Chapter 3
Kinetics of Electrode Reactions

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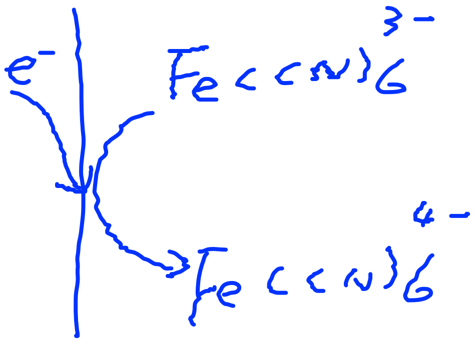
Types of electrode reactions

1. Simple electrode reactions-
   1) products dissolved in the ionic conductor
   2) Products dissolved in the electron conductor
2. Formation a new phase
   1) Solid phase
   2) Gas phase
3. Electronic conductor is destroyed
4. Film transformation

Simple Electrode rxns

(1) $Fe^{3+}(CN)_6^{3-}(aq) + e = Fe^{2+}(CN)_6^{4-}(aq)$



(2) $O = \langle O \rangle = O + 2H^+ + 2e = HO - \langle O \rangle - OH$

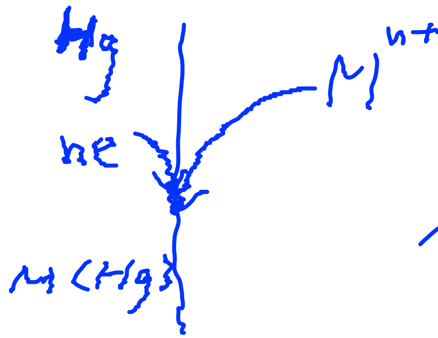
quinone (Q) — Hydroquinone (HQ) — reference electrode

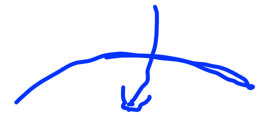
$Q + 2H^+ + 2e = HQ$

Nonaqueous soln

(3) $Ce^{4+}(aq) + e = Ce^{3+}(aq)$

(4) $M^{n+}_{(aq)} + ne^-(Hg) = M(amal.)$

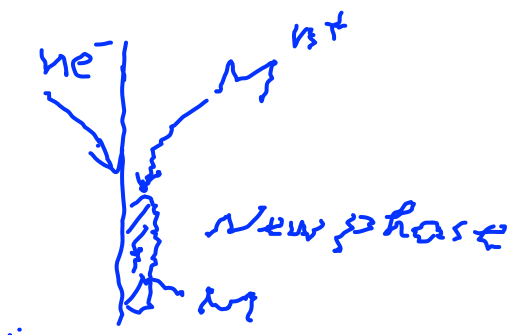




Formation of New phase

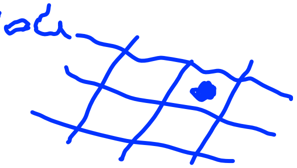
(5)

$M^{n+}_{(aq)} + ne^-(Pt) = M_{Pt}$

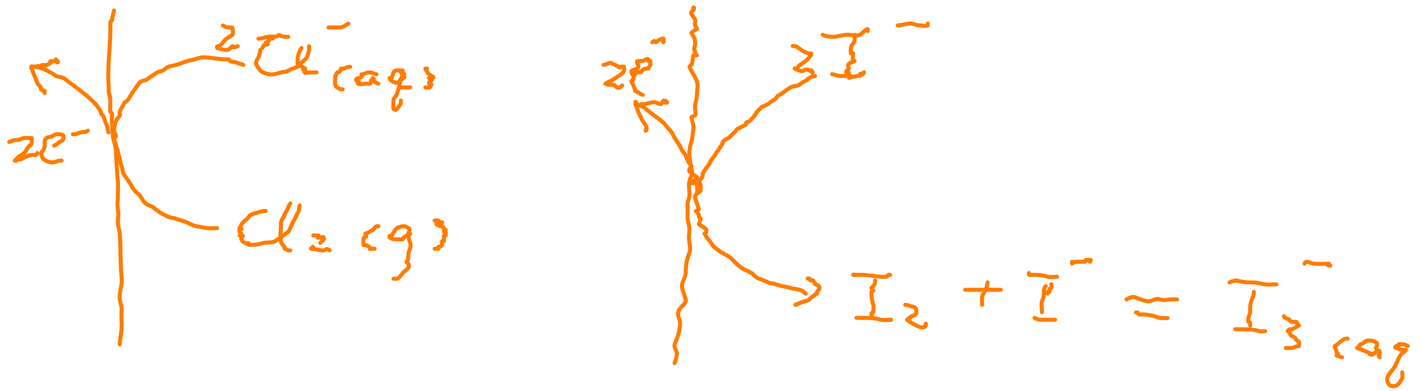


$H_2O_{(aq)} + e^-(Pd) = H(Pd) + OH^-$

Metal Hydride

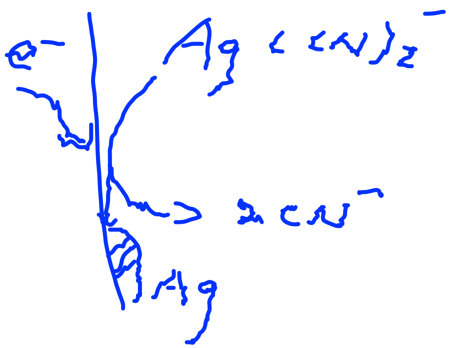


(6) $2Cl^-_{(aq)} \longrightarrow 2e + Cl_{2(g)}$



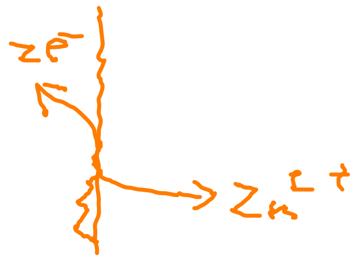
(7) $Ag(CN)_2^-{}_{(aq)} + e \longrightarrow Ag_{(s)} + 2CN^-_{(aq)}$

$Ag^+_{(aq)} + e \longrightarrow Ag_{(s)}$



Electrode is destroyed

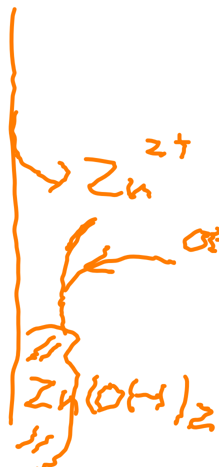
(1) $Zn \longrightarrow Zn^{2+} + 2e^-$



Metal dissolution

corrosion

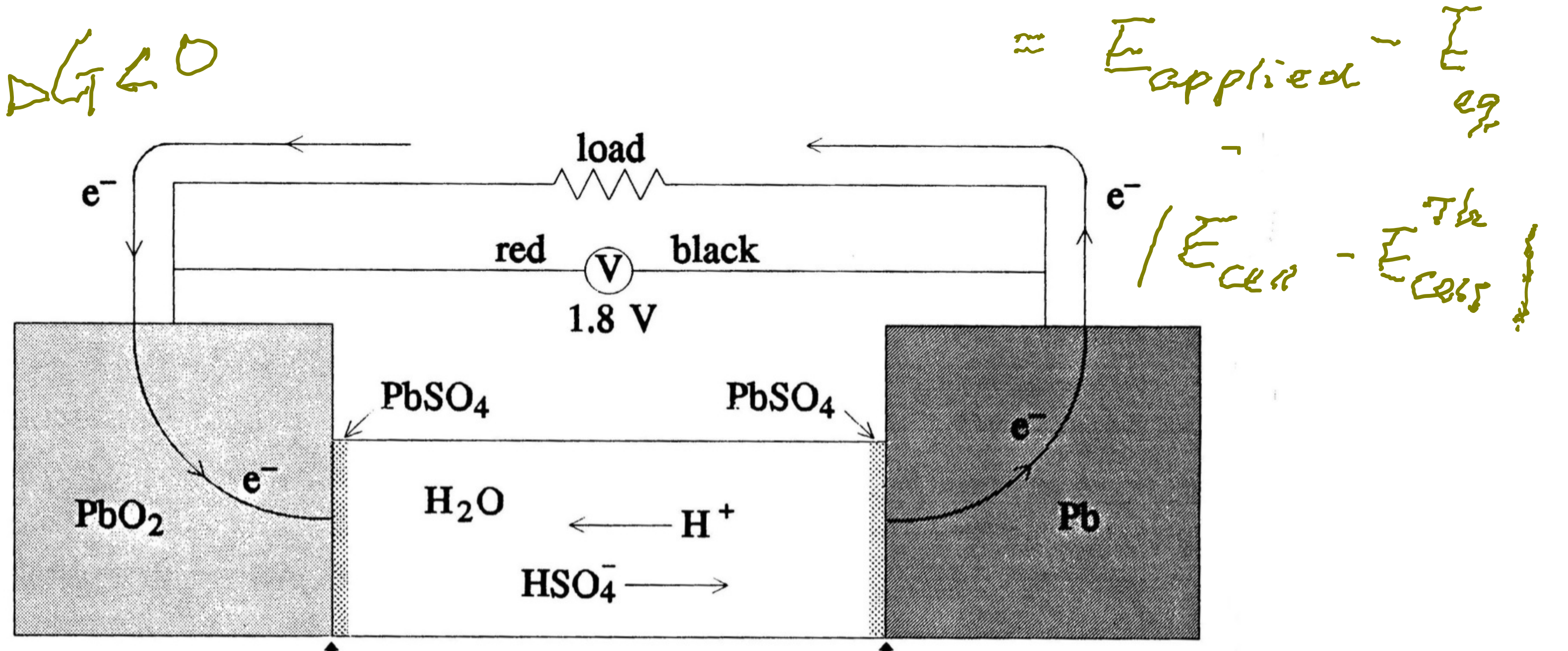
(acid)



(Intermediate pH)

passivation

Polarization-Discharging



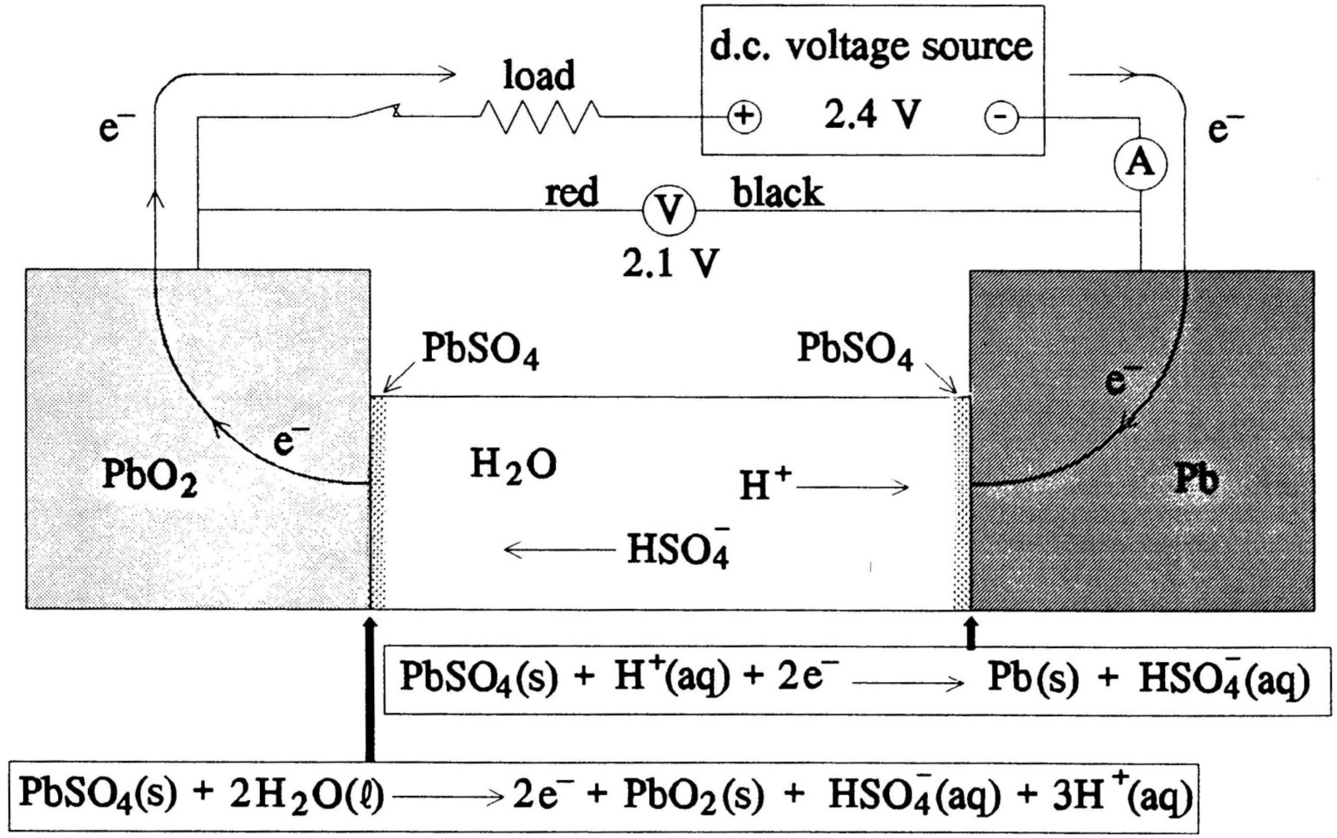
$Pb(s) + HSO_4^-(aq) \longrightarrow 2e^- + PbSO_4(s) + H^+(aq)$

$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) + 2e^- \longrightarrow PbSO_4(s) + 2H_2O(\ell)$

Polarization: their voltages decrease in magnitude when the energy is taken from them.

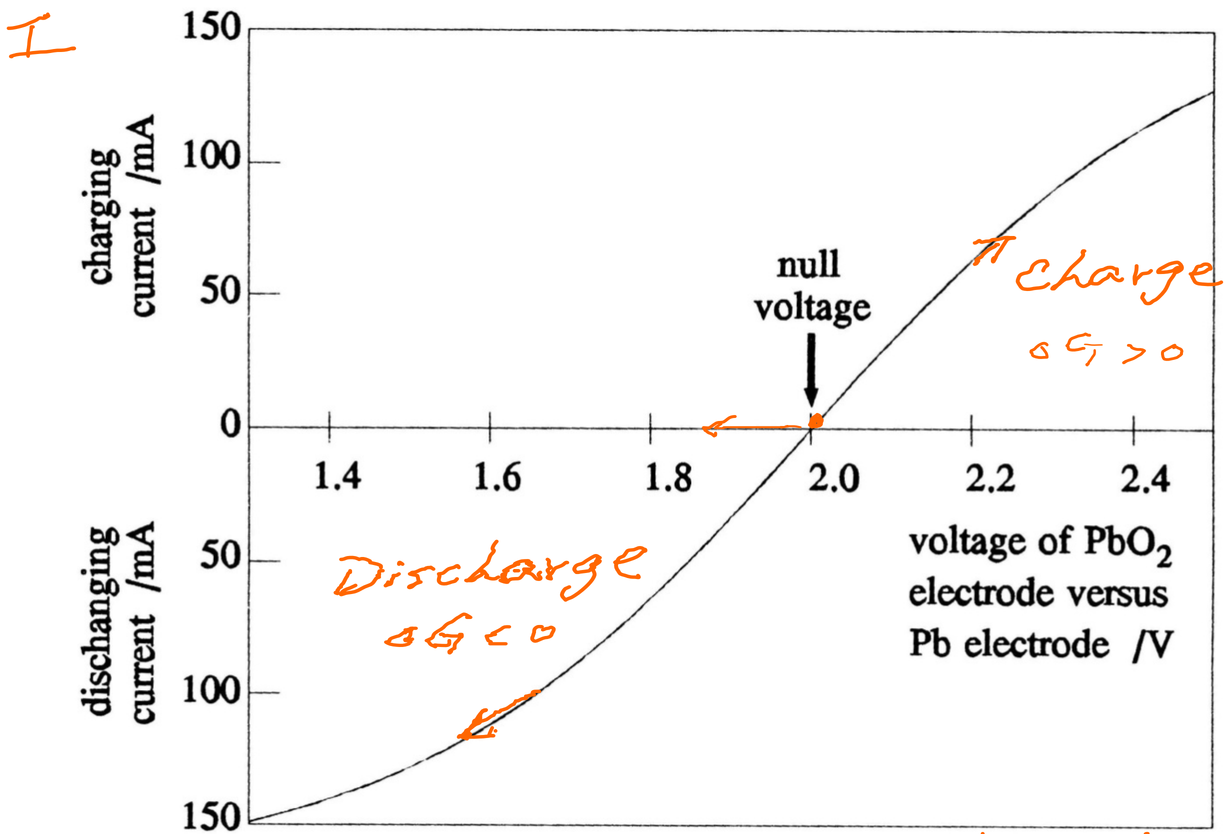
Polarization: a potential departures from its equilibrium potential

Electrolytic cell: $\Delta G>0$



Voltammogram

(I-V curve) plot



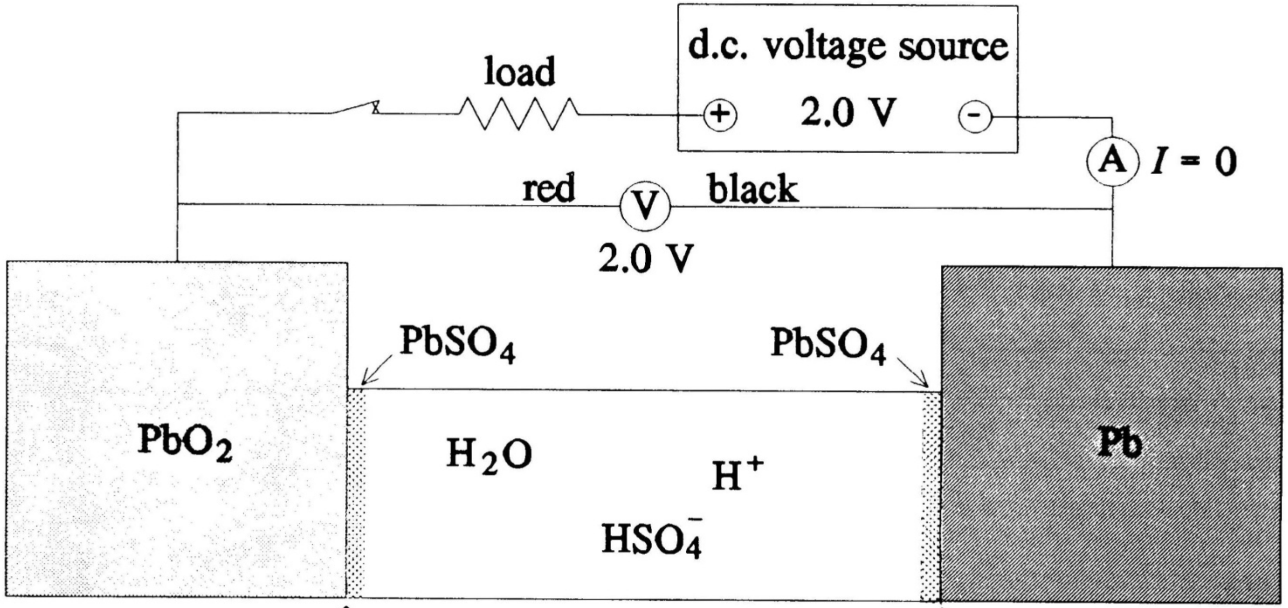
Cell voltage:

open circuit potential (OCP) ← E

Equilibrium cell voltage; Reversible cell voltage; Rest voltage; Null Voltage; Open-circuit voltage

(OCV) ← Ecell

An Equilibrium Cell



$$PbSO_4(s) + H^+(aq) \underset{}{\overset{\pm 2e^-}{\rightleftarrows}} Pb(s) + HSO_4^-(aq)$$

$$PbO_2(s) + HSO_4^-(aq) + 3H^+(aq) \underset{}{\overset{\pm 2e^-}{\rightleftarrows}} PbSO_4(s) + 2H_2O(\ell)$$

Homogeneous Reactions

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B$$

$$v_f = k_f C_A$$

$$v_b = k_b C_B$$

$$v_{net} = k_f C_A - k_b C_B$$

At equilibrium $v_{net} = 0$

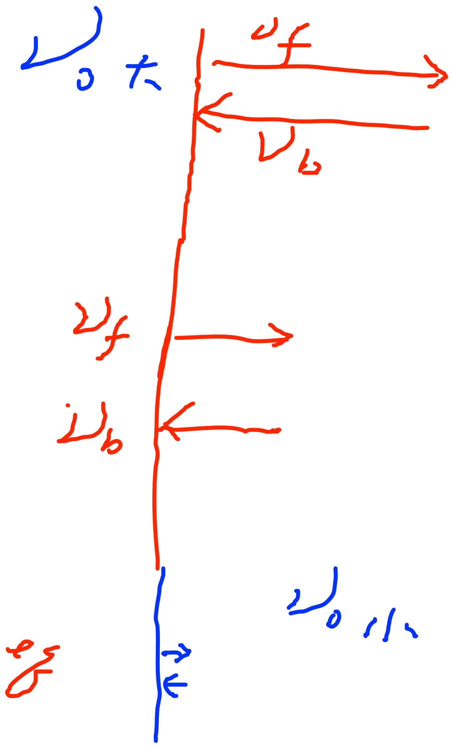
$$K = \frac{k_f}{k_b} = \frac{(C_B)_{eq}}{(C_A)_{eq}}$$

Kinetic parameter

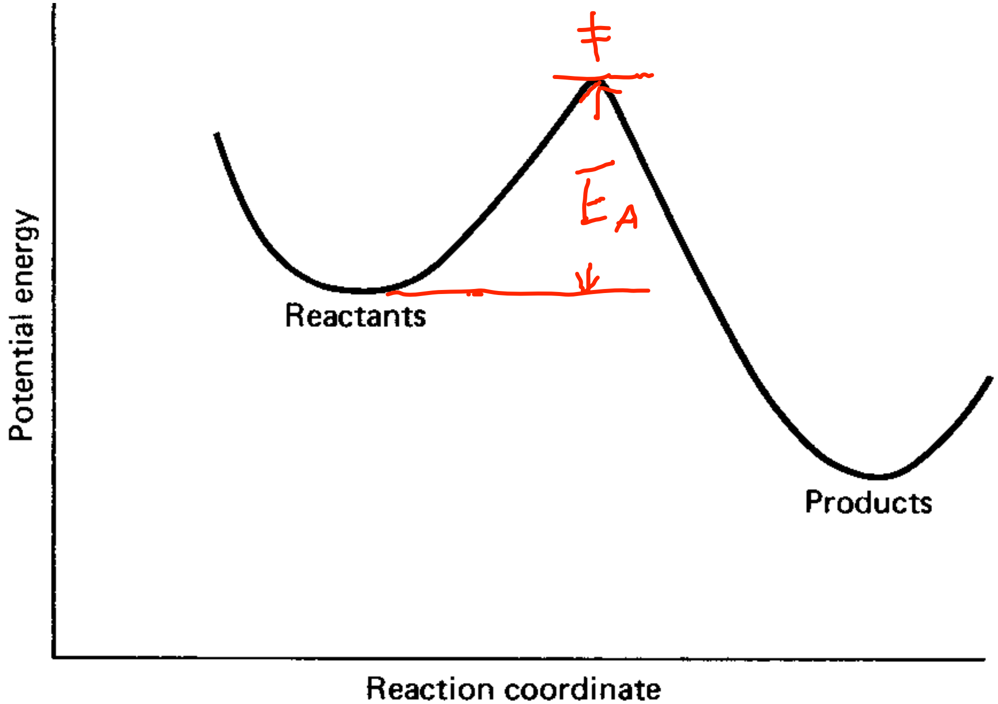
$$v_0 = k_f (C_A)_{eq} = k_b (C_B)_{eq}$$

exchange velocity

$$(v_f)_{eq} = (v_b)_{eq}$$



Arrhenius equation and potential energy surfaces



$$k = A\, e^{-E_A/RT}$$

↓

$$A'\, e^{-\Delta G^\ddagger/RT}$$

Transition state - theory

$$k = \kappa \frac{k_B T}{h} e^{-\Delta G^\ddagger/RT}$$

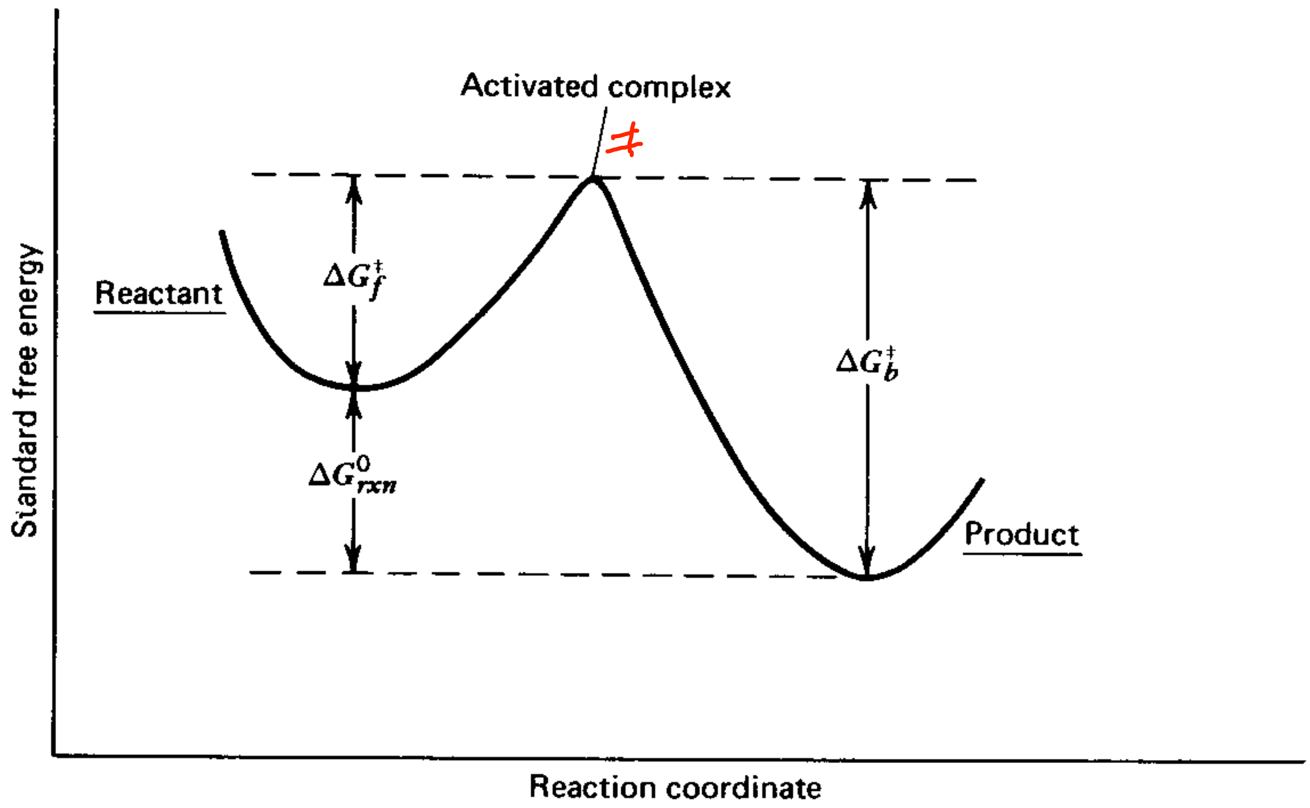
chemical rxn

$$\Delta G^\ddagger = f(\text{catalyst})$$

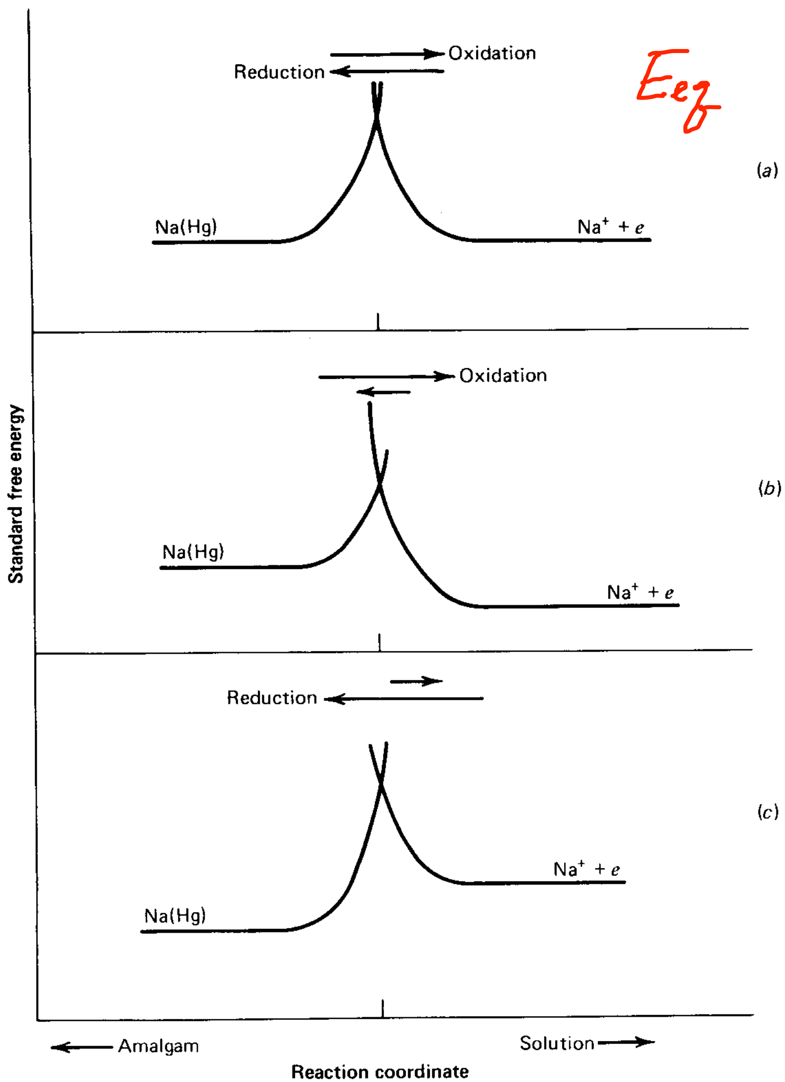
Electrochemical rxn

$$\Delta G^\ddagger = f'(\text{cat. electrode surface}, \underline{\underline{E}})$$

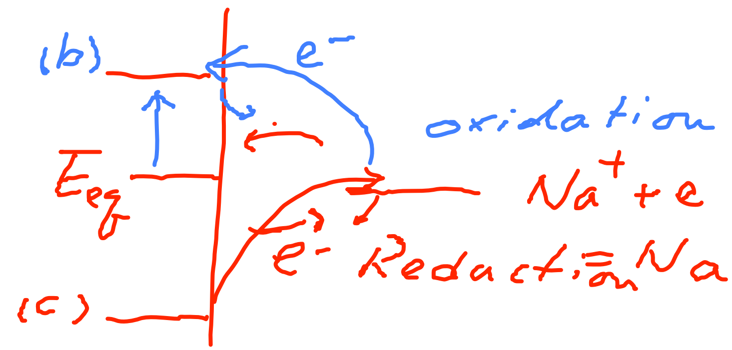
Transition state theory



Effect of potential on energy barriers



$Na^+ + e \xrightarrow{Hg} Na(Hg)$



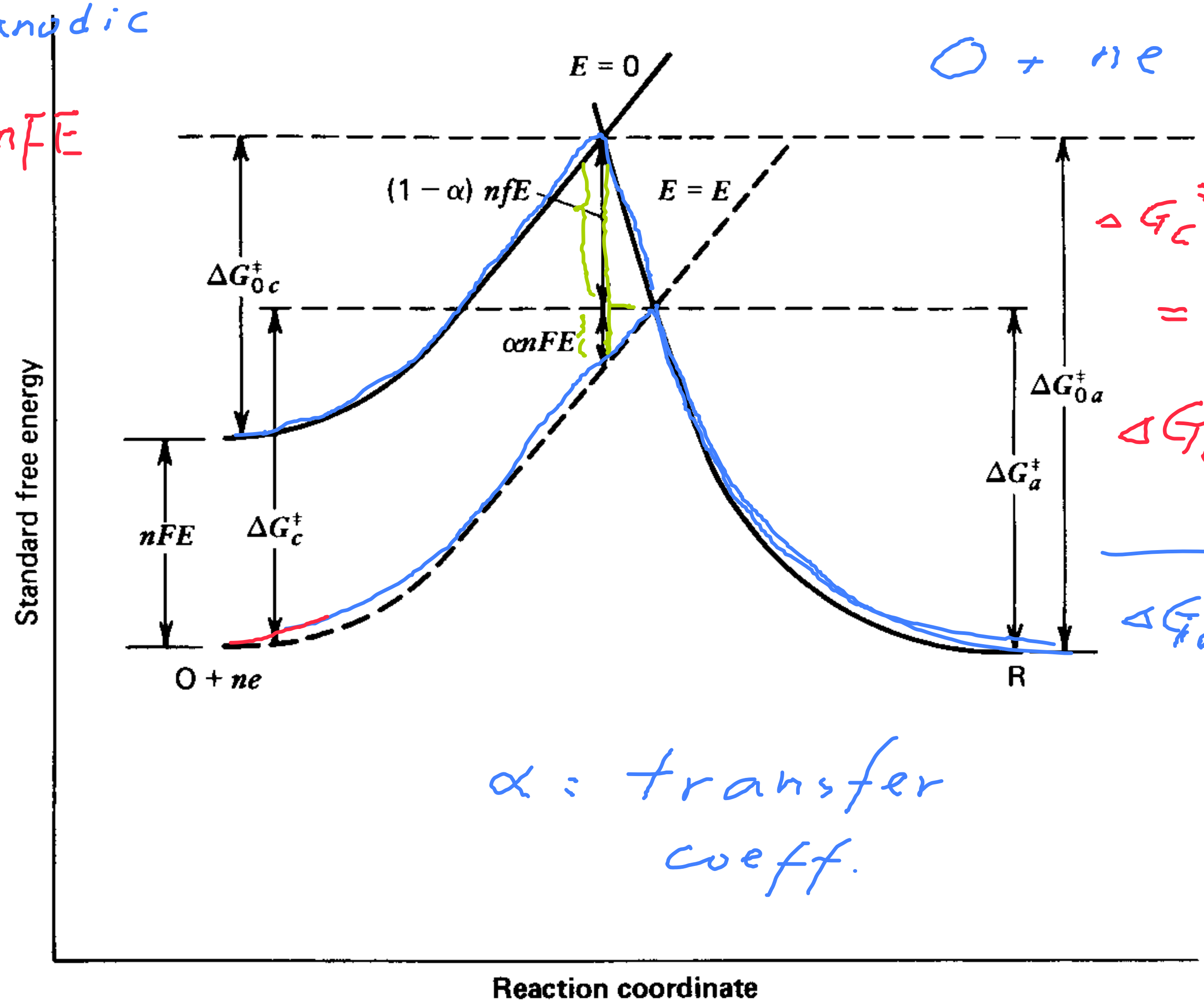
potential

One-step, one-electron reaction

c : cathodic
a : anodic

$\Delta G = -nFE$

$O + e = R$
$O + ne = R$



$\Delta G_c^{\neq} + (1-\alpha) nFE = nFE + \Delta G_{0c}^{\neq}$

$\Delta G_c^{\neq} = \Delta G_{0c}^{\neq} + \alpha nFE$

$\Delta G_a^{\neq} = \Delta G_{0a}^{\neq} - (1-\alpha) nFE$

α : transfer coeff.

Electrochemical Reactions

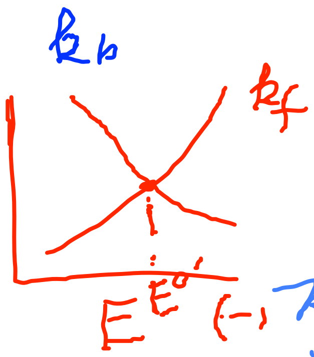
$$O + e \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R$$

$$k_f = A_f \, e^{-\Delta G_c^{\neq}/RT}$$

$$k_b = A_b \, e^{-\Delta G_a^{\neq}/RT}$$

$$f = \frac{F}{RT}$$

$(n=1)$



$$k_f = A_f \exp(-\Delta G_{oc}^{\neq}) \, e^{-\alpha f E}$$

$$k_b = A_b \exp(-\Delta G_{oa}^{\neq}) \, e^{(1-\alpha) f E}$$

$C_O(x,t)$

$C_R(x,t)$

$$\frac{i}{nFA} = r_{net} = k_f C_O(0,t) - k_b C_R(0,t)$$

mol / s·cm²

$$i = nFA\left(k_f C_O(0,t) - k_b C_R(0,t)\right) = i_c - i_a$$

$$n=1 \quad i = FA\left[A_f e^{-\Delta G^{\ddagger}_{0c}/RT} e^{-\alpha f E} C_O(0,t) - A_b e^{-\Delta G^{\ddagger}_{0a}/RT} e^{+(1-\alpha) f E} C_R(0,t)\right]$$

at equilibrium, $E = E^{0'}$, $i = 0$

$$k_f C_O^* = k_b C_R^*$$

$$A_f e^{-\Delta G^{\ddagger}_{0c}/RT} e^{-\alpha f E^{0'}} C_O^*$$

$$k^0 = A_b e^{-\Delta G^{\ddagger}_{0a}/RT} e^{(1-\alpha) f E_0'} C_R^*$$

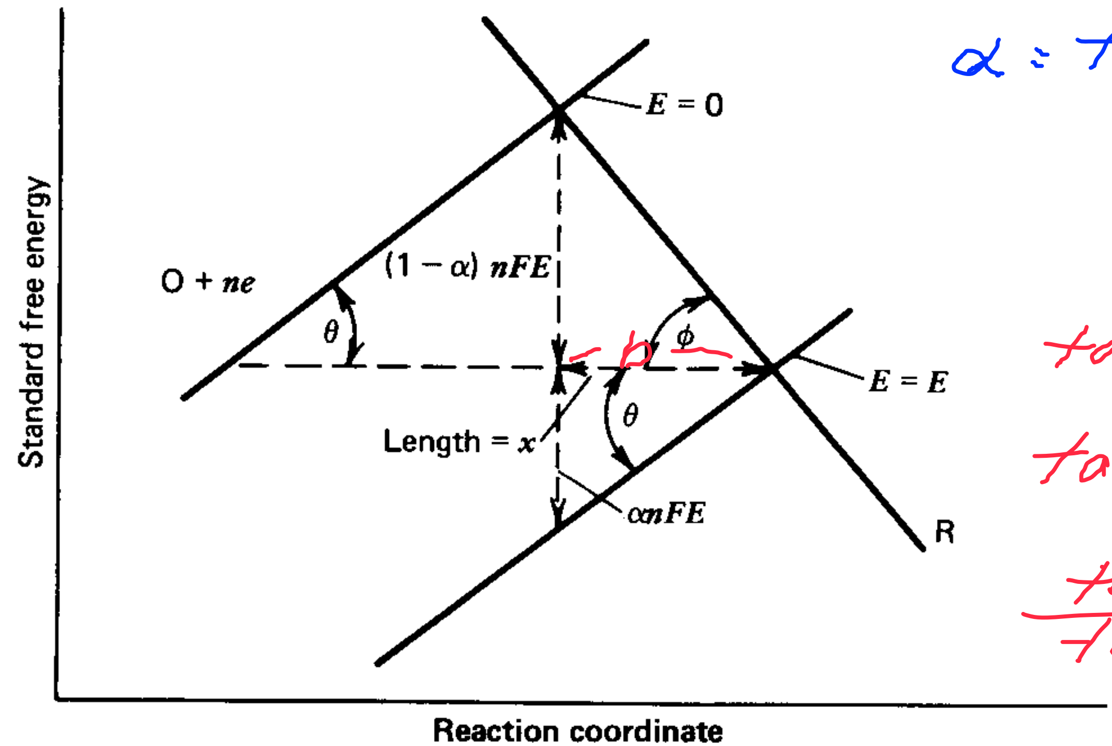
$$i = nFk^0\left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f(E-E^{0'})} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f(E-E^{0'})}\right]$$

at $E = E^{o'}$

$$k_f = k_b = k^0$$ standard rate const

$$i = nFAk^0 \left[C_O(0,t)\, e^{-\alpha f(E-E^{o'})} - C_R(0,t)\, e^{(1-\alpha)f(E-E^{o'})} \right]$$

Effect of angle of intersection of the free energy curves on transfer coefficients

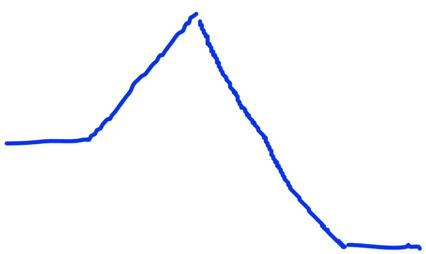


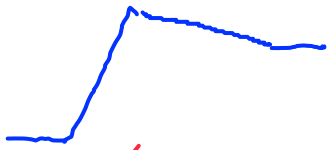
α : transfer coeff.

$$\tan\theta = \frac{\alpha FE}{b}$$

$$\tan\phi = \frac{(1-\alpha)FE}{b}$$

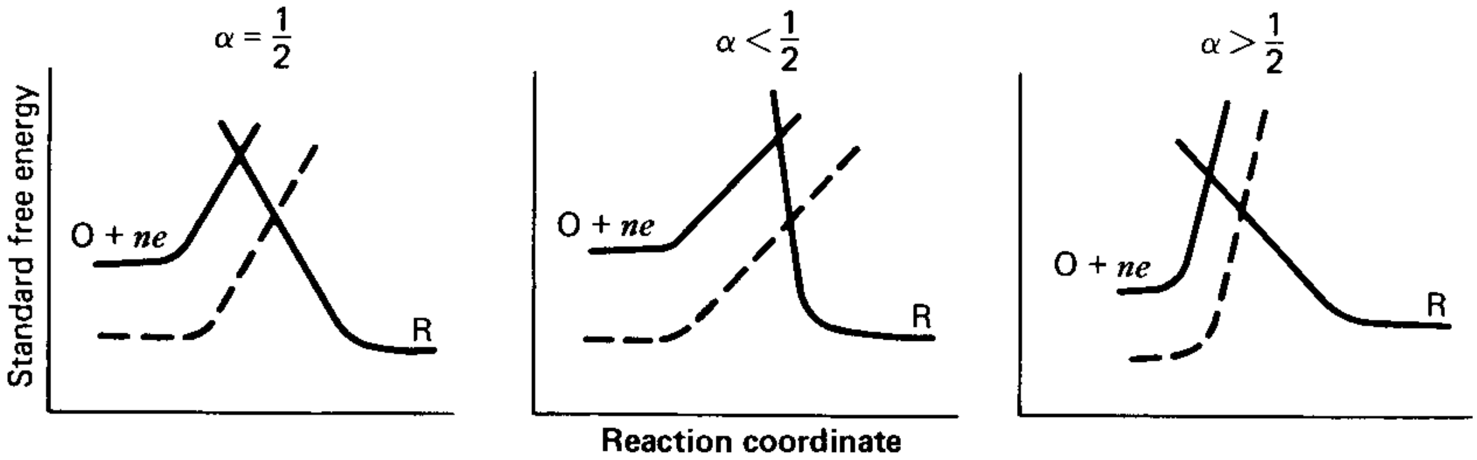
$$\frac{\tan\theta}{\tan\phi} = \frac{\alpha}{1-\alpha}$$





$$\frac{\tan\theta}{\tan\theta + \tan\phi} = \alpha$$

Effect of transfer coefficient



Butler-Volmer model for the one-step, one electron process

$$i = FAk^0\left[C_O(0,t)e^{-\alpha f(E-E^{0'})} - C_R(0,t)e^{(1-\alpha)f(E-E^{0'})}\right] = i_c - i_a$$

$$O + e = R$$

at $E = E_{eq}$ $\quad \left(k_f(E_{eq}) C_O^* = k_b(E_{eq}) C_R^* \right)$

$i = 0$ $\quad i_c(E_{eq}) = i_a(E_{eq}) = i_o$ exchange current

Nernst eq

$$E = E^{0'} + \frac{RT}{F}\ln\frac{C_O^*}{C_R^*}$$

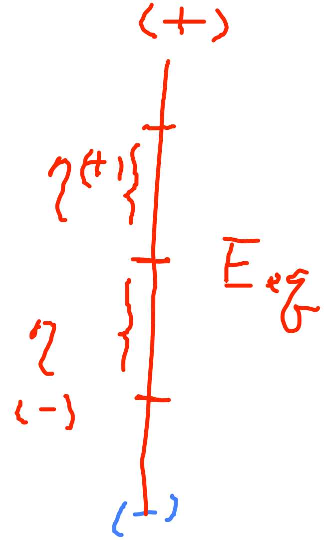
$$\frac{C_O^*}{C_R^*} = \exp f(E_{eq} - E^{0'})$$

$$i = i_o\left[\frac{C_O(0,t)}{C_O^*}e^{-\alpha f(E-E_{eq})} - \frac{C_R(0,t)}{C_R^*}e^{(1-\alpha)f(E-E_{eq})}\right]$$

Driving force

$$\eta = E - E_{eq}$$

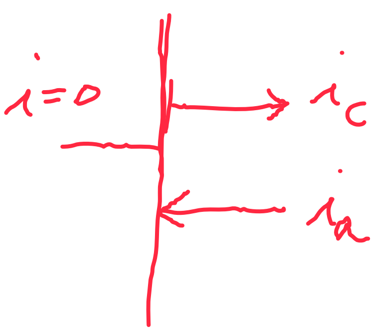
overpotential



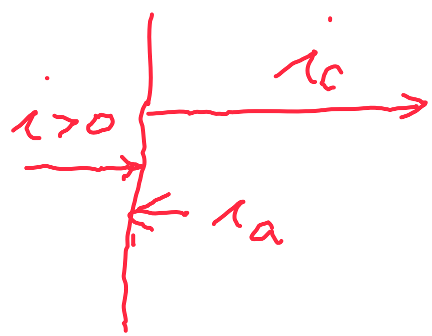
i-E curve

$$i = i_0 \left[\frac{C_O(0,t)}{C_O^*} e^{-\alpha f \eta} - \frac{C_R(0,t)}{C_R^*} e^{(1-\alpha) f \eta} \right]$$

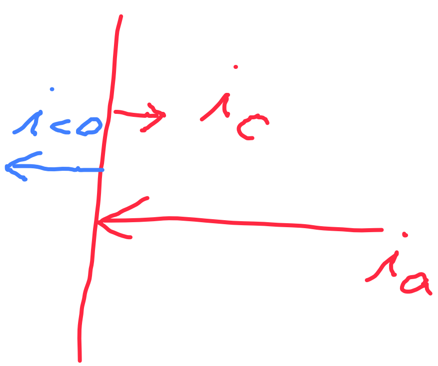
$\eta = 0$ E_{eq}



$\eta < 0$



$\eta > 0$



No Mass transfer effect

$C_O(0,t) = C_O^*$

$C_R(0,t) = C_R^*$

$R_m \ll R_{ct}$

↓

Mass transfer resistance

Charge transfer resistance

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

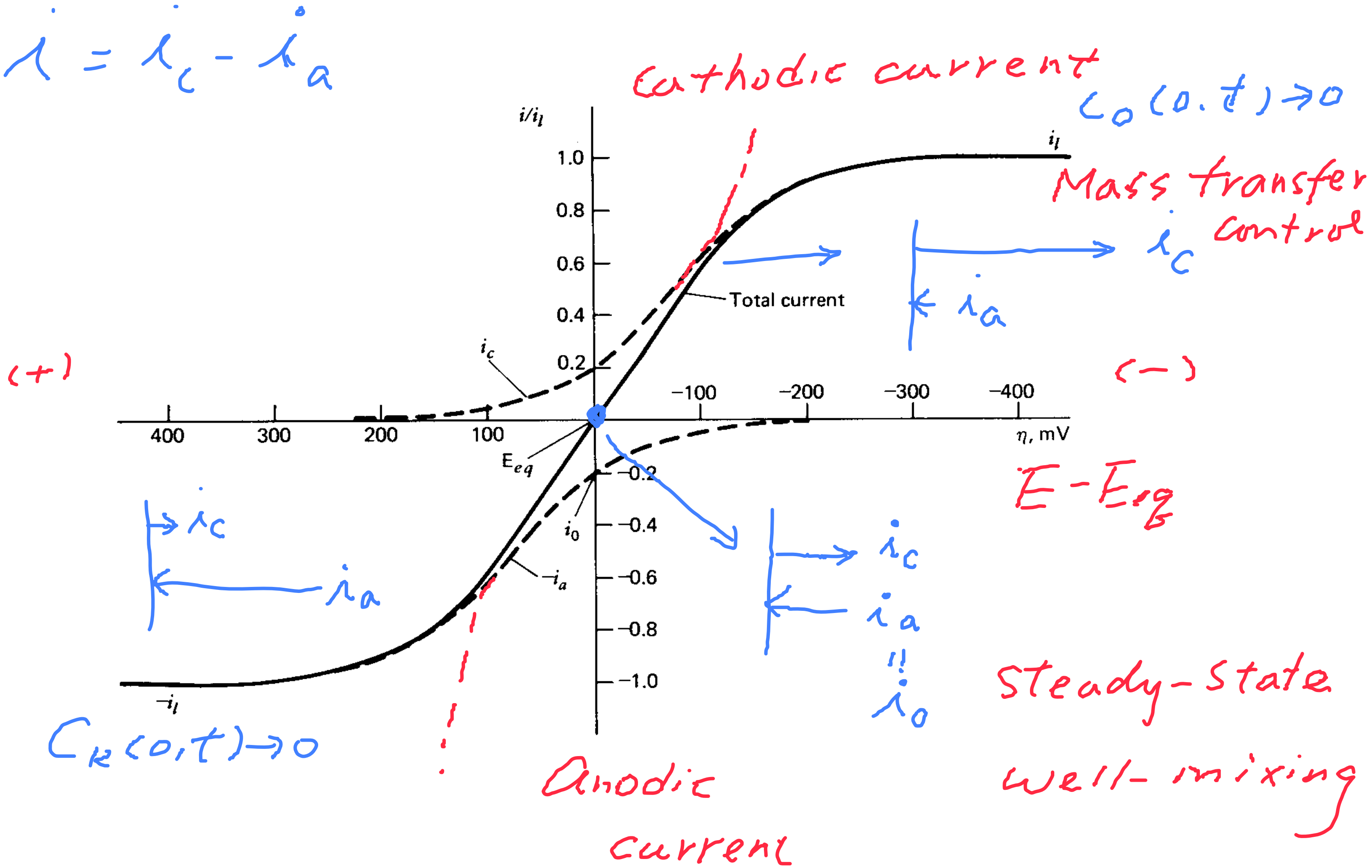
← Butler-Volmer eq

i_0 :

α :

Current-potential curves

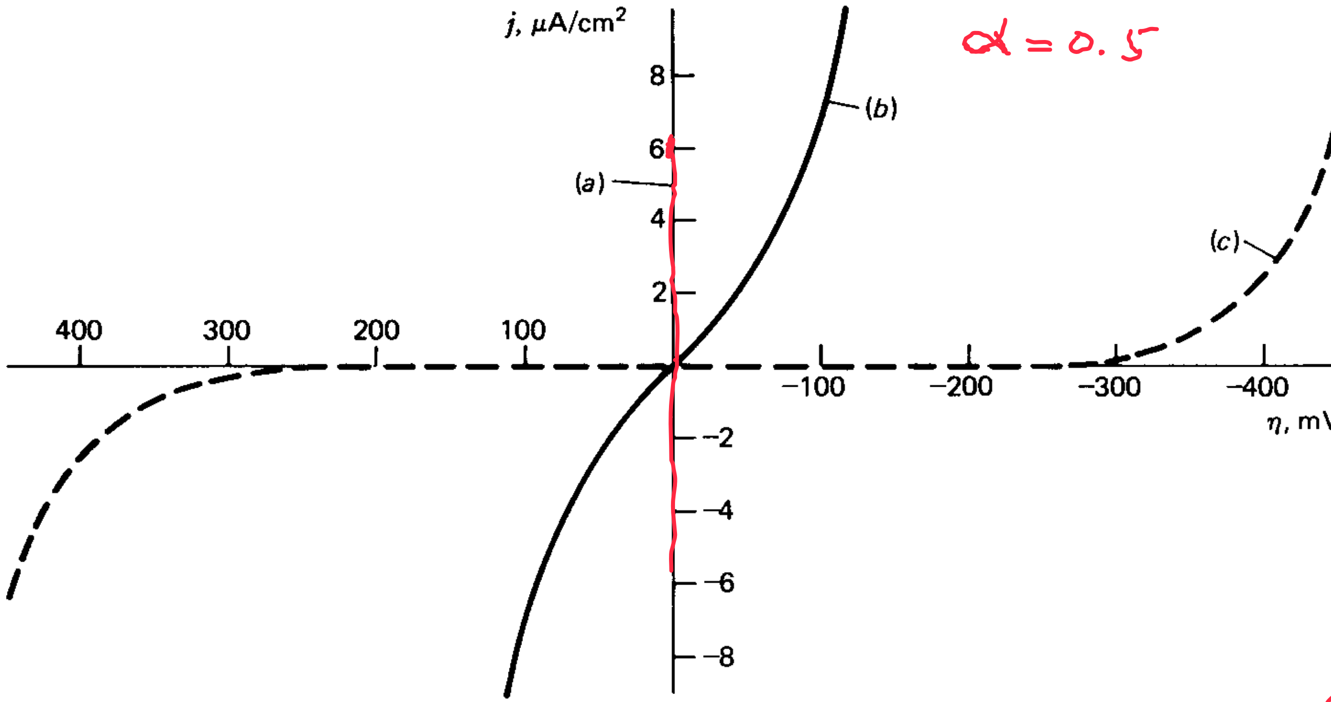
$i = i_c - i_a$



No Mass transfer effects- Effect of exchange current density

j_0 : 10^{-3} ~ 10^{-9} (a) (c) A/cm^2

$\alpha = 0.5$

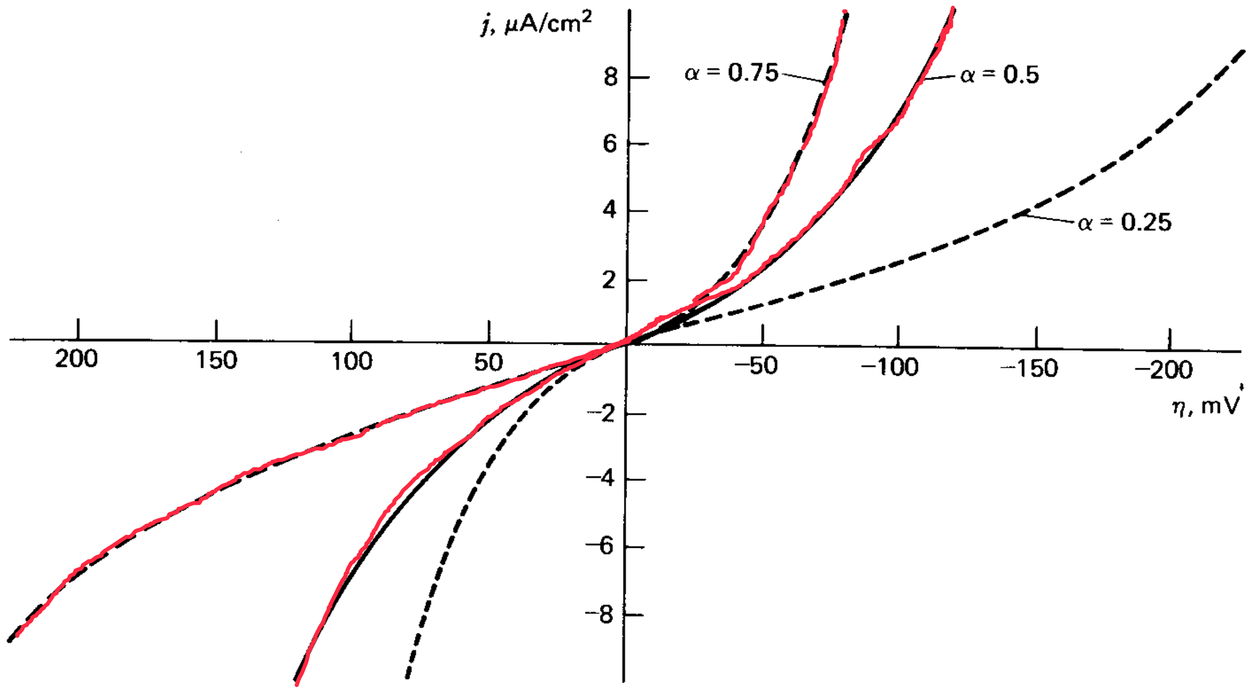


j_0 : exchange current density

$$i = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

$$j = j_0 \left[\quad \right]$$

Effect of transfer coefficient

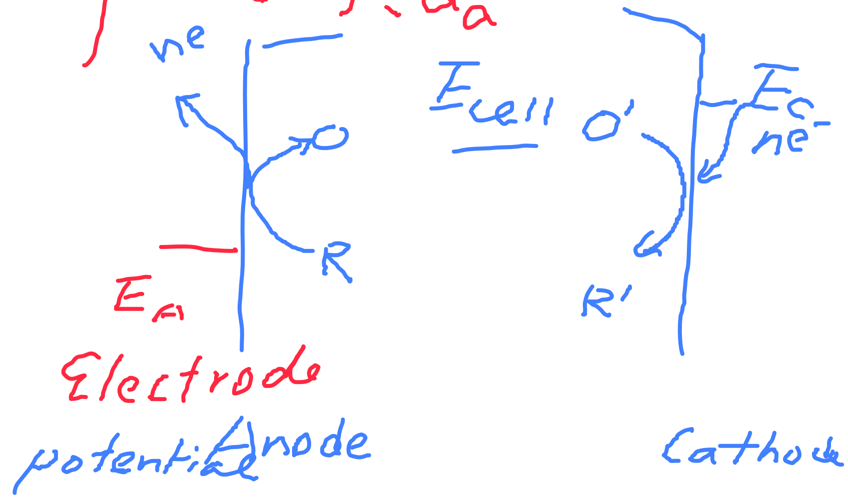


$$i_A = i_0 \left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta} \right]$$

$$i'_C = i'_0 \left[e^{-\alpha' f \eta'} - e^{(1-\alpha') f \eta'} \right]$$

$\alpha : \alpha_c$

$(1-\alpha) : \alpha_a$

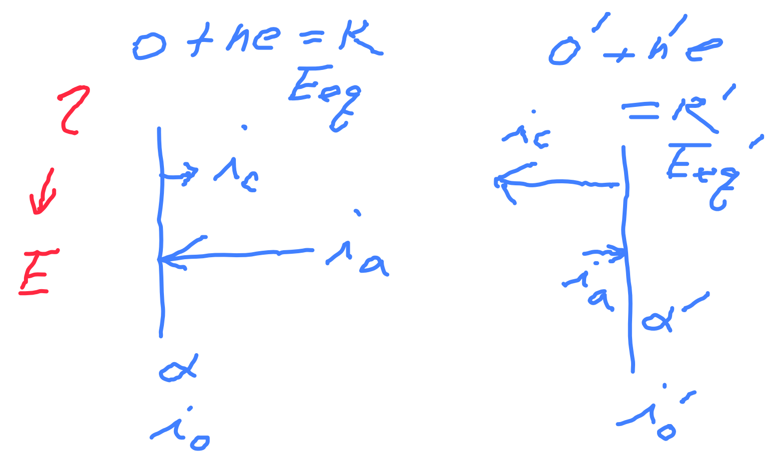


Anode: $\eta = E_A - E_{eq}$

Cathode $\eta' = E_C - E'_{eq}$

$$E_{cell} = E_C - E_A$$

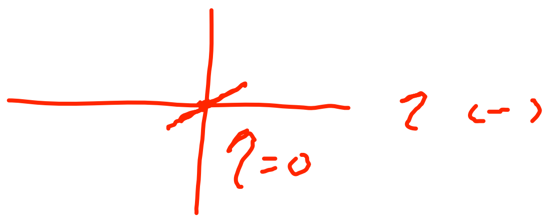
$$i_{measured} = |i_A| = |i'_C|$$



$$i = i_0\left[e^{-\alpha f\eta} - e^{(1-\alpha)f\eta}\right]$$

Case 1: $\eta \to 0$ $\qquad f = \frac{F}{RT}$

$$i = -i_0 f\eta \Rightarrow R_{ct} = \frac{|\eta|}{i} = \frac{RT}{F i_0}$$



$\eta = a + b\log i$

Tafel

Case 2: $|\eta| > 118$ mV

$\eta(-)$: $\quad i \doteq i_0 e^{-\alpha f\eta}$

$\eta(+)$: $\quad i \doteq i_0 e^{(1-\alpha)f\eta}$

$$\ln i = \ln i_0 - \alpha f\eta$$

$$\eta = \frac{RT}{\alpha F}\ln i_0 - \frac{RT}{\alpha F}\ln i = a + b\log i$$

Tafel plots

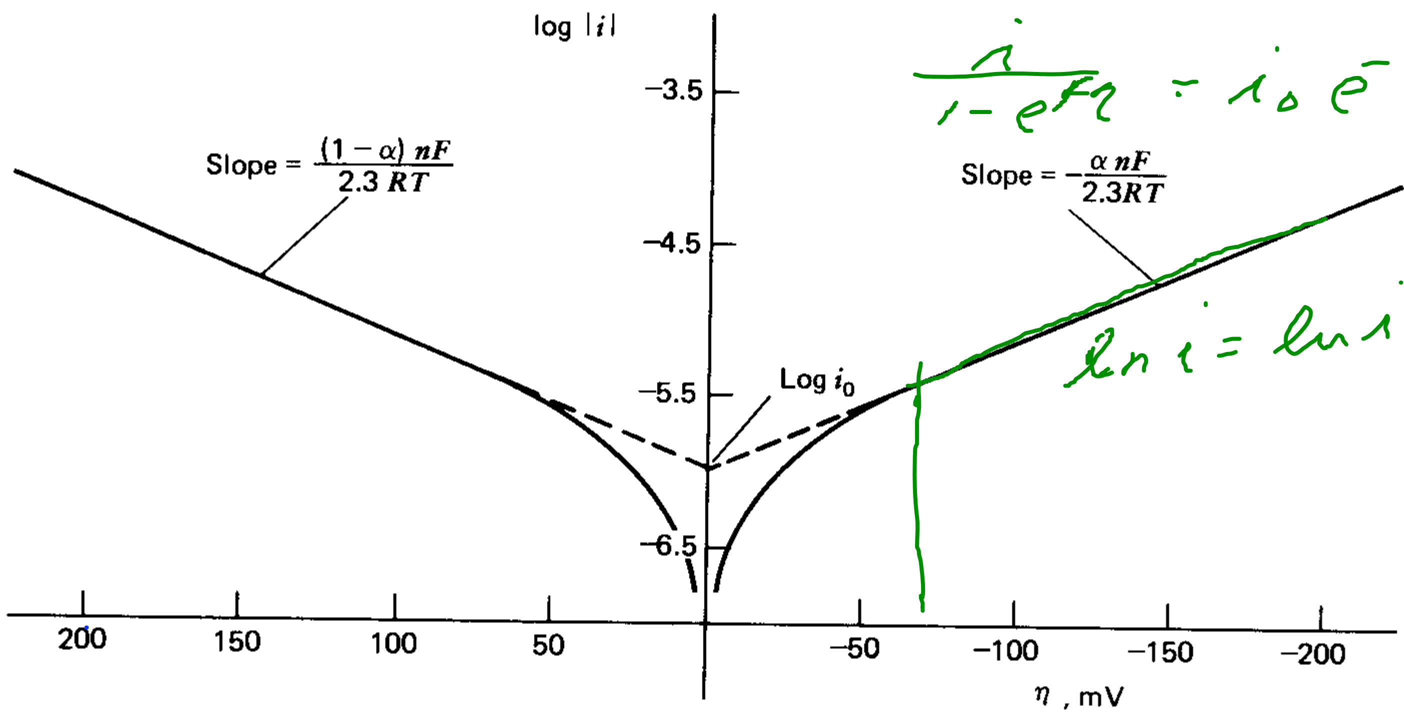
$$\log \frac{i}{1 - e^{nf\eta}} = \log i_0 - \frac{\alpha n F \eta}{2.3RT}$$

$$i = i_0\left[e^{-\alpha f \eta} - e^{(1-\alpha) f \eta}\right]$$

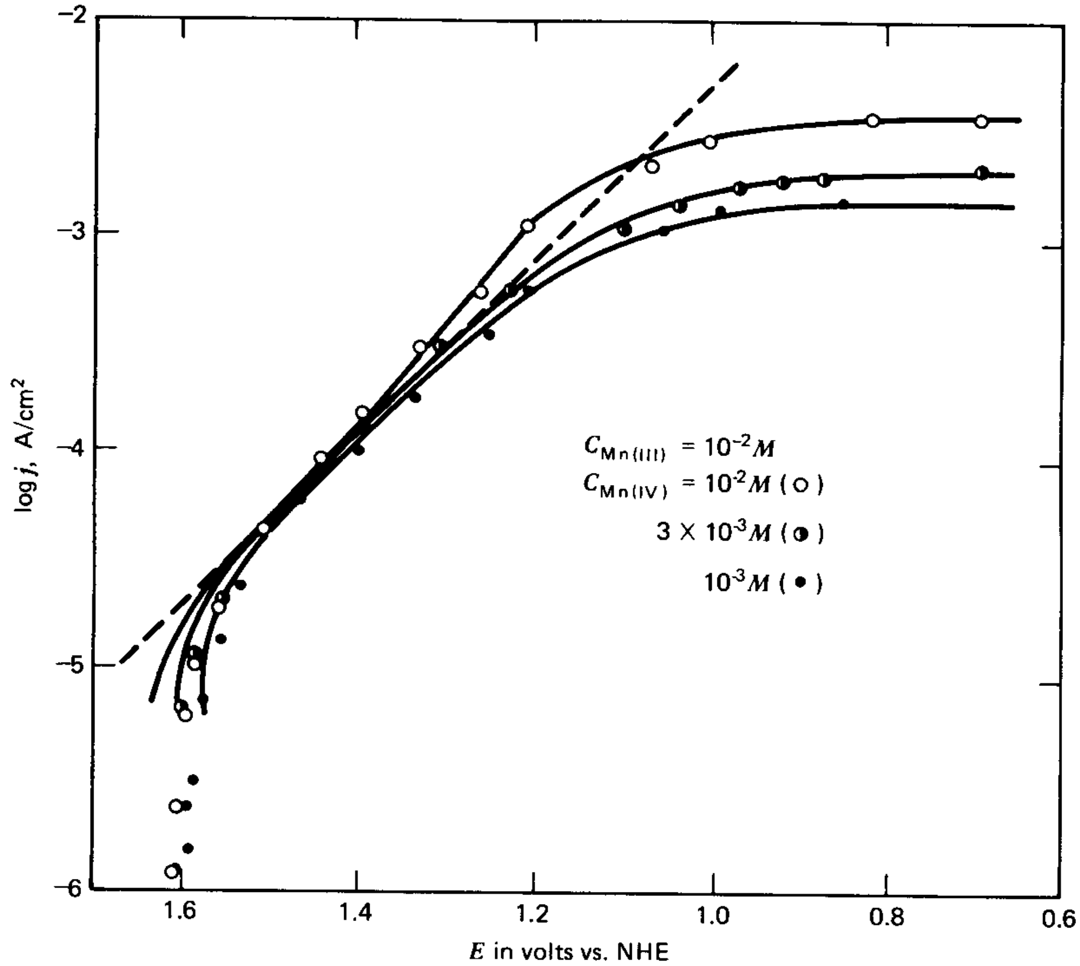
$$= i_0 e^{-\alpha f \eta}\left[1 - e^{f\eta}\right]$$

$$\frac{i}{1 - e^{f\eta}} = i_0 e^{-\alpha f \eta}$$

$$\ln i = \ln i_0 - \alpha f \eta$$



Tafel plots for the reduction of Mn(IV) to Mn(III)



Mn(IV) + e = Mn(III)

$$I = nFAk_0\{C_o(0,t)\exp[-\alpha nF(E-E_0)/RT] - \{C_R(0,t)\exp[(1-\alpha)nF(E-E_0)/RT]\}$$

$$= i_0\,\{C_o(0,t)/C_{o,eq}\exp[-\alpha nF\eta/RT] - \{C_R(0,t)/C_{R,eq}\exp[(1-\alpha)nF\eta\,/RT]\}$$

$$= i_c - i_a$$

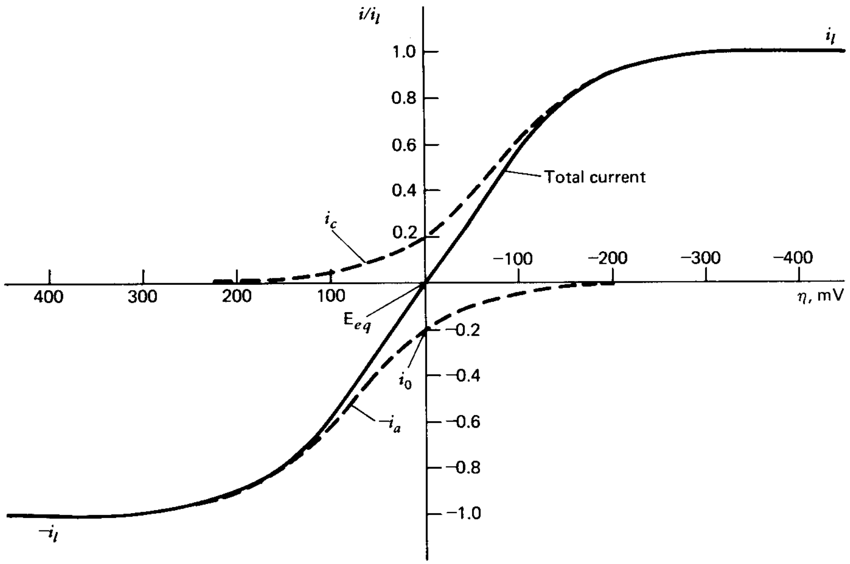
Where i_0 = exchange current

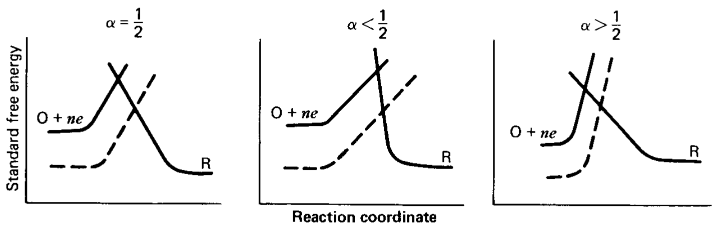
i_c = cathodic current

i_a = anodic current

α = transfer coefficient

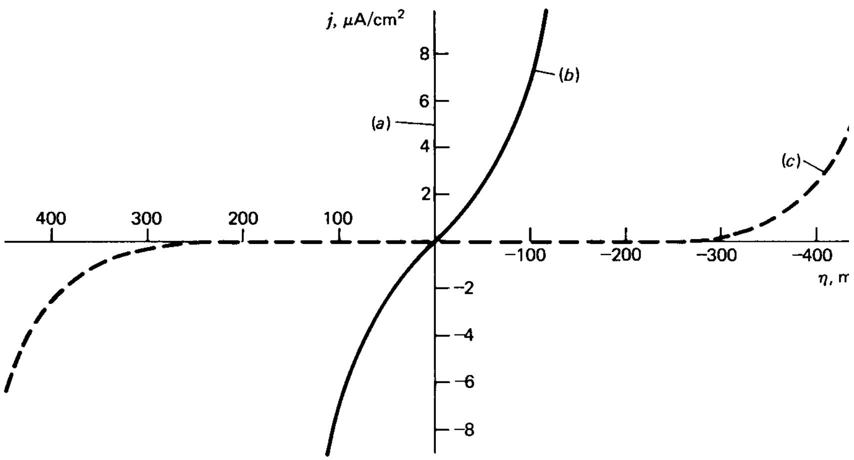
$\eta = E - E_{eq}$ = overpotential

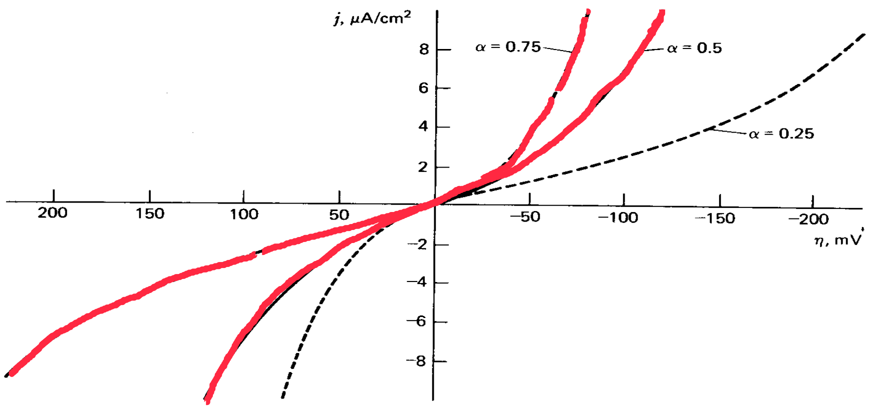




A. J. Bard and L. R. Faulkner, "Electrochemical Methods - Fundamentals and Applications"

1. $I = I_0[\exp(-\alpha_c nF\eta/RT) - \exp(\alpha_a nF\eta/RT)]$





A. J. Bard and L. R. Faulkner, “Electrochemical Methods - Fundamentals and Applications”

Butler Volmer Equation

1. At low overpotential region (called "polarization resistance", i.e., when $E \approx E_{eq}$), where the Butler–Volmer equation simplifies to:

$$i = i_0 \frac{nF}{RT}(E - E_{eq})$$

2. At the high overpotential region, where the Butler–Volmer equation simplifies to the Tafel equation:

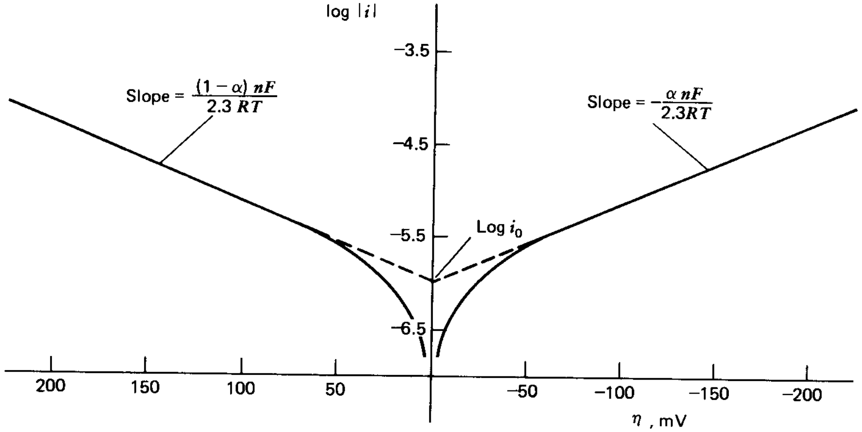
(a)for a cathodic reaction, when $E \ll E_{eq}$,

$$E - E_{eq} = a + b\log(i)$$

or

(b) for an anodic reaction, when $E \gg E_{eq}$

$$E - E_{eq} = a - b\log(i)$$



A. J. Bard and L. R. Faulkner, "Electrochemical Methods - Fundamentals and Applications"

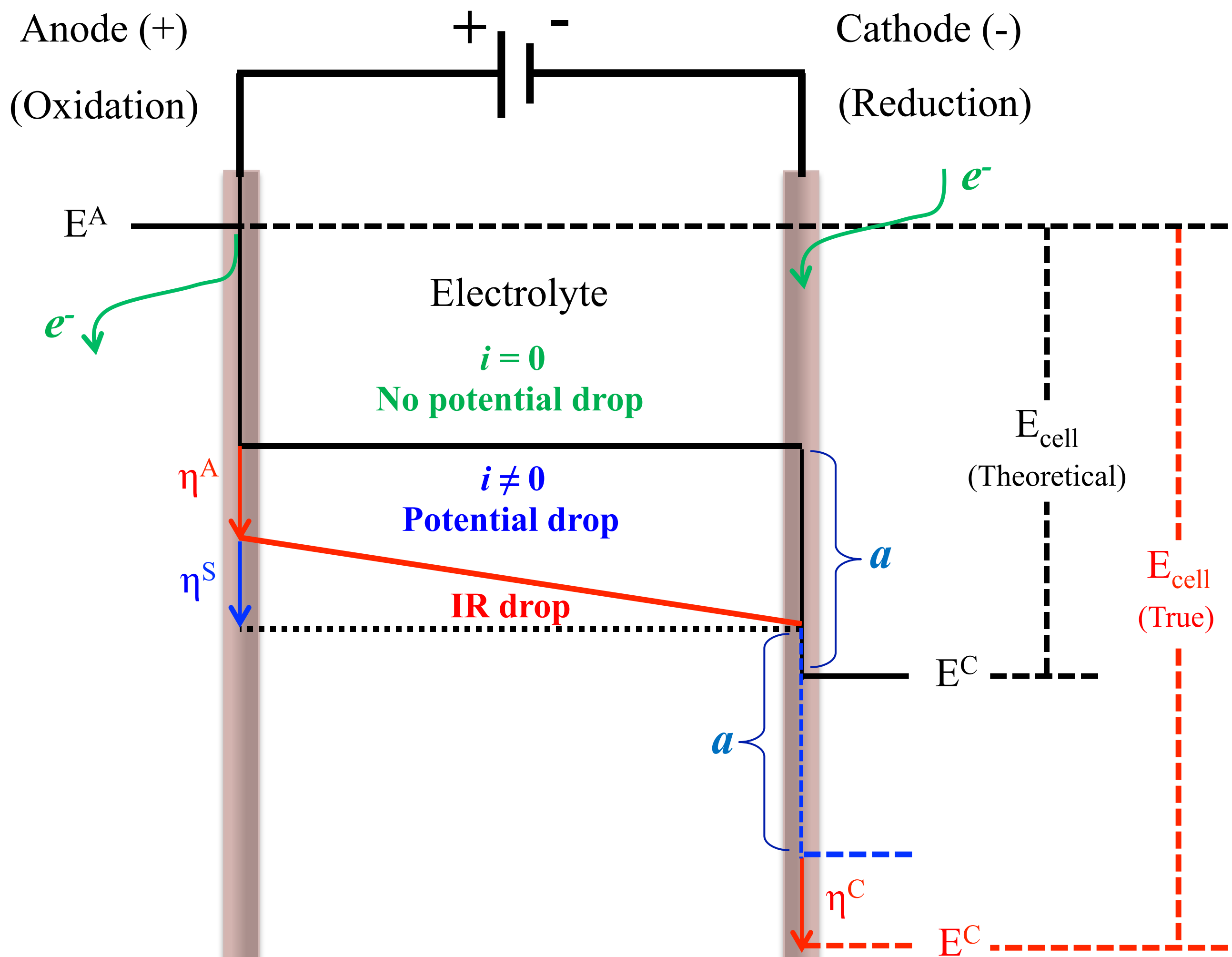
Basic Terminology (II)

1. Equilibrium potential (E_{eq})
2. Open circuit potential (OCP)
3. Exchange current density (i_o)
4. Transfer coefficient (Symmetric factor) (α)
5. Overpotential s
6. Charge transfer (activation) overpotential or polarization (η_{ct} or η_a)
7. Concentration overpotential or polarization (η_c)
8. Ohmic overpotential or polarization (η_Ω)

Potential Drop in Electrolytic cell

Electrolytic cell (ΔG>0)

Potential drop (overpotential)

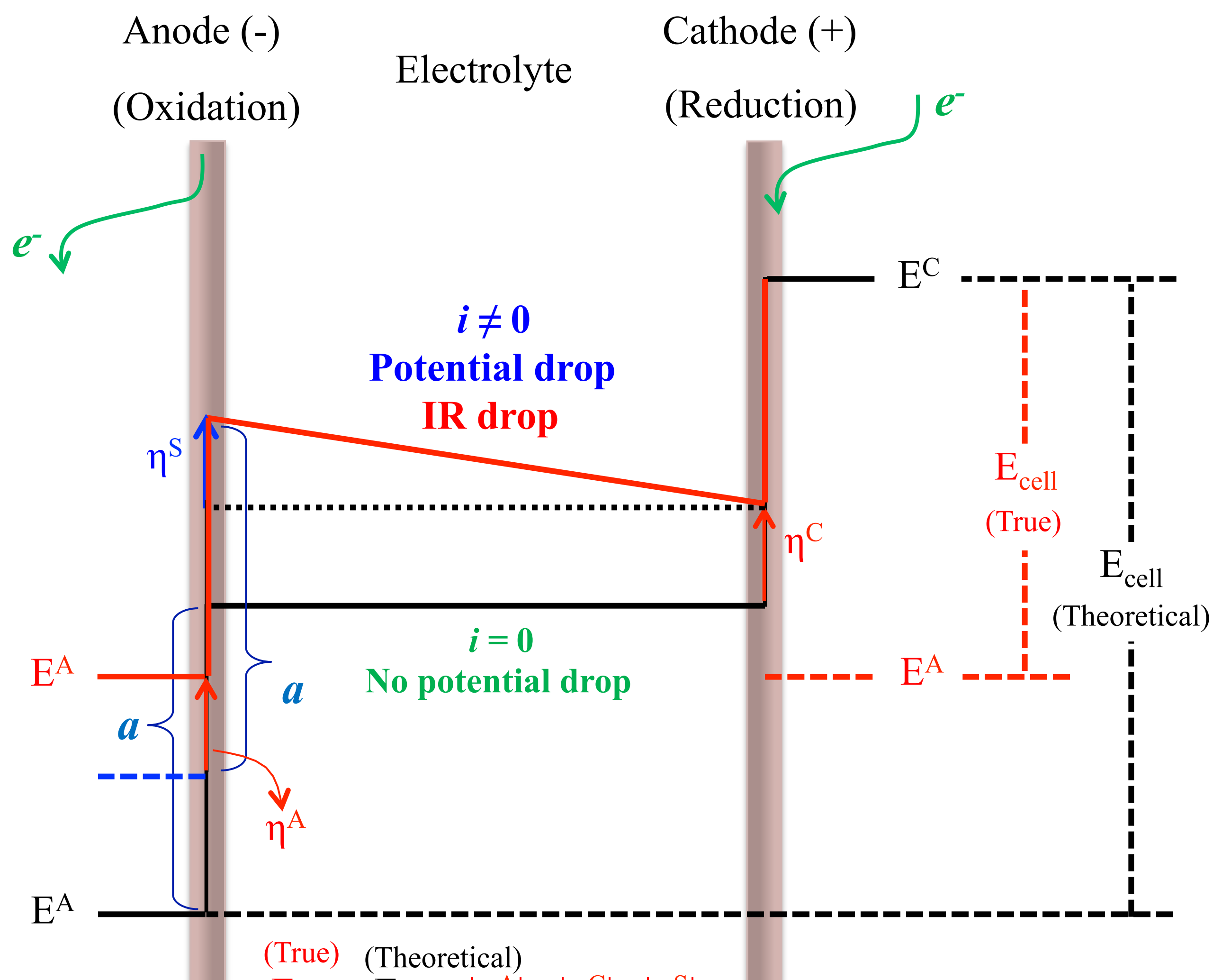


$$|E_{cell}^{(True)}| = |E_{cell}^{(Theoretical)}| + |\eta^A| + |\eta^C| + |\eta^S| = f(i)$$

Potential Drop in Galvanic cell

Galvanic cell (ΔG<0)

Potential drop (overpotential)



(True) (Theoretical)

$$E_{cell} = E_{cell} - |\eta^A| - |\eta^C| - |\eta^S|$$

Kinetic parameters of electrode reactions

Kinetic parameters of electrode reactions

Reaction	Solution	Electrode	α	$k^{o\prime}$/m s^{-1}
$Fe^{3+}(aq) \underset{}{\overset{\pm e^-}{\rightleftarrows}} Fe^{2+}(aq)$	0.5 M $HClO_4$	Pt	0.50	9×10^{-8} at 25°C
$Fe^{3+}(aq) \overset{\pm e^-}{\rightleftarrows} Fe^{2+}(aq)$	1.0 M HCl	C	0.59	1.2×10^{-6} at 21°C
$Ce^{4+}(aq) \overset{\pm e^-}{\rightleftarrows} Ce^{3+}(aq)$	1.0 M H_2SO_4	C	0.28	3.8×10^{-6} at 25°C
$V^{III}(aq) \overset{\pm e^-}{\rightleftarrows} V^{II}(aq)$	1.0 M $HClO_4$	Hg	0.52	3.2×10^{-5} at 20°C
$MnO_4^-(aq) \overset{\pm e^-}{\rightleftarrows} MnO_4^{2-}(aq)$	1.0 M KOH	Pt	–	1.2×10^{-6} at 20°C
$Ag^+(aq) \overset{\pm e^-}{\rightleftarrows} Ag(s)$	1.0 M $HClO_4$	Ag	–	2×10^{-4} at 25°C
$Fe(CN)_6^{3-}(aq) \overset{\pm e^-}{\rightleftarrows} Fe(CN)_6^{4-}(aq)$	1.0 M KNO_3	Pt	0.49	6.6×10^{-4} at 35°C

Multistep mechanisms

$$i = i_0 \left[\frac{C_O}{C_O^*} e^{-\alpha n f \eta} - \frac{C_R}{C_R^*} e^{(1-\alpha) n f \eta} \right]$$

$O + ne = R$ (simple one step)

$Fe(CN)_6^{3-} + e = Fe(CN)_6^{4-}$

$Te^+ + e \overset{Hg}{=} Hg$

Multi-step rxns

$Ag^+ + e = Ag$

$2H^+ + 2e = H_2$

$H^+ + e = H_{ads}$ (E)

$H_{ads} + H_{ads} = H_2$ (C)

$H_{ads} + H^+ + e = H_2$

Rate determining electron transfer

Overall rxn

$$O + ne = R$$

r_1: $O + n'e \rightleftharpoons O'$

r_2: $O' + e \rightleftharpoons R'$ (RDS)

r_3: $R' + n''e \rightleftharpoons R$

$$O + (1 + n' + n'')e \rightleftharpoons R$$

($1 + n' + n'' = n$)

i_t: $i_1 = n' i_{rds}$, i_{rds}, $i_3 = n'' i_{rds}$

$$i_t = (1 + n' + n'') i_{rds}$$

psedo steady-state assumption

$$i_{rds} = nFA k^0_{rds} \left[C_{O'}(0,t) e^{-\alpha f (E - E^{0'}_{rds})} - C_{R'} e^{(1-\alpha) f (E - E^{0'}_{rds})} \right]$$

Multi-step process at equilibrium

$r_1 = k_1^0 \cdots \Rightarrow \frac{r_1}{k_1^0} \to 0$

$\parallel$

$r_2 = k_{rds}^0 \cdots$

$\parallel$

$r_3 = k_3^0 \cdots\cdots \qquad \frac{r_3}{k_3^0} \to 0$

$k_1^0, k_3^0 \gg k_{rds}^0$

$R' + n''e = R$

$O + n'e \rightleftarrows O'$

$$E_{eq} = E_1^{0'} + \frac{RT}{n'F} \ln \frac{C_O}{C_{O'}}$$

$$C_{O'} = C_O \, e^{-(E_{eq} - E_1^{0'}) n'F/RT}$$

$$C_{R'} = C_R \, e^{(E_{eq} - E_3^{0'}) n''F/RT}$$

$$C_R = C_{O'} \, e^{-(E_{eq} - E_{rds}^{0'}) F/RT}$$

Nernstian Multistep processes

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$$i = nF\overset{A}{\vee}k^{0}_{rds}\Big[C_O\, e^{-(E-E_1^{0'})n'F/RT - \alpha F(E-E^{0'}_{rds})/RT}$$

$$C_O\, e^{-(n'+\alpha)FE/RT + (n'E_1^{0'} + \alpha E^{0'}_{rds})F/RT}$$

$$- C_R\, e^{(E-E_3^{0'})n''F/RT + (1-\alpha)F(E-E^{0'}_{rds})/RT}\Big]$$

$$C_R\, e^{(n''+(1-\alpha))FE/RT - (n''E_3^{0'} + (1-\alpha)E^{0'}_{rds})F/RT}$$

Formal potential $E = E^{0'}$

$$C_O = C_R = 1$$

$$E^{0'} = \frac{E^{0'}_{rds} + n'E_1^{0'} + n''E_3^{0'}}{n}$$

$$O + ne = R$$

$$i = nFA[k_f C_O - k_b C_R]$$

Quasi-reversible and Irreversible Multi-step processes

$$i = i_0 \left[\frac{C_O}{C_O^*} e^{-(n'+\alpha) f \eta} - \frac{C_R}{C_R^*} e^{(n''+1-\alpha) f \eta} \right]$$

$$O + n'e \rightleftharpoons O'$$

$$\text{(RDS)} \quad O' + e \rightleftharpoons R'$$

$$R' + n''e \rightleftharpoons R$$

$$O + n'e - O' = 0 \quad \text{zero}$$

$$O' + \alpha e \rightleftharpoons R' + (1-\alpha)e$$

$$0 = R - R' - n''e$$

$$O + (n'+\alpha) e = R - (n''+1-\alpha)e$$

(C) $O \rightleftharpoons O'$

(E) $O' + e \rightleftharpoons R'$ (RDS)

(E) $R' + n'' e \rightleftharpoons R$

$O - O' = \Theta$

$O' + \alpha e = R' - (1-\alpha) e$

$\Theta = R - R' - n'' e$

$O + \alpha e = R - (n''+1-\alpha) e$

$$i = i_0 \left[\frac{C_O}{C_O^*} e^{-\alpha f \eta} - \frac{C_R}{C_R^*} e^{(n''+1-\alpha) f \eta} \right]$$

General rules to derive kinetic equation

Key steps to derive the kinetic equations for a complex reaction

(1) Write down the rate determining step.

(2) Each of the mechanistic steps that precedes the rds is in equilibrium.

(3) Conversely, rewrite all the steps that follow the rds by transferring, with a sign change, all the species from the left-hand side to the right hand side.

(4) Leaving the rds unmodified, multiply each of the other equations, if necessary, by a small integer such that the intermediates will disappear when rule (V) below is implemented.

(5) Add the equations to generate the stoichiometric equation.

Complex electrode reactions

Overall reaction

$$O + P + 2e = 3R$$

ECEC mechanism

$$O + e = W$$

$$W + P = V + R$$

$$V + e = 2U \quad \text{(rds)}$$

$$U = R$$

Kinetic equations

$$O - W + e =$$

$$W + P - V - R =$$

$$V + \alpha e = 2U - (1-\alpha)e \quad (rds)$$

$$= 2R - 2U$$

They sum to

$$O + P - R + (1+\alpha)e = 2R - (1-\alpha)e$$

$i =$

$$2Fk[(C^s{}_R)^2/C^o \exp\{(1-\alpha)nF(E-E^{o'})/RT\} - C^s{}_O C^s{}_P/C^s{}_R \exp\{(-(1+\alpha)nF(E-E^{o'})/RT$$