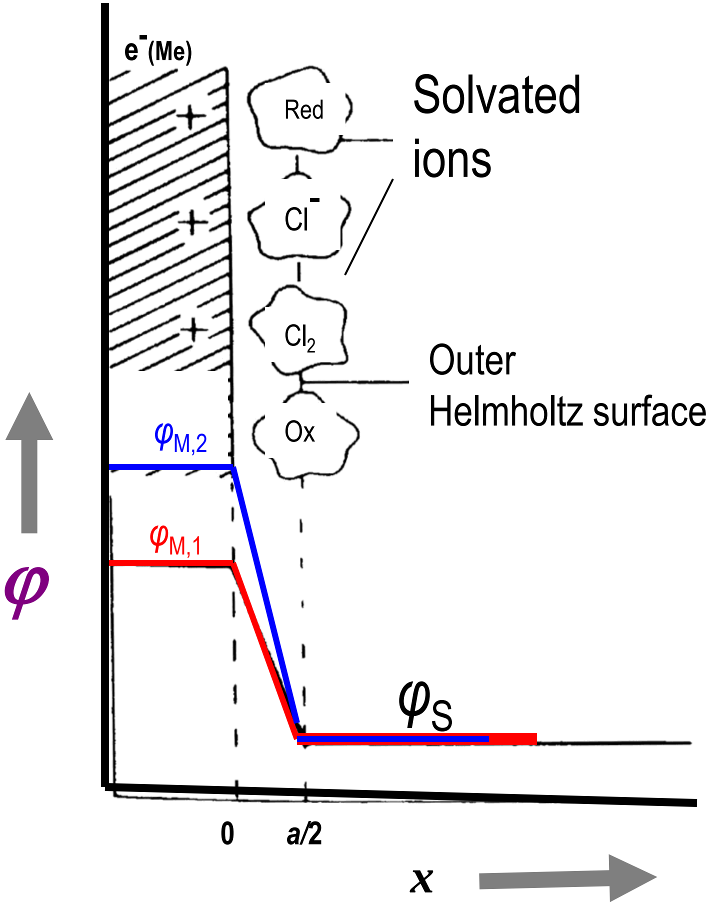
Electron-Transfer is a quantum mechanical effect:

•*cathodic reaction*, an electron transfers from the conduction band of the metal directly into an unoccupied molecular orbital of an ion or neutral molecule in the electrolyte on the electrode

•*anodic process* is the reverse of this, with an electron transferred from an occupied molecular orbital of an ion or neutral molecule in the electrolyte on the electrode

Consider a simple electron transfer process

Initially, we will restrict ourselves to metallic electrodes and to electrolyte solutions with high concentrations of salt, so that the change in potential between electrode and electrolyte is essentially restricted to within the Helmholtz layer. In this model, if electrode potential goes from E_1 to E_2, then potential in metal changes but is constant in the bulk leading to the potential distribution shown in modified Fig. 3.15, below.



Modified Fig 3.15. Potential distribution between electrode and outer Helmholtz surface

For the half reaction below there is an electrode potential, E

$$\mathrm{Ox} + ne^- \leftrightarrow \mathrm{Red} \qquad E_{\mathrm{Ox/red}}$$

$$\mathrm{Cl_2} + 2\,e^- \rightarrow 2\,\mathrm{Cl}^- \qquad E_{\mathrm{Cl2/Cl-}}$$

What are the effects of starting at potential, E_1, then changing to E_2 ?

$$\mathbf{E_2} = \varphi_{M,2} - \varphi_S$$

$$\mathbf{E_1} = \varphi_{M,1} - \varphi_S$$

- The energy of charge ze_0 is $ze_0 E$
- Electrode potential, $E = \Delta\varphi$, *inner potential drop*
- The free energy change on going from $\mathbf{E_1}$ to $\mathbf{E_2}$ is equal to $\Delta G = -nF\,\Delta E$.

Note: in Fig 4.5, sometimes β or $1-\beta$ is used for the reduction process

Initially, we will restrict ourselves to metallic electrodes and to electrolyte solutions with high concentrations of salt, so that the change in potential between electrode and electrolyte is essentially restricted to within the Helmholtz layer.

Let now consider a simple chemical reaction:

A + B → AB → products

(which is general case of
Ox + ne$^-$ → activated complex → Red)

Rudolf Marcus (CalTech Nobel prize 1990)
Al Anderson (CWRU)
J O'M Bockris (Texas A&M)
Perla Balbuena (Texas Austin)

The rate, $\nu = k_f\, c_A\, c_B$. Eyring activated complex rate theory says, $k_f = k_f^o \exp(-\Delta G_f^\ddagger/RT)$, so the overall rate of this reaction is:

Eqn. 4.8
$$\nu = k_f^0 c_A c_B \exp\left(\frac{-\Delta G_f^\ddagger}{RT}\right)$$

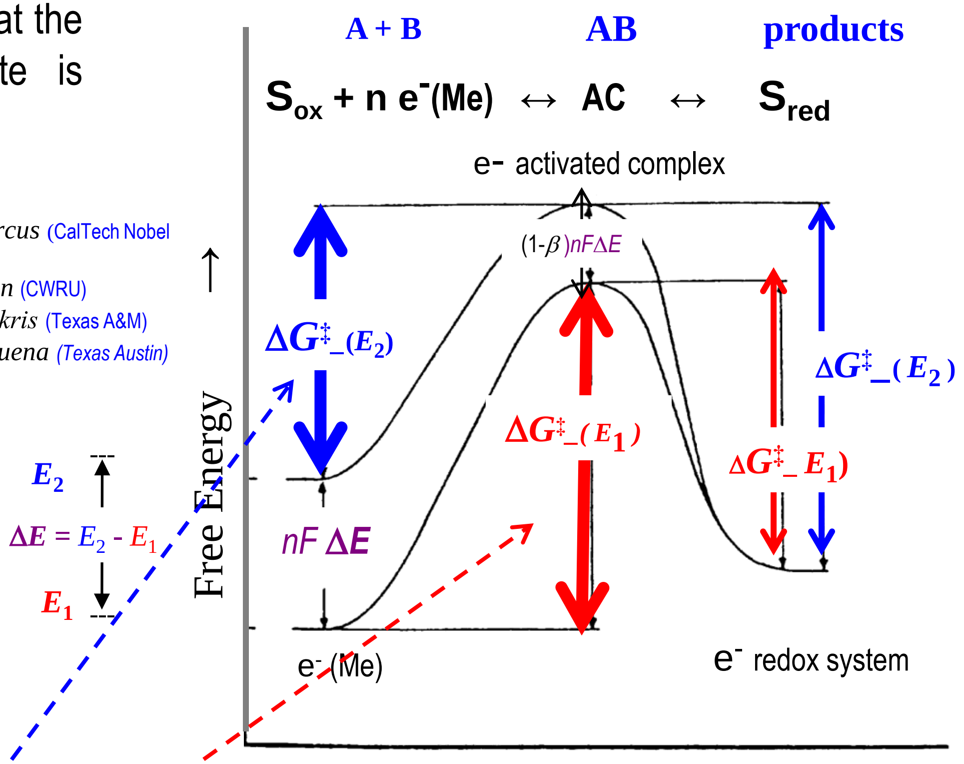


Fig. 4.5. Internal energy of an electron in an electrode during its transition from the electrode to a component of a suitable redox couple in solution and during the reverse process occurring by an outer sphere process.

If now the electrode potential is altered from E_1 to E_2

- for a cathodic process:

Eqn. 4.9
$$\Delta G^\ddagger_-(E_2) = \Delta G^\ddagger_-(E_1) + (1-\beta)\, nF\ \Delta E$$

Note well: Since **ΔE is negative** $\Delta G^\ddagger\_(E_2)$ *becomes less than* $\Delta G^\ddagger\_(E_1)$

- for an anodic process:

Eqn. 4.10
$$\Delta G^\ddagger_+(E_2) = \Delta G^\ddagger_-(E_1) - \beta\, nF\ \Delta E$$

Note well: The change in potential from E_1 to E_2, corresponds in this figure to an electrode potential shift to more negative values (resulting in a higher overpotential, lower forward barrier to electron transfer , $\Delta G^\ddagger\_(E_2) < \Delta G^\ddagger\_(E_1)$ and higher forward *reduction rate* [net increases in reduction current]).

Note: β is the so called asymmetry parameter (β= 0.5 for a *SYMMETRIC* TRANSITION)

Electron-Transfer (cont.)

We can proceed by calculating, the rate of the cathodic and anodic reactions using the Eyring rate equation (eqn 4.8). The flux density of Ox is $j^-(E_1)$ at a potential, E_1, so then j^- will be:

$$J^-(E_1) = -c_{\mathrm{Ox}} k_0^{\prime -} \cdot \exp\left(\frac{-\Delta G_-^{\ddagger}(E_1)}{RT}\right)$$

Eqn. 4.11, p. 164

Knowing the straightforward relationship between the current density and the flux density, $j = nFJ$ gives the expression for the current density, $j^-(E_1)$, in A/m^2 in which a –sign is for reduction current:

$$j^-(E_1) = -nFc_{\mathrm{Ox}} k_0^{\prime -} \cdot \exp\left(\frac{-\Delta G_-^{\ddagger}(E_1)}{RT}\right)$$

Eqn. 4.12, p. 164

Introducing the potential change from E_1 to E_2 the current density becomes:

$$j^-(E_2) = -nFc_{\mathrm{Ox}} k_0^{\prime -} \cdot \exp\left\{-\frac{\overbrace{\Delta G_-^{\ddagger}(E_1) + (1-\beta)nF \cdot \Delta E}^{\Delta G^{\ddagger}_-(E_2)}}{RT}\right\}$$

Eqn. 4.13, p. 164

If the potential E_1 is set equal to zero for the reference potential scale used in the experiment, then since the reference electrode does not depend on factors such as c_{ox}, the value of exp $-\Delta G^{\ddagger}_-(E_1)$ can be treated as a *constant and incorporated into our rate constant* $k_o^{\prime -}$ *to make a new constant* k_o^- and replacing E_1 and ΔE by a general potential E gives for the reduction current density.

$$j^-(E) = -nFc_{\mathrm{Ox}} \cdot k_0^- \cdot \exp\left\{-\frac{(1-\beta)nFE}{RT}\right\} \qquad 4.14$$

By an analogous process, we obtain for the anodic current:

$$j^+(E) = nFc_{\mathrm{Red}} \cdot k_0^+ \cdot \exp\left\{\frac{+\beta nFE}{RT}\right\} \qquad 4.16$$

Note: value of rate constant k_o^- has an embedded *constant* and so k_o^- depends on choice of zero of potential

Exchange current density, j_o

Equations (4.14) and (4.16) describe the two partial current densities $j^-(E)$ and $j^+(E)$ of opposite algebraic sign at each potential. It follows that at the rest potential, E_r, when the net current is zero, the two partial currents must be numerically equal and have the magnitude of the so-called <u>*exchange current density*</u>, j_0. It is important to recognize that the rest potential corresponds to a dynamic equilibrium and not to zero activity. At the rest potential, E_r, then, we have expression for the exchange current densities, $-j_o$ and $+j_o$, given in eqns. 4.17 and 4.18.

$-j_o$

$$j^-(E_r) = -j_0 = -nFc_{Ox}k_0^- \cdot \exp\left\{-\frac{(1-\beta)nFE_r}{RT}\right\} \qquad 4.17$$

$+j_o$

$$j^+(E_r) = +j_0 = +nFc_{Red}k_0^+ \cdot \exp\left\{+\frac{\beta nFE_r}{RT}\right\} \qquad 4.18$$

Interesting side point…After some rearrangement of the above equations and solving for E_r re-gives eqn. 3.19

$$E_r = \frac{RT}{nF}\ln\frac{k_0^+}{k_0^-} + \frac{RT}{nF}\ln\frac{c_{Ox}}{c_{Red}}$$

where $E^0 = \frac{RT}{nF}\ln\frac{k_0^+}{k_0^-}$

The Nernst Equation,

Eqn. 4.19 , p.165

Eqn. 3.19 , p. 81

If we now write the actual electrode potential, E, as $E_r + \eta$, where η is the overpotential and E_r the rest potential as defined above, then 4.17 and 4.18 become…

$$j^-(E) = -nFc_{Ox}k_0^- \cdot \exp\left\{-\frac{(1-\beta)nFE_r}{RT} - \frac{(1-\beta)nF\eta}{RT}\right\} \qquad 4.20$$

$$j^+(E) = nFc_{Red}k_0^+ \cdot \exp\left\{\frac{\beta nFE_r}{RT} + \frac{\beta nF\eta}{RT}\right\} \qquad 4.21$$

Eqns. 4.20 and 4.21 are simplified next …

Finally, for a metal electrode in contact with its ions into the solution we can simplify Eqns. 4.20 and 4.21 using equations 4.14, 4.16 and the definition of exchange current density 4.17 and 4.18 :

- upon application of a negative overpotential we obtain (cathodic reaction)

$$j^{-}(E) = -j_0 \cdot \exp\left\{-\frac{(1-\beta)\, n\, F\, \eta}{RT}\right\} \qquad 4.22a$$

- upon application of a positive overpotential we obtain (anodic reaction)

$$j^{+}(E) = j_0 \cdot \exp\left\{+\frac{\beta\, n\, F\, \eta}{RT}\right\} \qquad 4.22b$$

The net current, *j* , for a redox process with both red and ox form in the solution, is the sum of $j^{-}(E)$ and $j^{+}(E)$, which is eqn. 4.23, the Butler–Volmer Equation. The Butler–Volmer Equation is the electrochemical rate equation.

The electrochemical rate equation, *the Butler - Volmer Equation* p.166

The Butler – Volmer equation gives the current when an electrode (poised at a potential, *E*) **is *controlled by the rate of electron transfer .***

$$j = j^{+} + j^{-} = j_0\left[\exp\left\{\frac{\beta n F \eta}{RT}\right\} - \exp\left\{-\frac{(1-\beta) n F \eta}{RT}\right\}\right] \qquad 4.23,\ \text{p.166}$$

Take a breath

The Meaning of the Exchange Current Density j_0 and the Asymmetry Parameter β

From the Butler-Volmer equation (eqn4.23), it is clear that …

- the partial (+ or -) current densities increase or decrease exponentially with overpotential
- the steepness of the rise or fall depend on the asymmetry parameter, β as shown in Fig4.6 (experimentally β is usually found to be between 0.4 and 0.6).
- By contrast. the exchange current density, j_0, is a multiplicative factor, affecting both branches (+or -) of the curve equally. j_0 is given in terms of the + and - j branches in eqn. 4.24, below.

$$j_0 = nFc_{\mathrm{Ox}}k_0^{/-} \exp\left\{-\frac{\Delta G_-^{\ddagger}(E_\mathrm{r})}{RT}\right\} = n\mathbf{F}c_{\mathrm{Red}}k_0^{/+} \exp\left\{-\frac{\Delta G_+^{\ddagger}(E_\mathrm{r})}{RT}\right\}$$

eqn. 4.24

- j_0 depends on concentration of species and the ΔGactivation at E_r and it is j_0 that is increased when a reaction is catalyzed.

High overpotential, $|\eta| >> RT/nF$, and Tafel Equation

For reduction with a negligible anodic current, the total current can be written as:

$$j = -j_0 \exp\left\{-\frac{(1-\beta)nF\eta}{RT}\right\}$$

Taking logarithms to the base 10, we obtain:

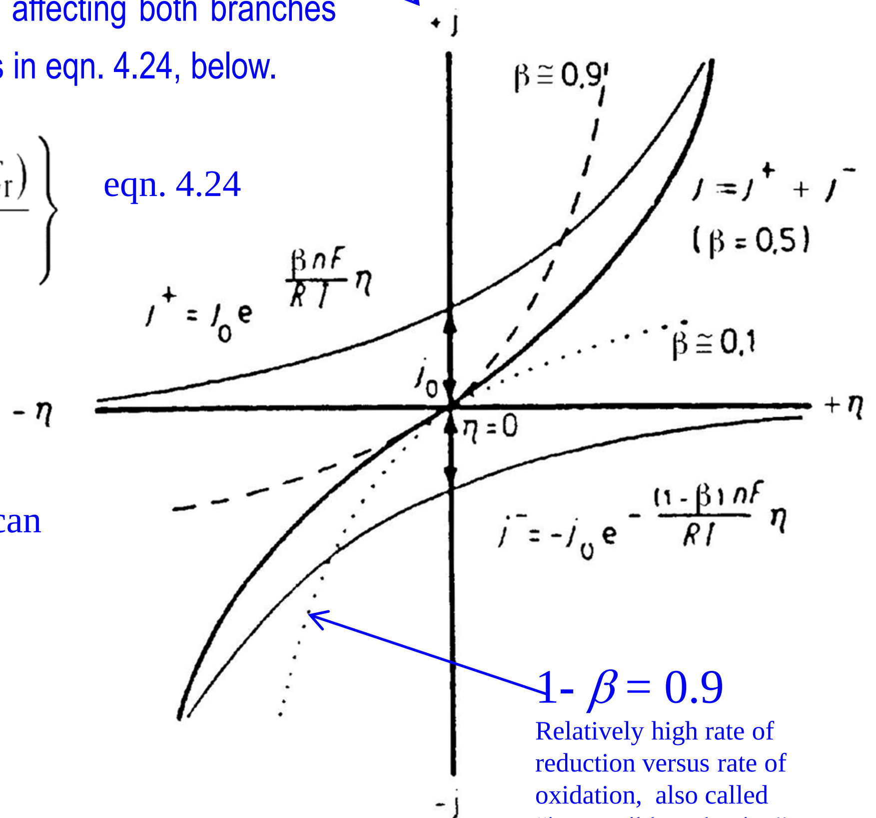
$$\eta = \left\{\frac{2.303RT}{(1-\beta)nF}\right\} \cdot \log_{10} j_0 - \left\{\frac{2.303RT}{(1-\beta)nF}\right\} \cdot \log_{10}|j|$$

$$\eta = A + B \cdot \log_{10}|j|$$

Eqn. 4.27 – *the Tafel Equation*

$$-\frac{(1-\beta)nF}{2.303RT} = -0.118V$$

0.118 V is the Tafel slope, B, for n=1 and β=0.5 at 25°C.



1- β = 0.9

Relatively high rate of reduction versus rate of oxidation, also called "irreversible reduction"

Fig. 4.6 Graphical representation of the two partial equations and the ButlerVolmer equation,

Tafel Equation Analysis p167

The Tafel Equation *for a cathodic process* can be rearranged to give eqn. 4.28:

$$\log_{10}|j| = \log_{10} j_0 + \frac{(1-\beta)\, n\, F}{2.303RT}\cdot|\eta| \qquad \text{Eqn. 4.28}$$

and plotting $\log_{10}|\ j\ |$ versus $|\ \eta\ |$ (as in Fig 4.7) gives …

- j_0 as the intercept on the y-axis for $|\ \eta\ | \to 0$
- β from evaluation of the slope.

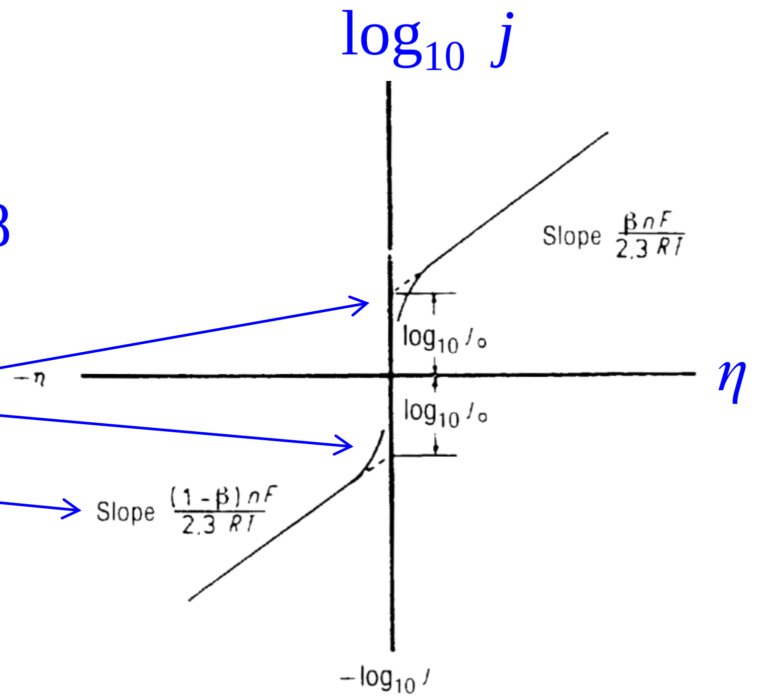


Fig. 4.7 Graphical representation of the Tafel equation for β=0.5 with the current plotted on a logarithmic scale.

By an analogous way of proceeding, we can derive the Tafel Equation *for an anodic process at* $\eta >> \frac{RT}{nF}$

$$\eta = -\frac{2.303RT}{\beta nF}\cdot\log_{10} j_0 + \frac{2.303RT}{\beta\ n\ F}\cdot\log_{10} j$$

Eqn. 4.30,
Anodic Tafel

$$\log_{10} j = \log_{10} j_0 + \frac{\beta nF}{2.303RT}\cdot\eta$$

Eqn. 4.31,
Anodic β

Directly Measuring exchange current density, j_o

$$j = j^{-} + j^{+} = j_0 \left[\exp\left\{\frac{\beta nF\eta}{RT}\right\} - \exp\left\{-\frac{(1-\beta)nF\eta}{RT}\right\}\right]$$

B-V eqn.
Eqn. 4.23,
p.166

At very small overpotentials ($\eta <$ ~10 mV), the exponents in the Butler-Volmer equation are small enough to allow expansion of the exponential terms. (using $e^x \approx 1+x$) so

$$j = j_0 \left\{1 + \left(\frac{\beta nF\eta}{RT}\right) - \left[1 - \frac{(1-\beta)nF\eta}{RT}\right]\right\} = j_0 \cdot \frac{nF\eta}{RT}$$

Eqns. 4.32, 4.33

in the low overpotential region ($|\eta| \leq 10$ mV) the current-potential plot is linear, with a slope that depends only on the value j_0 and not on β. The value of j_0 can be directly determined solely from a knowledge of the current at low overpotentials.

Note:

The quantity $RT/(j_0nF)$ is called "electron transfer resistance" because $j = j_0(nF/RT)\eta$ has the form I = (1/R) E so the quantity RT/j_0nF has units of Ohm-cm^2

At high overpotentials , the situation for determining j_0 is more complicated because β plays a role.

The Concentration Dependence of the Exchange Current Density p169

The exchange current density j_0 is a measure of the rate of electron transfer at equilibrium, and from 4.17 or .4.18 can be related to the reducing or oxidizing ranch of the BV Eqn, respectively, Starting with 4.17, the reducing branch

$$j^-(E_r) = -j_0 = -nFc_{Ox}k_0^- \cdot \exp\left\{-\frac{(1-\beta)nFE_r}{RT}\right\} \qquad 4.17$$

and remembering the definitions for E_r (eqn. 4.19) , 4.18 (oxidative branch) and setting $n = 1$, we have for the oxidative (anodic) branch:

$$j_0 = Fc_{Red}k_0^+ \cdot \exp\left\{\frac{\beta FE^0}{RT} + \beta \ln \frac{c_{Ox}}{c_{Red}}\right\}$$

$$= Fk_0^+(c_{Ox}^{\beta} \cdot c_{Red}^{1-\beta}) \cdot \exp\left\{\frac{\beta FE^0}{RT}\right\} \qquad 4.35 \text{ anodic part}$$

Following the same approach we get for the cathodic branch:

$$-j_0 = -Fk_0^-(c_{Ox}^{\beta} \cdot c_{Red}^{1-\beta} \cdot \exp\left\{-\frac{(1-\beta)FE^0}{RT}\right\} \qquad 4.36 \text{ cathodic part}$$

Knowing j_0 is equal for the cathodic and anodic part:

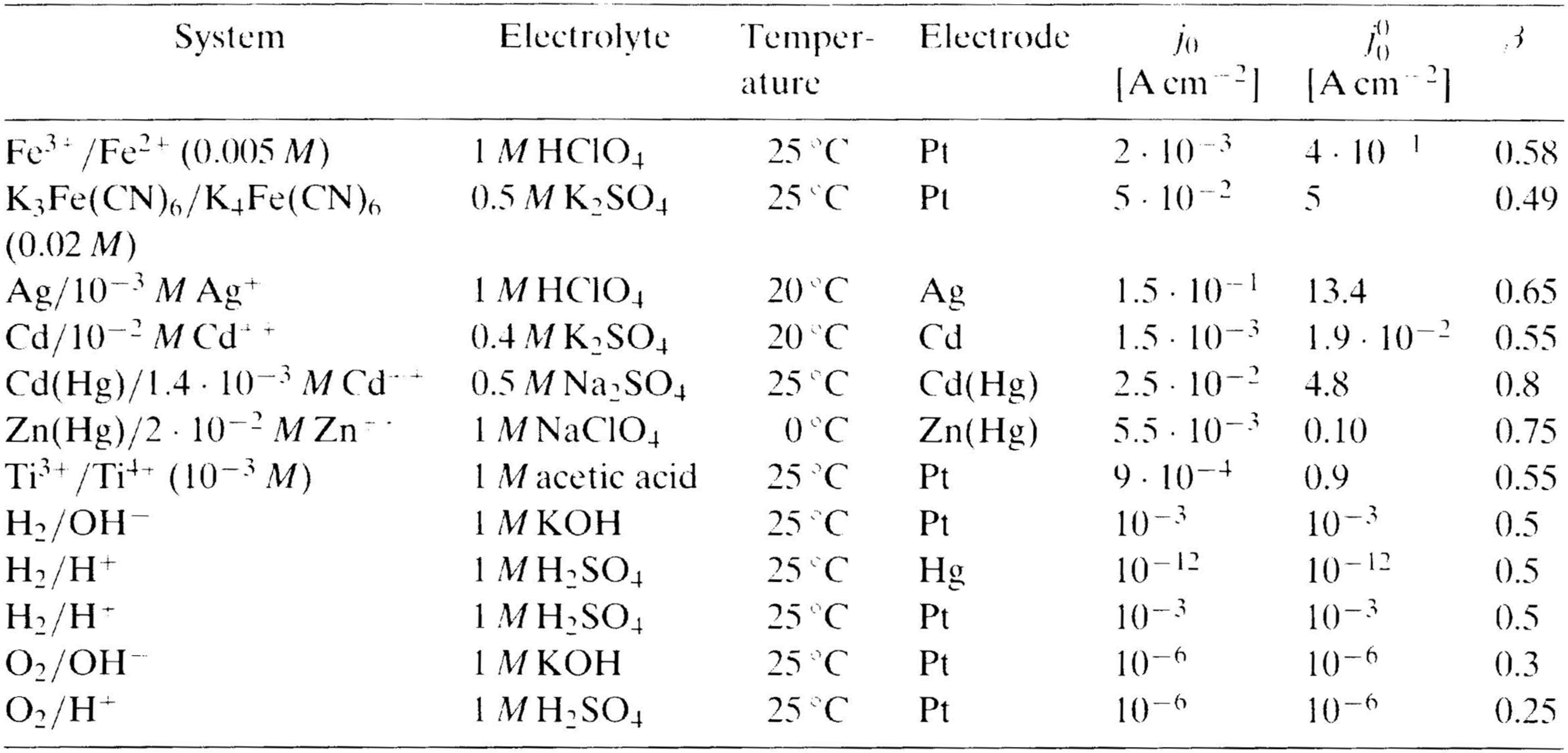
$$Fk_0^+ \cdot \exp\left\{\frac{\beta FE^0}{RT}\right\} = Fk_0^- \cdot \exp\left\{-\frac{(1-\beta)FE^0}{RT}\right\} \equiv Fk_0$$

we finally get:

$$j_0 = Fk_0 c_{Ox}^{\beta} \cdot c_{Red}^{1-\beta} \qquad 4.38$$

which is an expression for value of the *exchange current density at a particular concentration of reactants and products*. By analogy, the standard exchange current density, j_0^o, is the value of j_0 when all species are in their standard state.

Table 4.1 Examples of Values of Exchange Current Density, j_o



System	Electrolyte	Temperature	Electrode	j_0 [A cm^{-2}]	j_0^0 [A cm^{-2}]	β
Fe^{3+}/Fe^{2+} (0.005 *M*)	1 *M* $HClO_4$	25 °C	Pt	$2 \cdot 10^{-3}$	$4 \cdot 10^{-1}$	0.58
$K_3Fe(CN)_6/K_4Fe(CN)_6$ (0.02 *M*)	0.5 *M* K_2SO_4	25 °C	Pt	$5 \cdot 10^{-2}$	5	0.49
$Ag/10^{-3}$ *M* Ag^+	1 *M* $HClO_4$	20 °C	Ag	$1.5 \cdot 10^{-1}$	13.4	0.65
$Cd/10^{-2}$ *M* Cd^{++}	0.4 *M* K_2SO_4	20 °C	Cd	$1.5 \cdot 10^{-3}$	$1.9 \cdot 10^{-2}$	0.55
$Cd(Hg)/1.4 \cdot 10^{-3}$ *M* Cd^{++}	0.5 *M* Na_2SO_4	25 °C	Cd(Hg)	$2.5 \cdot 10^{-2}$	4.8	0.8
$Zn(Hg)/2 \cdot 10^{-2}$ *M* Zn^{++}	1 *M* $NaClO_4$	0 °C	Zn(Hg)	$5.5 \cdot 10^{-3}$	0.10	0.75
Ti^{3+}/Ti^{4+} (10^{-3} *M*)	1 *M* acetic acid	25 °C	Pt	$9 \cdot 10^{-4}$	0.9	0.55
H_2/OH^-	1 *M* KOH	25 °C	Pt	10^{-3}	10^{-3}	0.5
H_2/H^+	1 *M* H_2SO_4	25 °C	Hg	10^{-12}	10^{-12}	0.5
H_2/H^+	1 *M* H_2SO_4	25 °C	Pt	10^{-3}	10^{-3}	0.5
O_2/OH^-	1 *M* KOH	25 °C	Pt	10^{-6}	10^{-6}	0.3
O_2/H^+	1 *M* H_2SO_4	25 °C	Pt	10^{-6}	10^{-6}	0.25

j_o^o is the exchange current density, j_o , with all species in their standard states

Note:

Leave effects of

- consecutive electron transfer
- coupled chemical reactions and
- geometric rearrangement

on kinetics to your reading

Determination of Activation Parameters and the T- dependence of Electrochemical Reactions p184

Recall eqn. 4.24 and $\Delta G = \Delta H - T\Delta S$, so the expression for the exchange-current density could be written as:

$$j_0 = nFc_{\mathrm{ox}}k_0'^{-} \exp\left\{-\frac{\Delta H_-^\ddagger(E_\mathrm{r})}{RT}\right\}\cdot\exp\left\{\frac{\Delta S_-^\ddagger(E_\mathrm{r})}{R}\right\}$$

eqn. 4.24

Considering the pre-exponential terms and $\Delta H^\ddagger_-$ and $\Delta S^\ddagger_-$ are invariant with respect to temperature; taking the ln of 4.24 and the partial derivative with respect to 1/T, we get:

$$d \ln j_o / d\,(1/T) = -\Delta H^\ddagger / R$$

which allows to evaluate the enthalpy of activation from a plot of ln j_o versus 1/T

The experimental values of activation enthalpy vary considerably, even for the same electrochemical reaction on different electrodes, For example, for the hydrogen electrode, the $\Delta H^\ddagger$ values are …

- ~ 70 kJ mol^{-1} found on mercury
- ~ 25 kJ mol^{-1} found on nickel.

Note: For accurate $\Delta H^\ddagger$ values, these must be determined at the exchange current density, j_o, measure at the reversible potential, E_r. If $\Delta H^\ddagger$ is determined for j measured at some overpotential, η, then $\Delta H^\ddagger$ will be in error from the true value by about $\beta n F\eta$ … which is ~50 kJ/mole for $\beta = 0.5$ and $n = 1$, since

$$j = -j_0 \exp\left\{-\frac{(1-\beta)nF\eta}{RT}\right\}$$

Next

Concentration Overpotential p185

The effect of Transport of Material on the Current-Voltage Curve