Electrode Kinetics
Background

• Consider the reaction given below:

\[ \text{A} \quad \text{↔} \quad \text{B} \quad (1) \]

• Let $k_f$ and $k_b$ are the rate constants of the forward and backward reactions
Reaction rates

• Rate of the forward reaction is given by:

\[ R_f = k_f \times C_A \] (2)

• Rate of the backward reaction is given by:

\[ R_b = k_b \times C_B \] (3)
Net reaction rate

- The net rate of reaction is given by:

\[ R_{\text{net}} = R_f - R_b \]

- Thus, \( R_{\text{net}} \) can be written as:

\[ R_{\text{net}} = k_f \times C_A - k_b \times C_B \quad (4) \]
Equilibrium

Equilibrium is defined as the point at which the net reaction rate is zero

- From equation 4, we obtain an equilibrium concentration ratio

\[ \frac{k_f}{k_b} = K = \frac{C_B}{C_A} \quad (5) \]

- $K$ is a constant, and is called the equilibrium constant ($K$)
Requirement

Every kinetic theory requires that the kinetic equations collapse to thermodynamic relations at equilibrium

• Equation similar to (5) required of any kinetic theory
Thermodynamics vs. kinetics

• Thermodynamics provides a description of the behaviour at equilibrium
• Predicts whether a reaction is feasible (spontaneous),
• Information about the reaction rates is provided by kinetic equations
• For a kinetic expression to be valid, reduction to thermodynamic equations at equilibrium is essential
The Arrhenius theory

- Rate constants vary with temperature (generally increase with T)
- Most common relationship between rate constant (k) and temperature is of the form:

\[ k = A e^{-\frac{E_a}{RT}} \]  

- \( E_a \) - activation energy
- \( R \) - gas constant.
- \( A \) - pre exponential factor
Activation energy

• Above relationship - called Arrhenius relationship

• **Activation energy**: Energy barrier that has to be surmounted by the reactants before they can be converted to product

• Larger the activation energy - more energy needed by reactants to surmount barrier
Significance

\[ k = A e^{-\frac{E_a}{RT}} \] (6)

• Exponent term \( (e^{-\frac{E_a}{RT}}) \) - a probabilistic feature - represents the probability that the energy barrier will be surmounted.

• Pre exponential factor \((A)\) - represents the number of attempts made at surmounting the barrier - also called the frequency factor
Activation energy

![Diagram of reaction energy profile showing reactants, activation energy (E_a), and products.
Requirements of kinetic theories

• Consider the general reversible electrode reaction

\[ \text{O} + n\text{e} = \text{R} \] (7)

with \( k_f \) and \( k_b \) as the forward and backward reaction rate constants

• This is a typical redox reaction

Note that \( \text{O} \) and \( \text{R} \) stand for Oxidized state and Reduced state respectively
For this reaction, the equilibrium state is governed by the Nernst equation - See section on thermo:

\[ E_{eq} = E^\circ - \frac{RT}{nF} \ln \left( \frac{C_R^*}{C_O^*} \right) \]  (8)

Relates the equilibrium potential of the electrode (\(E_{eq}\)) to the concentration of the reactants and products (O and R)
Any electrode kinetics theory must reduce to the Nernst equation when equilibrium conditions are placed upon it - 1st requirement of an electrode kinetic theory
E vs. i

- Electrode kinetic theory - must provide information about the dependence of current on electrode potential

- When a current is passed, some electrochemical change occurs at the electrode
Overvoltage

• Due to irreversibility - sustaining a given current requires that a penalty be paid in terms of electrode potential – penalty called overvoltage

$$\eta = E_{eq} - E \ (9)$$

$E_{eq}$ - expected (equilibrium) electrode potential
$E$ - actual electrode potential
Tafel equation

• Experimental observation: At low currents, the current is exponentially related to the overpotential

\[ \eta = a + b \log i \] (10)

• \(a\) and \(b\) are constants, \(i\) is the current density
• Called the Tafel equation
• Any successful electrode kinetic theory must also explain Tafel behaviour – 2\textsuperscript{nd} requirement of an electrode kinetic theory
Recap

1. Any electrode kinetics theory must reduce to the Nernst equation when equilibrium conditions are placed upon it.
2. Any electrode kinetic theory must also explain Tafel behaviour.
3. Rate equations must reduce to the Nernst and Tafel equations when the appropriate conditions are introduced.
Kinetics of Electrode Reactions
Rates of forward and backward reaction

\[ O + ne = R \quad (7) \]

- For the above reaction, the rate of the forward reaction is given by:

\[ R_f = k_f \ C_O (0, t) = \frac{i_c}{nF} \quad (11) \]

Where \( C_O (0, t) \) is the surface concentration of O

- Similarly the rate of the backward reaction is given by:

\[ R_b = k_b \ C_R (0, t) = \frac{i_a}{nF} \quad (12) \]

Recall that reaction rate and current are interlinked – also recall that reduction occurs at the cathode and oxidation at the anode
Net reaction rate

- The net reaction rate (and hence the net current) is given by

\[ R_{\text{net}} = R_f - R_b = \frac{i}{nF} = \frac{[i_c - i_a]}{nF} \]

\[ = [k_f C_O (0, t) - k_b C_R (0, t)] \] (13)
Potential dependence of $k_f$ and $k_b$

- Both $k_f$ and $k_b$ are potential dependent functions.
- The forward reaction (a reduction) is an electron accepting process - the rate increases as the electrode potential becomes more negative.
- This is because the electrode can give away electrons more easily.
• The opposite trend is seen for the backward (oxidation) reaction - the rate increases as the electrode potential becomes more negative

This potential dependence needs to be qualified to obtain a true picture of electrochemical kinetics
Potential dependence of $k_f$ and $k_b$

Value of $k$

More positive $E$
At equilibrium

• It is possible to adjust the electrode potential and O and R concentrations make net reaction rate zero. At this point:

\[ i_c = i_a ; R_f = R_b \] (14)

In other words:

\[ k_f \ C_O (0, t) = k_b \ C_R (0, t) \] (15)
Relating the rate constants to potential

- Rearranging equation 15, and taking logarithms on both sides:

\[ \ln (k_b) - \ln (k_f) = \ln \left[ \frac{C_O (0, t)}{C_R (0, t)} \right] \] (16)

- Equation 16 is stated under conditions of equilibrium (zero net current)
- Therefore, invoking the Nernst equation:

\[ \ln (k_b) - \ln (k_f) = \ln \left[ \frac{C_O (0, t)}{C_R (0, t)} \right] = \frac{F}{RT} (E - E^\circ) \] (17)
• Differentiation of eqn 17 with respect to E (first and last terms only) yields:

$$\frac{RT}{F} \left[ \frac{d}{dE} \{\ln (k_b)\} + \frac{d}{dE} \{\ln (1/k_f)\} \right] = 1 \quad (18)$$

$$1-\alpha + \alpha = 1$$

• The two terms on the left sum up to one - are called symmetry factors in the case of an one electron transfer reaction.
Symmetry factors

\[ \alpha = \frac{1}{2} \] \[ \alpha < \frac{1}{2} \] \[ \alpha > \frac{1}{2} \]

\( \alpha \) as an indicator of the symmetry of the energy barrier – the dashed lines show the shift in the curve for O + e (reactants) as the potential is made more positive.
Reductive and oxidative symmetry factors

• The reductive symmetry factor - associated with the forward reaction - represented by the Greek alphabet $\alpha$

$$\frac{RT}{F} \frac{d}{dE} \{\ln \left( \frac{1}{k_f} \right) \} = \alpha \ (19)$$

• The oxidative symmetry factor therefore becomes $1 - \alpha$

$$\frac{RT}{F} \frac{d}{dE} \{\ln \left( k_b \right) \} = 1 - \alpha \ (20)$$
Significance

• The term $\alpha$ is a measure of the symmetry of the energy barrier

• If the effect of changing the potential is identical on both sides of the barrier, then $\alpha = 0.5 = 1 - \alpha$.

• Any asymmetry results in other (fractional) values of $\alpha$. 


Influence on kinetics

Will return to this picture after detailed understanding of kinetic expressions
Standard rate constants

• Equation 19 on integration gives:

\[ \ln \left( \frac{1}{k_f} \right) = \alpha \frac{FE}{RT} + c \quad (21) \]

• If \( k_f = k_f^\circ \) @ \( E = E^\circ \)

\[ k_f = k_f^\circ \, e^{-\left[ \frac{\alpha F}{RT} \right] \left( E - E^\circ \right)} \quad (22 - a) \]

Similarly:

\[ k_b = k_b^\circ \, e^{\left( (1-\alpha) F/RT \right) \left( E - E^\circ \right)} \quad (22 - b) \]
• $k_f^\circ$ and $k_b^\circ$ are termed the standard (or conditional) rate constants

• If the concentrations of O and R are equal, and the potential is maintained at $E^\circ$ to prevent current flow:

from equation 15, $k_f^\circ = k_b^\circ$

Can be replaced by a single symbol $k^\circ$. 
Significance of $k_0$

- $k^\circ$ - very important parameter in electrode kinetics.
- Measure of the “kinetic facility” of the redox couple –
- The larger the value of $k^\circ$, the faster equilibrium will be attained.
- Systems with small standard rate constants are typically sluggish
• The standard rate constant is large for simple redox couples

• e.g.: reactions involving a single electron transfer – such as:

\[ \text{H}_2 = 2 \text{H}^+ + 2e \]

in a PEM fuel cell.

• The largest measured values of these constants are on the order of 1-10 cm/s.
• These values drop rapidly with increasing reaction complexity, and can be as lower as $10^{-9}$ cm/s in certain cases.

$$\text{O}_2 + 4 \text{H}^+ + 4\text{e} = \text{H}_2\text{O}$$

• The oxygen reduction reaction - a 4 electron process - has a lower value of $k^\circ$ than the hydrogen oxidation reaction – increased complexity
Sluggish cathode kinetics

- $k^\circ$ for oxygen reduction $\ll k^\circ$ for hydrogen oxidation
- Note however that forward and backward rate constants can still be large

\[
k_f = k^\circ \ e^{- \left[ \frac{\alpha F}{RT} \right] (E - E^\circ)} \quad (22-a)
\]

\[
k_b = k^\circ \ e^{\left[ (1-\alpha) \frac{F}{RT} \right] (E - E^\circ)} \quad (22-b)
\]

- Thus, for small $k^\circ$ s, need a larger overpotential to maintain a given $k$
- Larger overpotential – lower net cell voltage - less efficient fuel cell

Urgent need to improve oxygen reduction kinetics – increase $k^\circ$
The Butler – Volmer Theory
End Result

\[ i = nF \, k^o \, [C_O (0, t) \, e^{- [\alpha nF/RT] (E-E^o)}] \]

\[ - \, C_R (0, t) \, e^{[(1-\alpha)nF/RT] (E-E^o)}} \]  (25)

(n – stands for no. of electrons transferred)

This formulation is called the Butler – Volmer formulation of electrode kinetics

• Note – two components (anodic and cathodic) of current
• Note – exponential dependence on potential
Typical V-I relationship
Derivation

• Writing an expression for net reaction rate:

\[ R_{\text{net}} = \frac{i}{nF} = [k_f \ C_O (0, t) - k_b \ C_R (0, t)] \] (23)

• Thus:

\[ i = nF [k_f \ C_O (0, t) - k_b \ C_R (0, t)] \] (24)
Substituting the values for $k_f$ and $k_b$ from 22 in 23:

$$i = nF k^o [C_O (0, t) e^{- \frac{anF}{RT} (E-E^o)}]$$

$$- C_R (0, t) e^{\left\{\left[(1-\alpha)nF/RT\right](E-E^o)\right\}}$$ (25)

n – stands for no. of electrons transferred

This formulation is called the Butler – Volmer formulation of electrode kinetics
B-V Theory

• This formulation links four important parameters:
  - Faradaic current
  - Electrode potential
  - Concentration of reactant
  - Concentration of product.
At equilibrium

Equation 25 can be rewritten (after some arithmetic) as:

\[ C_0 (0, t) - C_R (0, t) \ e^{\left[ \frac{nF}{RT} (E-E^\circ) \right]} = \left[ \frac{i}{nF \ k^\circ} \right] \ e^{\left[ \frac{\alpha nF}{RT} (E-E^\circ) \right]} \] (26)

- At equilibrium, \( i = 0 \)
- Right hand side (R.H.S) = 0
- L.H.S. rearranges to give the Nernst equation
Tafel kinetics

• For very large overpotentials ($\eta = E - E^\circ$), one or the other of the exponents on the R.H.S. of equation 25 goes to zero

• Depending on whether the overpotential is positive or negative, either the cathodic or anodic component vanishes

• B-V formulation reduces to the form:

$\eta = a + b \log i$ (27)
• Thus the B-V formulation satisfies the following requirements:

  - Reduces the Nernst equation at equilibrium
  - Explains Tafel behaviour

Has the makings of a good electrode kinetics theory
The exchange current

Current that flows (equal magnitude in opposite directions) at equilibrium

• Recall - at equilibrium - net current is zero
• Also - surface concentrations of O and R = bulk concentrations

\[ i = nF \, k^\circ \, [C_O(0, t) \, e^{-[\alpha nF/RT](E-E^\circ)}] - C_R(0, t) \, e^{[(1-\alpha)nF/RT](E-E^\circ)} \] (25)

Now becomes:

\[ nFk^\circ C_O \, e^{-[\alpha nF/RT](E_{eq}-E^\circ)}} = nFk^\circ C_R \, e^{[(1-\alpha)nF/RT](E_{eq}-E^\circ)}} \] (28)
• Eqn. 28 reduces to:

\[ e^{\frac{nF}{RT}[E_{eq}-E^\circ]} = \frac{C_O^*}{C_R^*} \]  \hspace{1cm} (29)

• Restatement of the Nernst equation (8)
• Though the net current is zero, faradaic activity is still in progress at the electrode surface

An equal magnitude of anodic and cathodic current flows
This current density is referred to as the exchange current ($i_o$)

- Thus the exchange current may be written as:

\[
i_o = nFk^\circ C_0 \cdot e^{\left[-\frac{\alpha nF}{RT} (E_{eq} - E^\circ)\right]} \quad (30)
\]
\[ e^{(nF/RT)(E_{eq}-E^\circ)} = C_O^*/C_R^* \quad (29) \]

- Raise both sides of equation 29 to the power \(-\alpha\), substitute for the term \(e^{-\left[\alpha nF/RT\right](E_{eq}-E^\circ)}\) to yield:

\[ i_0 = nFk^\circ C_O^{*(1-\alpha)} C_R^{*\alpha} \quad (31) \]

- In the case where \(C_O^* = C_R^* = C\):

\[ i_0 = nFk^\circ C \quad (32). \]
Significance of $i_o$

- $i_o$ is directly proportional to the standard rate constant $k^o$
- Frequently used as an important kinetic parameter in place of $k^o$

Ideally, one would like to have as high an exchange current density as possible for fast kinetics
Effect of exchange current density on kinetics

Const. $\alpha$ (0.5);
(a) $i_0 = 10^{-3}$ A/cm$^2$; (b) $i_0 = 10^{-6}$ A/cm$^2$; (c) $i_0 = 10^{-9}$ A/cm$^2$
Current – overpotential equation

• Especially convenient - provides direct relationship between current and overpotential \((E - E_{eq})\)
• Unlike earlier formulation (B-V), where the relationship was between the current and the quantity \((E - E^\circ)\)
• Uses \(i_o\) instead of \(k^o\)
Current – Overpotential eqn. - Derivation

- Dividing the current density (eqn. 25) by the exchange current density (eqn. 31), we have:

\[
\frac{i}{i_o} = \frac{[C_O (0, t) / C_O^*]e^{-\left(\alpha nF/RT\right) (E-E^o)}[ C_O^* / C_O^*]^{\alpha}}{- [C_R (0, t)/ C_R^*] e^{\left[(1-\alpha)nF/RT\right](E-E^o)}[ C_O^* / C_O^*]^{-\alpha}} (33)
\]

using equation 29 to substitute for \([ C_O^* / C_O^*]^{\alpha}\) and \([ C_O^* / C_O^*]^{-\alpha}\):

\[
\frac{i}{i_o} = \frac{[C_O (0, t) / C_O^*]e^{-\left(\alpha nF/RT\right) \eta}}{- [C_R (0, t)/ C_R^*] e^{\left[(1-\alpha)nF/RT\right]\eta}} (34)
\]

Where \(\eta = E - E_{eq}\)
Typical current – overpotential curve
Effect of exchange current density

Const. $\alpha$ (0.5);
(a) $i_0 = 10^{-3}$ A/cm$^2$; (b) $i_0 = 10^{-6}$ A/cm$^2$; (c) $i_0 = 10^{-9}$ A/cm$^2$
Effect of the transfer coefficient

\[ i_o = \text{const.} = 10^{-6} \text{ A/cm}^2 \]
Limiting cases

• No mass transport effects - surface and bulk concentrations are identical - their ratio equals unity

• The current – overpotential eqn. (34) becomes:

\[ i = i_0 \left[ e^{- \left( \alpha nF/RT \right) \eta} - e^{\left[ (1-\alpha)nF/RT \right] \eta} \right] \]  (35)

• Known as the Butler - Volmer equation

Used as a good approximation to eqn. 34 i is smaller than 10% of the smaller of the anodic or cathodic limiting currents
Limiting cases

• For very small values of x, the exponent $e^x$ is approximately equal to 1+x.

• For very small values of $\eta$ the B-V equation can be written in a linear form as:

$$i = -i_0 F \frac{\eta}{RT} \text{ (36)}$$

• Linear relation between current and overpotential

• Ratio of the two - units of resistance - called the charge transfer resistance ($R_{ct}$).

$$R_{ct} = -\frac{\eta}{i} = \frac{RT}{i_0 F} \text{ (37)}$$
Limiting cases

• Very large values of $\eta$:
• One of the exponents in eqn 35 goes to 0
• For large positive $\eta$:

$$i = i_0 \left[ e^{[(1-\alpha)nF/RT] \eta} \right] \quad (38)$$

which becomes:

$$\ln \left( \frac{i}{i_0} \right) = (1-\alpha)nF \eta /RT \quad (39)$$
• Eqn. 39 reduces to:

\[ \hat{\eta} = \frac{RT}{(1-\alpha)nF} \ln i - \frac{RT}{(1-\alpha)nF} \ln i_o \] (40)

• Fits the Tafel formulation (eqn. 10), with

\[ a = -\frac{RT}{(1-\alpha)nF} \ln i_o \] and \[ b = \frac{RT}{(1-\alpha)nF} \]

Such an approximation is only valid for a given oxidation or reduction component when the other component contributes 1% or less to the total current.
Tafel plots

• A plot of log i vs. η is called a Tafel plot
• Shown in Fig.
• Comprises an anodic branch and a cathodic branch
• Slopes of \((1- \alpha)nF/2.3 \text{ RT}\) and \(\alpha nF/2.3 \text{ RT}\) respectively

**Sharp deviation from linearity as η approaches zero** – due to breakdown of assumptions
Tafel plot

\[ \text{Slope} = \frac{(1 - \alpha) F}{2.3 RT} \]

\[ \text{Slope} = \frac{-\alpha F}{2.3 RT} \]

\[ \log |i| \]

\[ \log i_0 \]

\[ \eta, \text{ mV} \]
Mass transport effects

• Equations (35 – 40) assumed no mass transport effects

• Mass transport effects are frequently present in electrochemical systems

• Need for corrections to account for mass transport effects
Recall from the electrochemistry notes (eqn. 40):

\[ C(x=0)/C^* = [1 - (i/i_l)] \]

Where \( i_l \) is the limiting current
\[
i/i_o = [C_O (0, t) / C_O^*] e^{-\left[\alpha nF/RT\right] \eta}
- [C_R (0, t)/ C_R^*] e^{\left[(1-\alpha)nF/RT\right] \eta} \] (34)

- Incorporating limiting currents into eqn 34:

\[
i/i_o = [1 - (i/i_{l,c})] e^{-\left[\alpha nF/RT\right] \eta}
- [1 - (i/i_{l,a})] e^{\left[(1-\alpha)nF/RT\right] \eta} \] (41)

**Current –overpotential equation corrected for mass transfer effects**
Limiting cases

- Very small overpotentials, this equation can be linearized
- Need to apply Taylor's series expansion
- This yields (derivation omitted):

\[ \dot{\eta} = \left[ \frac{RTi}{nF} \right] \left( \frac{1}{io} + \frac{1}{i_{l,c}} - \frac{1}{i_{l,a}} \right) \] (42)

- Transport corrected analog of linearized B-V eqn.
• Recall: $RT/F_i^o$ represents the resistance to charge transfer (37)

• Thus, eqn. 42 can be rewritten as:

$$\eta = -i (R_{ct} + R_{mt,c} + R_{mt,a}) \quad (43)$$

• $R_{mt,c} + R_{mt,a}$ are mass transfer resistances at the cathode and anode
Interpretation of eqn. 43

• When $i_o >> i_{l,c}$ and $i_{l,a}$:
  - Overpotential occurs mainly due to mass transport effects even at very close to equilibrium
  - Kinetics of the system are very fast

• If the reverse is true:
  - Kinetics of the reaction is very slow
  - The overpotential close to equilibrium is due to poor charge transfer.
Limiting cases

• For very large overpotentials a Tafel like expression can be obtained

• For insignificant anode overpotentials:

\[
\frac{i}{i_0} = [1 - (i/i_{l,c})] \ e^{\left\{ - \left[ \frac{\alpha n F}{RT} \right] \ \eta \right\}} \quad (44)
\]
• Eqn. 44 on rearrangement gives:

\[ \eta = \frac{RT}{\alpha nF} \ln \left( \frac{i_0}{i_{l.c}} \right) + \frac{RT}{\alpha nF} \ln \left( \frac{i_{l.c} - i}{i} \right) \]  

(45)

• Equation can be used to fit a mass transport corrected Tafel plot

• Can be used to obtain kinetic parameters in systems having mass transport effects.