

# KJM 3110 Electrochemistry

## Chapter 7. Electrode reactions

With exercises

# Ch. 6 Summary

By contriving one of the electrodes to remain stable despite current flow, a cell voltage  $\Delta E$  may be expressed as the difference between the potential  $E$  of the working electrode and the constant potential  $E_{\text{RE}}$  of the reference electrode, so that

6:42

$$\Delta E = E - E_{\text{RE}}$$

- Activities:

$$E_n = E^\circ - \frac{RT}{nF} \ln \left\{ \frac{a_Z^{v_Z} a_Y^{v_Y}}{a_A^{v_A} a_B^{v_B}} \right\} \quad \text{for the reaction} \quad v_A A + v_B B + n e^- \rightarrow v_Z Z + v_Y Y \quad \text{Nernst equation}$$

- Concentrations and partial pressures:

$$E_n = E^{\circ'} - \frac{RT}{nF} \ln \left\{ \frac{c_Z^{v_Z} c_Y^{v_Y}}{c_A^{v_A} c_B^{v_B}} \right\} \quad \text{for the reaction} \quad v_A A + v_B B + n e^- \rightarrow v_Z Z + v_Y Y$$

- ISEs utilise potentials over ion selective membranes:

$$\phi^{\text{inner}} - \phi^{\text{outer}} = \frac{RT}{z_i F} \ln \left\{ \frac{a_i^{\text{outer}}}{a_i^{\text{inner}}} \right\} \quad \text{membrane potential difference}$$

# Status

- Till now, we have been introduced to electricity, chemistry and thermodynamics, electrochemical cells and their operating modes, electrolytic cells (electricity to chemical energy) and galvanic cells (chemical energy to electricity).
  - We have realised that the textbook may have been written 10-20 years ago.
- We have started to look at electrodes, the most important and unique place in electrochemistry.
- We have looked at the thermodynamics of electrodes, and ways to describe it in tables and graphs.
  - We have realised some unexpected takes on Gibbs energies in the textbook, that we don't have to agree on.
- We have looked at the use of thermodynamics in potentiometric electrodes, in particular ion selective electrodes (ISEs).

# Electrode reactions

- In chemistry (Ch. 2) we ask the following questions

What electrode reactions occurs?  $\Rightarrow$  Electrochemical stoichiometry

Why does the reaction occur?  $\Rightarrow$  Electrochemical thermodynamics

How fast does the reaction occur?  $\Rightarrow$  Electrochemical kinetics

How does the reaction occur?  $\Rightarrow$  Mechanisms of electrode reactions

- In electrochemistry we may ask the same
- Answers emerge in electrochemical terms
- In Ch. 7 – Electrode reactions – we address the two latter questions

# Exercise

- What is Faraday's law?
- The amount (number of moles) of any substance produced or consumed in an electrode reaction is proportional to the quantity of charge passed
  - *Michael Faraday, 1832*
  - Faradaic currents
- Non-faradaic currents: What may be their reasons?

# Coulometry

- Analysis of concentration of a reactant species in a finite volume at fixed voltage

- The total charge converted is  $Q = -nFVc_i / v_i$

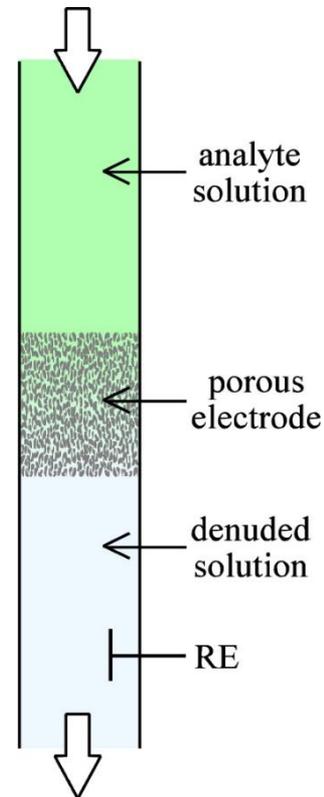
- $v_i$  is the number of molecules involved

- Integrated form:

$$c_i = \frac{v_i Q}{nFV} = \frac{v_i}{nFV} \int_0^{t_{\infty}} I dt$$

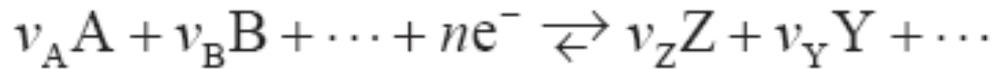
- Flowing coulometry

- Limiting current at given flow and fixed voltage



# Reaction

- General reaction

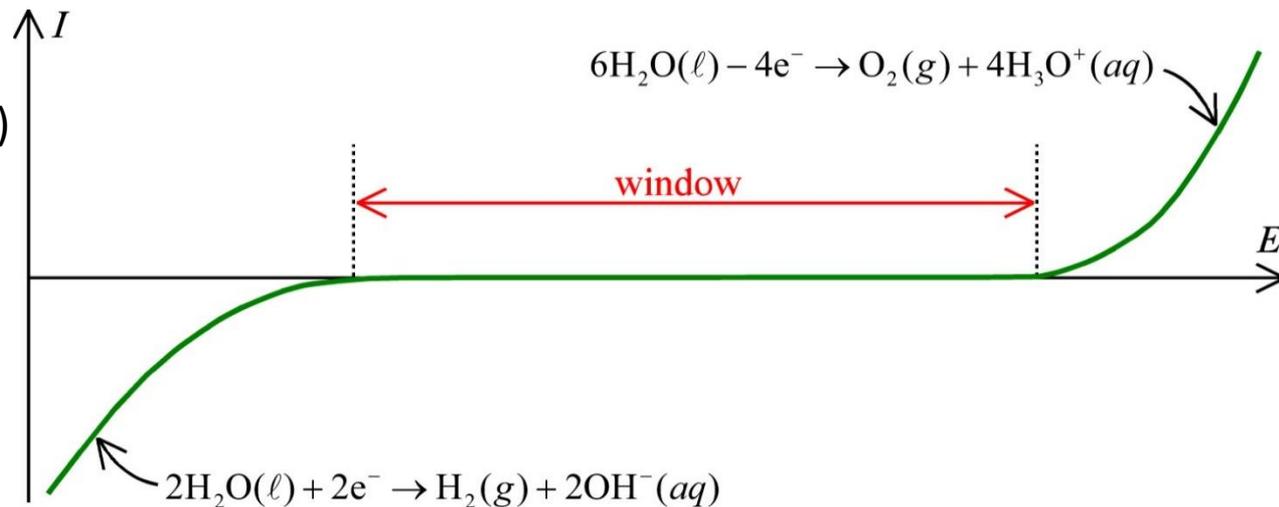
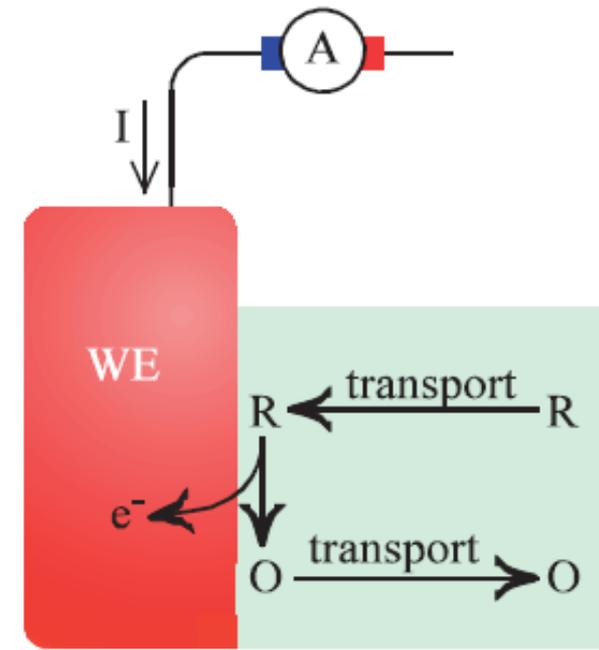


- Sign of  $n$  signifies cathodic and anodic direction
- Faraday's law:

$$\left\{ \begin{array}{l} \text{quantity of charge passed} = Q \\ \text{amount of Z produced} = n_Z^{\text{final}} - n_Z^{\text{initial}} = \Delta n_Z = -v_Z Q / nF \propto Q \\ \text{amount of A consumed} = n_A^{\text{initial}} - n_A^{\text{final}} = -\Delta n_A = -v_A Q / nF \propto Q \end{array} \right.$$

# A sustainable electrode reaction of study or use must have ...

- an adequate supply of reactants
  - Transport (mass transport)
- an adequate removal of products
- sufficient kinetics of the electrode reaction
- Conductive pathway for ions
  - Supporting electrolyte
- A potential window where it dominates alone
  - Totally polarized
  - Example: Au in  $\text{KNO}_3(\text{aq})$



# The Butler-Volmer equation

- Now, the book takes us through a derivation of the BV equation.
- It is as important as it is difficult, and there are as many versions and understandings as there are uses of it.
- It is difficult to derive, and many approaches to making it simpler.
- The book is one.
- Let us first take a look at the end result - what we will derive. Can we understand it qualitatively and does it makes sense even before we do it in more depth?

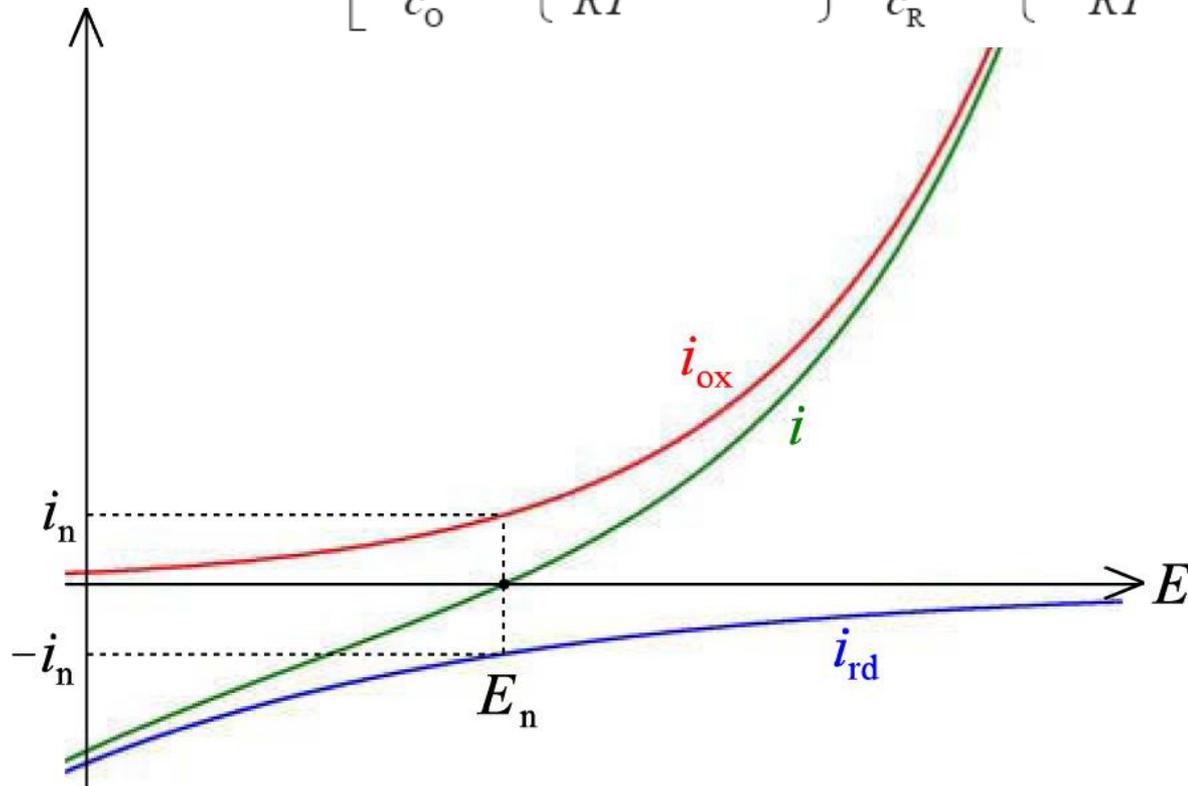
# Kinetics of electrode reaction – Butler-Volmer

- Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

- Butler-Volmer: 
$$\frac{I}{A} = i = Fk^{o'} \left[ -c_O^s \exp\left\{\frac{-\alpha F}{RT}(E - E^{o'})\right\} + c_R^s \exp\left\{\frac{(1-\alpha)F}{RT}(E - E^{o'})\right\} \right]$$

s = surface  
b = bulk

$$i = i_n \left[ -\frac{c_O^s}{c_O^b} \exp\left\{\frac{-\alpha F}{RT}(E - E_n)\right\} + \frac{c_R^s}{c_R^b} \exp\left\{\frac{(1-\alpha)F}{RT}(E - E_n)\right\} \right]$$



# Exercise

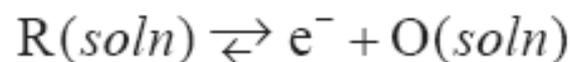
- Clarify as many as possible of the terms and behaviours of the two versions of the BV equations, and note the ones you don't understand.

# Kinetics of electrode reaction – rate and current

- For single electron transfer we will now derive the Butler-Volmer equation

- Simplest possible *oxidation* reaction

Reduced species                      Oxidised species



- *Net forward* oxidation reaction rate

$$v_{\text{net}}(E) = v_{\text{ox}}(E) - v_{\text{rd}}(E)$$

- Current density of electron production

$$\frac{i(E)}{F} = v_{\text{net}}(E) = v_{\text{ox}}(E) - v_{\text{rd}}(E)$$

- Definition: An *anodic* current (*oxidation*) at a working electrode (WE) is *positive*.

- Oxidation rate

$$v_{\text{ox}}(E) = k_{\text{ox}}(E)a_{\text{R}}^s = k_{\text{ox}}(E)\gamma_{\text{R}}c_{\text{R}}^s / c^{\circ} = k'_{\text{ox}}(E)c_{\text{R}}^s$$

- (All potential dependent)

## Exercise

$$v_{\text{ox}}(E) = k_{\text{ox}}(E)a_{\text{R}}^{\text{s}} = k_{\text{ox}}(E)\gamma_{\text{R}}c_{\text{R}}^{\text{s}}/c^{\circ} = k'_{\text{ox}}(E)c_{\text{R}}^{\text{s}}$$

- Draw the electrode (half cell) with reactants and products
- What are the units of the variables in the equations on the last slide?
- What are  $K_{\text{ox}}$  and  $K'_{\text{ox}}$  exactly?
- What determines  $K_{\text{ox}}$ ?
- What is it if  $E = 0$ ?
- Why and how does it vary with  $E$ ?

# Kinetics of electrode reaction - equilibrium

- Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

$$v_{ox}(E) = k_{ox}(E)a_R^s = k_{ox}(E)\gamma_R c_R^s / c^o = k'_{ox}(E)c_R^s$$

- Oxidation rate

- Reduction rate

$$v_{rd}(E) = k'_{rd}(E)c_O^s$$

- Substitute into the net current density:

$$v_{net}(E) = v_{ox}(E) - v_{rd}(E)$$

$$\frac{i(E)}{F} = v_{net}(E) = v_{ox}(E) - v_{rd}(E)$$

$$\frac{i(E)}{F} = k'_{ox}(E)c_R^s - k'_{rd}(E)c_O^s$$

- At equilibrium (open circuit, null condition):

$$0 = k'_{ox}(E_n)c_R^b - k'_{rd}(E_n)c_O^b$$

- Nernst:  $E_n = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{c_R^b}{c_O^b} \right\}$  becomes

$$E_n = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{k'_{rd}(E_n)}{k'_{ox}(E_n)} \right\}$$

# Exercise

- What are  $E_n$  (the null, or open circuit, or equilibrium potential) and  $E^\circ$  (the “formal” potential) exactly?
- What is the significance of the prime (‘) throughout here?
- We have seen that the mass action quotient  $Q$  can be expressed by different parameters, like
  - Activity, or concentration
  - Rate constant
  - More?
- Discuss how this works for normal chemical reactions and for electrochemical reactions.

# Kinetics of electrode reaction – formal rate constant

- Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

- Nernst:  $E_n = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{c_R^b}{c_O^b} \right\}$  becomes  $E_n = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{k'_{rd}(E_n)}{k'_{ox}(E_n)} \right\}$

- Similar for any potential:  $E = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{k'_{rd}(E)}{k'_{ox}(E)} \right\}$

One sees that at the formal potential  $E^{o'}$  the two rate constants are equal; this common value is given the symbol  $k^{o'}$  and the name **formal rate constant**<sup>720</sup>:  $k^{o'} = k'_{rd}(E^{o'}) = k'_{ox}(E^{o'})$ .

- Formal rate constant  $k^{o'}$  vs standard rate constant  $k^\circ$

# Kinetics of electrode reaction – transfer coefficients

- Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

- Rearrange  $E = E^{o'} - \frac{RT}{F} \ln \left\{ \frac{k'_{rd}(E)}{k'_{ox}(E)} \right\}$  to  $\frac{RT}{F} \ln \left\{ \frac{k^{o'}}{k'_{rd}} \right\} + \frac{RT}{F} \ln \left\{ \frac{k'_{ox}}{k^{o'}} \right\} = E - E^{o'}$

$$7:23 \quad \frac{RT}{F} \frac{d}{dE} \ln \left\{ \frac{k^{o'}}{k'_{rd}} \right\} + \frac{RT}{F} \frac{d}{dE} \ln \left\{ \frac{k'_{ox}}{k^{o'}} \right\} = 1$$

The first left-hand term in 7:23 is named the **reductive transfer coefficient** and represented by the symbol<sup>721</sup>  $\alpha$ . The second left-hand term is the **oxidative transfer coefficient**, which the equation shows to equal  $1 - \alpha$ . Thus

$$7:24 \quad \alpha = \frac{RT}{F} \frac{d}{dE} \ln \left\{ \frac{k^{o'}}{k'_{rd}} \right\} \quad \text{and} \quad 1 - \alpha = \frac{RT}{F} \frac{d}{dE} \ln \left\{ \frac{k'_{ox}}{k^{o'}} \right\}$$

whence on integration<sup>722</sup>

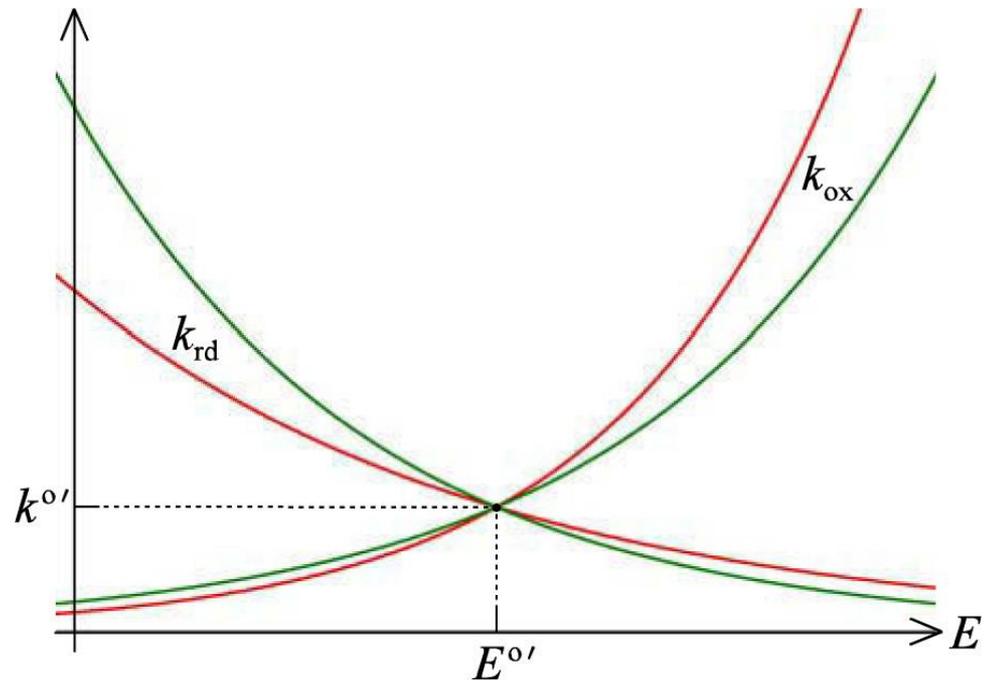
$$7:25 \quad k'_{rd} = k^{o'} \exp \left\{ \frac{-\alpha F}{RT} (E - E^{o'}) \right\} \quad \text{and} \quad k'_{ox} = k^{o'} \exp \left\{ \frac{(1 - \alpha) F}{RT} (E - E^{o'}) \right\}$$

# Kinetics of electrode reaction – transfer coefficients

• Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

• Rate constants at open circuit voltage  $E$  vs formal open circuit voltage  $E^{o'}$

$$k'_{rd} = k^{o'} \exp\left\{\frac{-\alpha F}{RT}(E - E^{o'})\right\} \quad \text{and} \quad k'_{ox} = k^{o'} \exp\left\{\frac{(1-\alpha)F}{RT}(E - E^{o'})\right\}$$



# Kinetics of electrode reaction – Butler-Volmer

• Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

• Substitution of  $k'_{rd} = k^{o'} \exp\left\{\frac{-\alpha F}{RT}(E - E^{o'})\right\}$  and  $k'_{ox} = k^{o'} \exp\left\{\frac{(1-\alpha)F}{RT}(E - E^{o'})\right\}$

Into  $\frac{i(E)}{F} = k'_{ox}(E)c_R^s - k'_{rd}(E)c_O^s$

Yields one version of the Butler-Volmer equation:

$$\frac{I}{A} = i = Fk^{o'} \left[ -c_O^s \exp\left\{\frac{-\alpha F}{RT}(E - E^{o'})\right\} + c_R^s \exp\left\{\frac{(1-\alpha)F}{RT}(E - E^{o'})\right\} \right]$$

Alternative:  $i = i_n \left[ -\frac{c_O^s}{c_O^b} \exp\left\{\frac{-\alpha F}{RT}(E - E_n)\right\} + \frac{c_R^s}{c_R^b} \exp\left\{\frac{(1-\alpha)F}{RT}(E - E_n)\right\} \right]$

Symbols	Meanings	Status during most experiments
$F, R$	Faraday's constant, gas constant	physical constants, known and invariant
$T, A, c_{\text{R}}^{\text{b}}, c_{\text{O}}^{\text{b}}$	temperature, electrode area, bulk concentrations of R and O	experimental parameters, known <sup>730</sup> and constant
$E^{\circ'}, k^{\circ'}, \alpha$	formal potential, formal rate constant, transfer coefficient	unknown parameters, usually treated as constants but subject to mild variation <sup>731</sup>
$I, E$	current, electrode potential	variables, either controlled or measured
$c_{\text{R}}^{\text{s}}, c_{\text{O}}^{\text{s}}$	concentrations of R and O at the electrode surface	variables, unknown and not measurable electrochemically

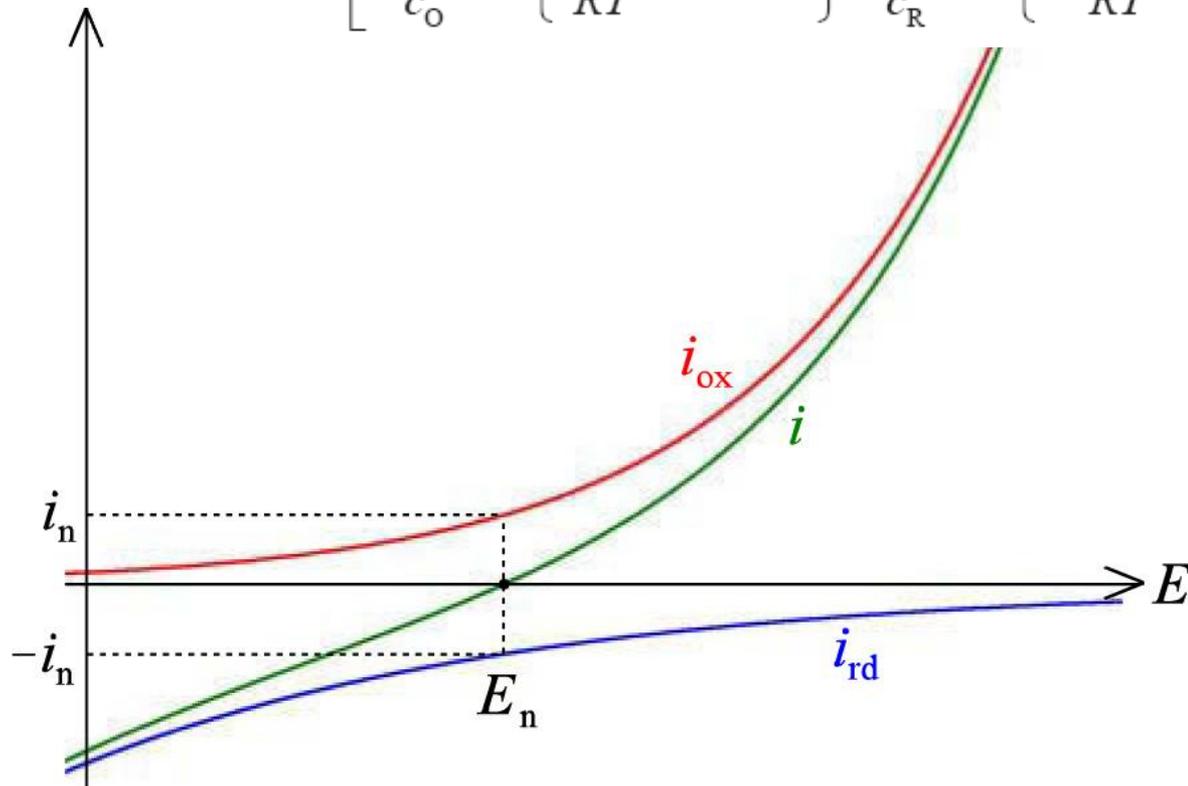
The term  $\exp\{-F(E - E^{\circ'})/RT\}$  may be thought of as the activity  $a_{e^-}$  of electrons in an electrode at potential  $E$ , compared with their activity at the formal potential  $E^{\circ'}$ . From this viewpoint, the Butler-Volmer equation may be written

$$7:28 \quad \frac{i}{F} = v_{\text{net}} = k^{\circ'} c_{\text{R}}^{\text{s}} a_{e^-}^{\alpha-1} - k^{\circ'} c_{\text{O}}^{\text{s}} a_{e^-}^{\alpha}$$

# Kinetics of electrode reaction – Butler-Volmer

- Simplest possible oxidation reaction  $R(soln) \rightleftharpoons e^- + O(soln)$

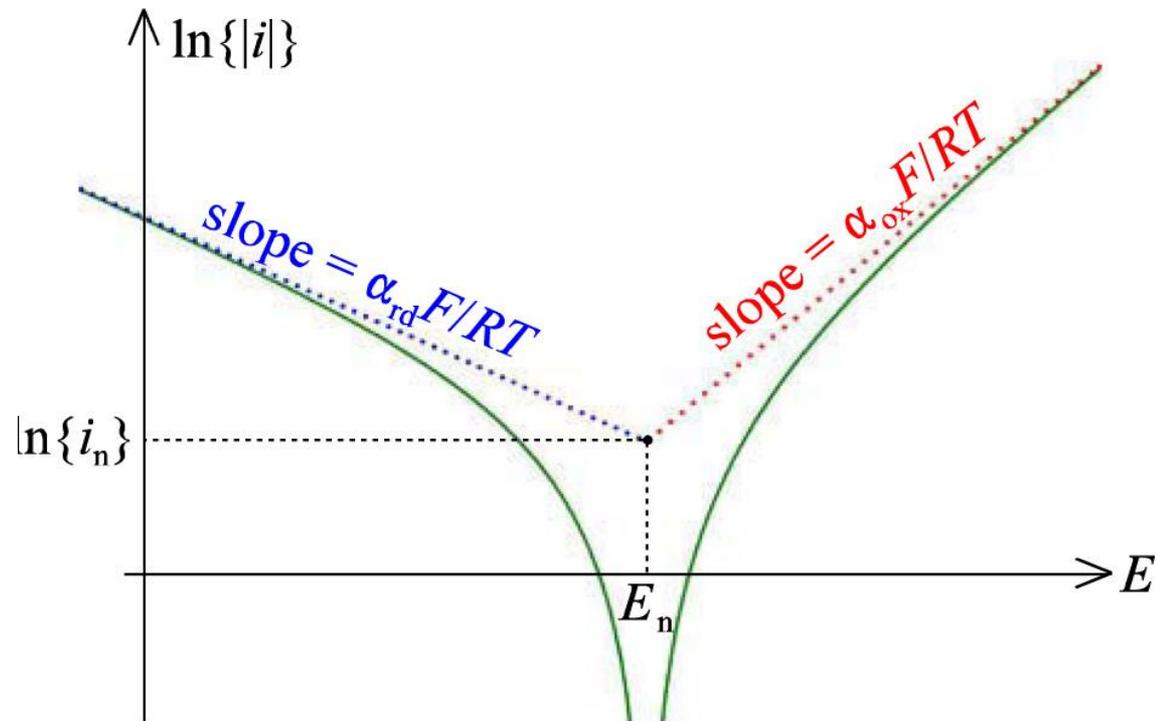
- Butler-Volmer: 
$$\frac{I}{A} = i = Fk^{o'} \left[ -c_O^s \exp\left\{\frac{-\alpha F}{RT}(E - E^{o'})\right\} + c_R^s \exp\left\{\frac{(1-\alpha)F}{RT}(E - E^{o'})\right\} \right]$$
- $$i = i_n \left[ -\frac{c_O^s}{c_O^b} \exp\left\{\frac{-\alpha F}{RT}(E - E_n)\right\} + \frac{c_R^s}{c_R^b} \exp\left\{\frac{(1-\alpha)F}{RT}(E - E_n)\right\} \right]$$



# Tafel plot

$$i = i_n \left[ -\frac{c_O^s}{c_O^b} \exp \left\{ \frac{-\alpha F}{RT} (E - E_n) \right\} + \frac{c_R^s}{c_R^b} \exp \left\{ \frac{(1-\alpha)F}{RT} (E - E_n) \right\} \right]$$

- $\ln|i|$  or  $\log|i|$  vs  $E$
- At large potentials, the oxidation or reduction dominates
- The current becomes exponentially dependent on  $E$



# Reaction order

- Example reaction



- For reactant A, for reduction,

$$\frac{\partial \ln \{-i_{\text{rd}}\}}{\partial \ln \{c_A^s\}} = \Omega_{A,\text{rd}}$$

- General rate law

$$i_{\text{ox}} \propto (c_A^s)^{\Omega_{A,\text{ox}}} (c_B^s)^{\Omega_{B,\text{ox}}} (c_Z^s)^{\Omega_{Z,\text{ox}}} \exp\left\{\frac{\alpha_{\text{ox}} F}{RT} E\right\}$$

$$i_{\text{rd}} \propto -(c_A^s)^{\Omega_{A,\text{rd}}} (c_B^s)^{\Omega_{B,\text{rd}}} (c_Z^s)^{\Omega_{Z,\text{rd}}} \exp\left\{\frac{-\alpha_{\text{rd}} F}{RT} E\right\}$$

general  
rate  
law

# Summary Ch 7. Electrode reactions

- Butler-Volmer equation

$$\frac{i}{F} = k'_{\text{ox}} c_{\text{R}}^s - k'_{\text{rd}} c_{\text{O}}^s = k^{o'} \left[ c_{\text{R}}^s \exp \left\{ \frac{(1-\alpha)F}{RT} (E - E^{o'}) \right\} - c_{\text{O}}^s \exp \left\{ \frac{-\alpha F}{RT} (E - E^{o'}) \right\} \right]$$

- $I$ - $E$  (or  $I$ - $V$  or  $I$ - $U$  or Butler-Volmer) plot

Tafel plot

