Electrochemistry

Electrode Reactions → Kinetics and tafel behavior

need to explain rates for these reactions and how they depended on electrode potential.

Basics:

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

Nernst Equation

$$E = E^{o} + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*}$$

E^{o} ↑ formal potential

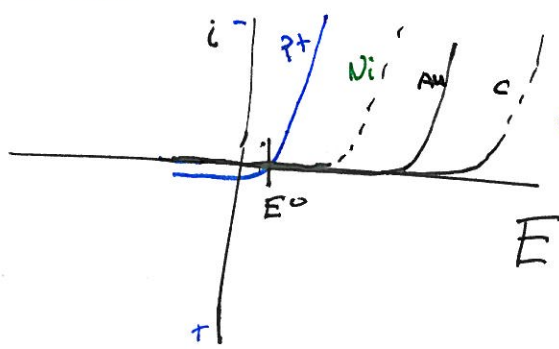
C_O^*, C_R^* → concentrations of species

When electrode kinetics (ie faradaic charge transfer is rate-limiting, the system does not obey the Nernst equation at the Electrode surface

Experimental observation:

Tafel 1905

$2H^+ + 2e^- \rightarrow H_2$



← different metals, for example, give very different responses.

must explain $i = a' e^{\eta/b'}$

η overpotential

Surface drastically affects observed i-E (i.e. rxn Rate)

Kinetics depends on surface!

Bard : Chapter 3 → Kinetics of Electrode Reactions

1.1 Review of Homogeneous kinetics

Consider elementary reaction

discrete chemical step

- several discrete steps make up a mechanism

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

rate forward

$$V_f = k_f C_A$$

$$V_b = k_b C_B$$

Rate backward

V_f units M/s

C_A units M

k_f units $\frac{1}{s}$

and :

$$\boxed{V_{net} = k_f C_A - k_b C_B}$$

k_f and k_b are the first order rate constants.

at Eq.

$$\frac{k_f}{k_b} = K = \frac{C_B}{C_A}$$

in the limit of Eq. kinetic theories collapse to the thermodynamic ones.

Define: exchange velocity

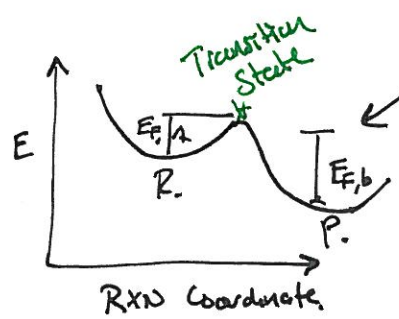
$$V_0 = k_f (C_A)_{eq} = k_b (C_B)_{eq}$$

consider like size of "pipe" connecting two reservoirs

1.2 Model → Arrhenius → Exp. observation!

$$\boxed{k = A e^{-E_a/RT}}$$

$$E_a \equiv \Delta G^{\ddagger}$$



potential barrier

* Simple model

E_a = Δ in Std. internal Energy in going from min to max.

Side note:

$H = U + PV$ → internal energy plus any PV work

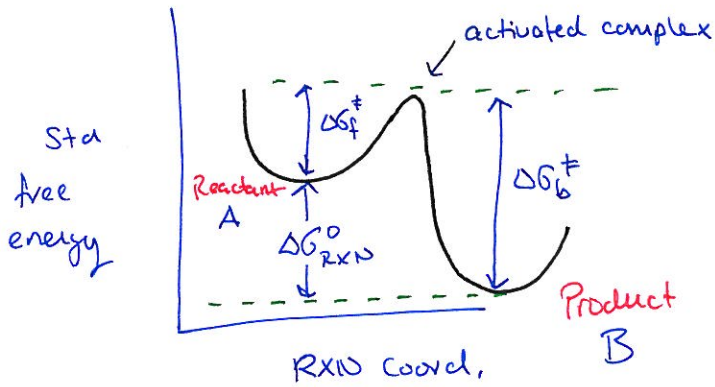
$G = H - TS$ ↑ includes entropy

~~$\Delta H^{\ddagger}$ → factor~~

3.1.3

Transition State Theory

- rxn proceeds through well-defined activated complex

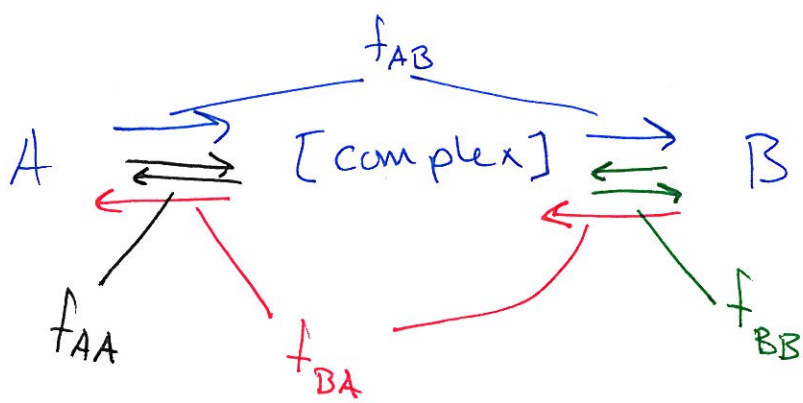


$A \rightarrow B$

Equillibrium Constants can be used to write out concentration of activated complex

$$K_f = \frac{[\text{complex}]}{[A]} = \exp\left(-\Delta G_f^{\ddagger}/RT\right)$$

$$K_b = \frac{[\text{complex}]}{[B]} = \exp\left(-\Delta G_b^{\ddagger}/RT\right)$$



4 different processes

$f_{AB} \equiv A \rightarrow [\text{complex}] \rightarrow B$

$f_{AA} \equiv A \rightarrow$ " " $\rightarrow A$

$f_{BA} \equiv B \rightarrow$ " " $\rightarrow A$

$f_{BB} \equiv B \rightarrow$ " " $\rightarrow B$

So net rate going to B

is

$$\underline{k_f [A]} = f_{AB}\, k' [\text{complex}]$$

rate going to A is

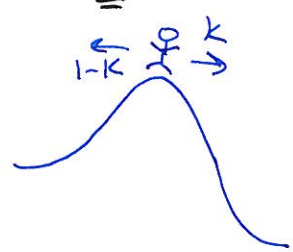
$$\underline{k_b [B]} = f_{BA}\, k' [\text{complex}]$$

at Equilibrium, $k_f [A] = k_b [B]$

$$\Rightarrow f_{AB} = f_{BA}$$

since $f_{AB} + f_{BA} + f_{BB} + f_{AA} = 1$ (all complexes must go somewhere!)

→ we define term $\underline{\underline{k}}$ the transmission coefficient



then $f_{AB} = f_{BA} = \frac{k}{2}$ and $f_{AA} = f_{BB} = \frac{1-k}{2}$

So sum $\underline{f_{AA} + f_{BA} + f_{BB} + f_{BA} = 1}$

So from before we wrote:

$$k_f [A] = f_{AB} k' [\text{complex}] = \frac{k' K}{2} [\text{complex}]$$

and also

$$\frac{[\text{complex}]}{[A]} = \exp(-\Delta G_f^{\ddagger}/RT)$$

$$k_f \cancel{[A]} = \frac{k'K}{2} \cancel{[A]} \exp(-\Delta G_f^{\ddagger}/RT)$$

$$\boxed{k_f = \frac{k'k}{2} \exp(-\Delta G_f^{\ddagger}/RT}$$

by analogy

$$\boxed{k_b = \frac{K k'}{2} \exp(-\Delta G_b^{\ddagger}/RT)}$$

$\Rightarrow$ using transition state theory and only considering the system at Equilibrium,

we now have expressions for the relation between k_f and k_b in terms of the potential barrier.

for simple cases statistical mechanics can be used to show that $k' = \frac{2kT}{h}$ (Boltzmann constant.)

- although derived at E.Q. holds away from E.Q.

3.2 Essential of Electrode Reactions (previous discussion was of homogeneous reactions)

For electrode EQ is characterized by Nernst equation – links Electrode potential to bulk solution concentrations

$$\boxed{O + ne^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} R}$$

and

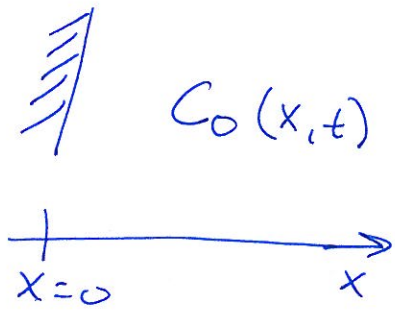
$$\boxed{E = E^\circ + \frac{RT}{nF} \ln \frac{C_O^*}{C_R^*}}$$

$\Rightarrow$ any kinetic theory must yield EQ. result

Theory must also explain experimental data shown earlier – i.e. "Tafel" equation (1905)

$$\boxed{\begin{array}{l} i = a' e^{\eta/b'} \\ \eta = \text{"overpotential"} \end{array}}$$

Consider an electrode:



$C_O(x,t)$ = concentration as function of position and time

the reaction rate, therefore:

rate of surface reactions

$$V_f = k_f C_O(0,t) = \frac{i_c}{nFA}$$

(reduction) cathodic current

electrode area

$$V_b = k_b C_R(0,t) = \frac{i_a}{nFA}$$

anodic current (oxidation)

unit analysis: $\frac{C}{s} \cdot \frac{mol}{C} \cdot \frac{1}{cm^2} = \frac{mol}{s\,cm^2}$

what are the units of k_f and k_b?

units of $C_O = \frac{mol}{cm^3}$, so k_f units are $\boxed{\frac{cm}{s}}$

the net reaction rate is thus

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

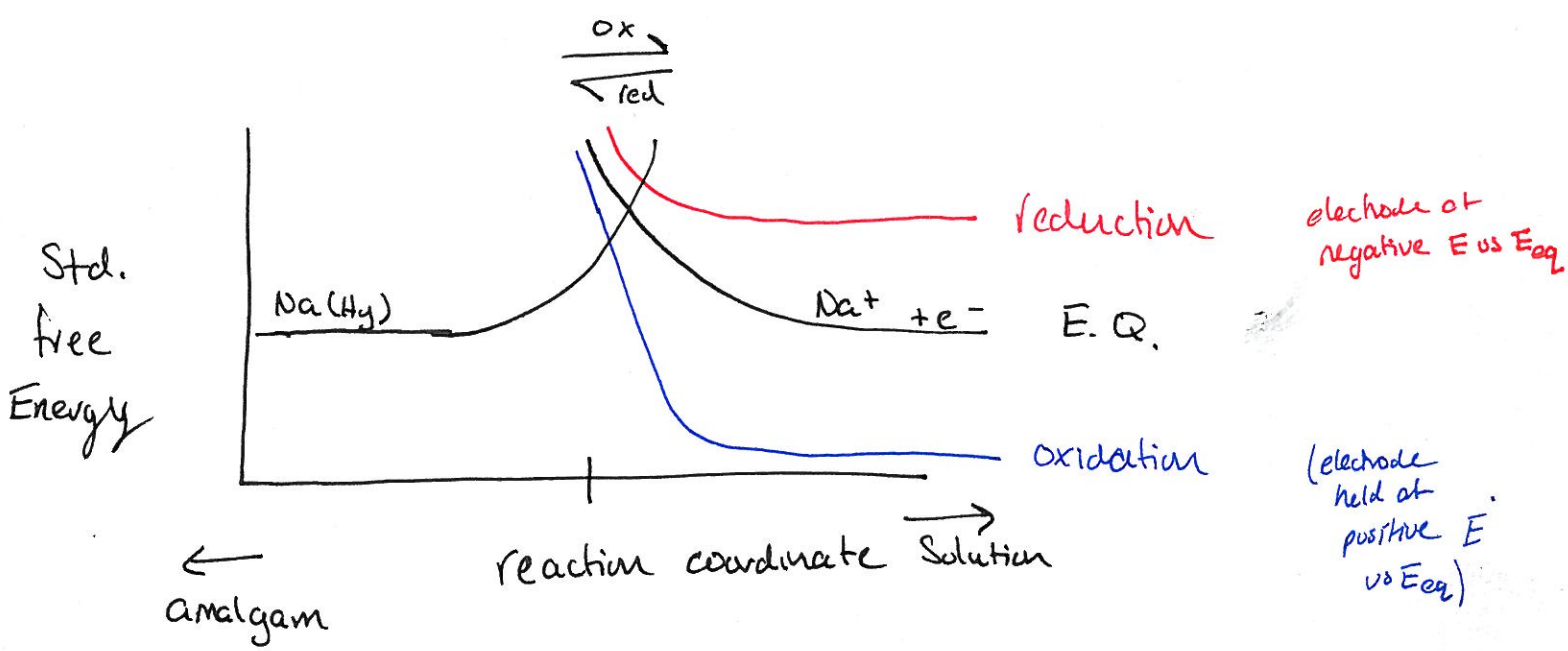
total current measured at the electrode.

3.3 Butler - Volmer Model of Electrode Kinetics

- k_f and k_b depend on potential (i.e. think of Tafel)
- we want to be able to describe that dependence.

We showed earlier that reactions can be visualized in terms of progress along an <u>energy surface</u>.

However → that energy surface depends on electrode potential!

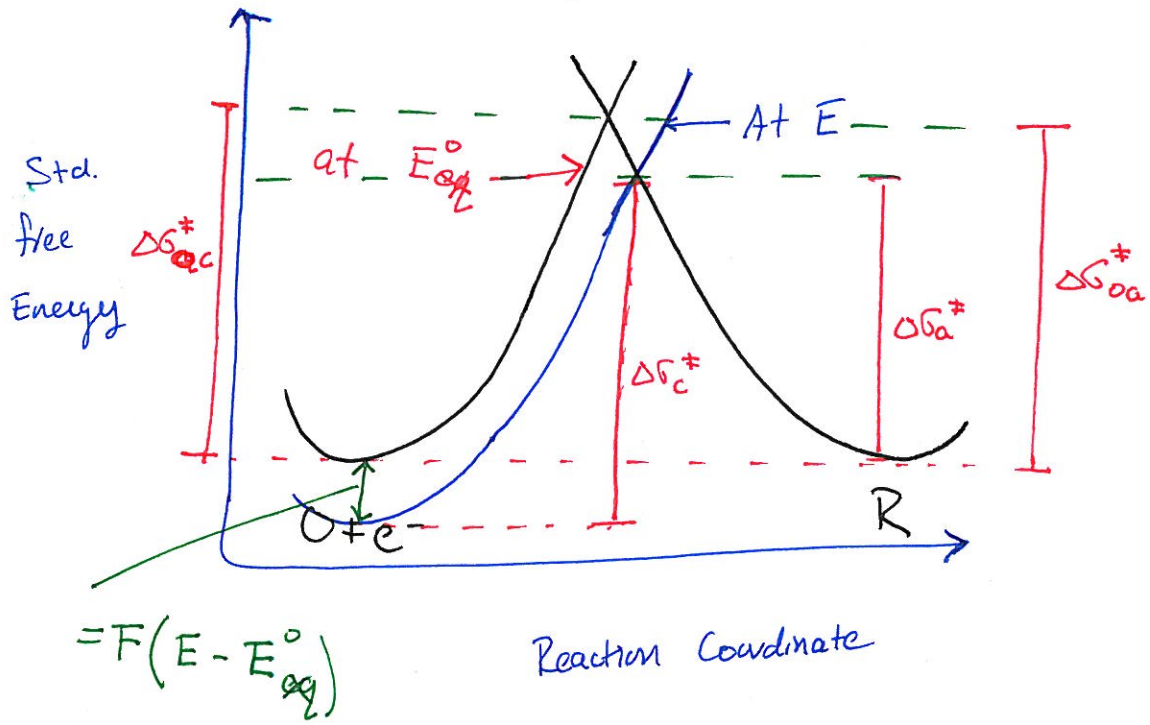


* How does the activation energy for the forward and reverse reactions depend on the applied electrode potential?

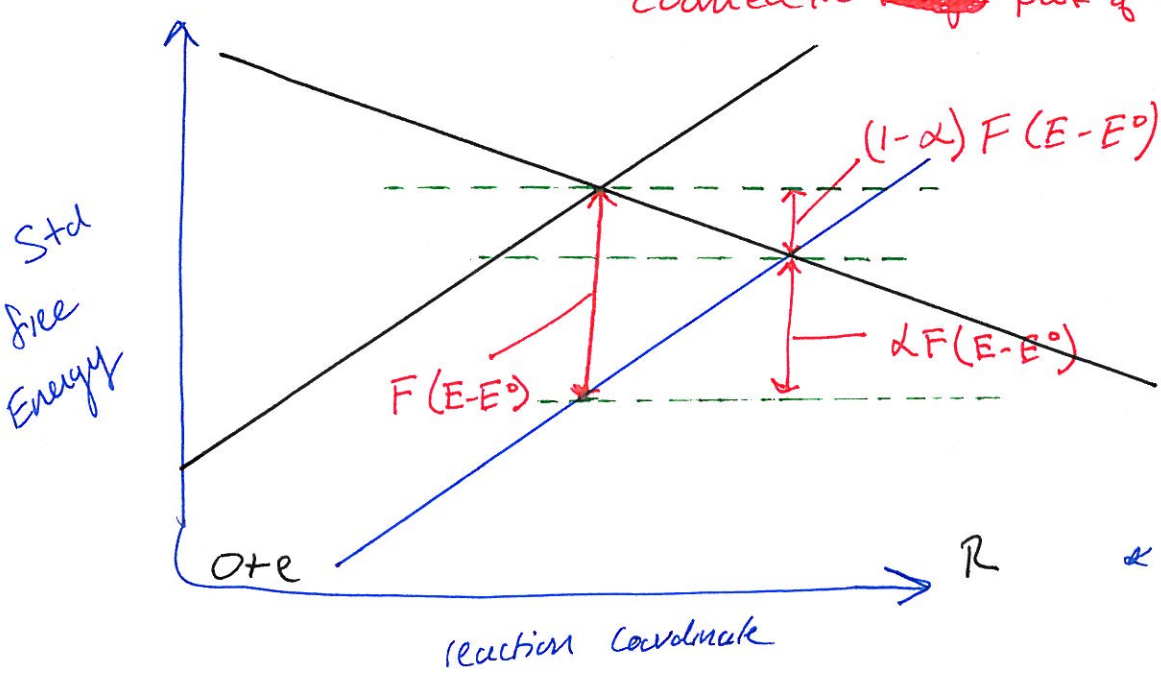
3.3.2 one-step one electron process

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

Potential changes affect the free-energy of activation



Zoomed in plot of barrier peak:



* α usually est to be 0.5

α, the transfer coefficient, varies from 0 to 1 depending on shape of barrier*

Now consider the case at equilibrium:

$$C_O^* = C_R^* \quad \text{so} \quad E = E^\circ$$

at EQ forward and reverse rates are the same so that:

$$k_f C_O^* = k_b C_R^* \Rightarrow \boxed{k_{f,eq} = k_{b,eq}} \text{ at } E^\circ.$$

E° is the potential where forward and reverse rate constants have the same value!

we define $k_f\,(\text{at } E^\circ) = k_b\,(\text{at } E^\circ) = k^\circ$

k° is the standard rate constant

k° is a measure of the kinetic facility of a given redox couple.

→ large k° – EQ achieved on short time-scale

→ small k° – EQ achieved on a long time scale.

again analogy to water level e.g. through big/small pipe

Complete current potential description of Electrode kinetics:

$$\text{so} \begin{cases} k_f = \underbrace{A_f \exp(-\Delta G^{\ddagger}_{oc})}_{= k^o} \exp[-\alpha f (E - E^o)] \\ k_b = \underbrace{A_b \exp(-\Delta G^{\ddagger}_{oc})}_{} \exp[(1-\alpha) f (E - E^o)] \end{cases}$$

$$f = \frac{F}{RT}$$ (used to simplify expression)

$$k_f = k^o \exp[-\alpha f (E - E^o)]$$
$$k_b = k^o \exp[(1-\alpha) f (E - E^o)]$$

$$\boxed{\text{now} \quad i = i_c - i_a = nFA[k_f C_o(0,t) - k_b C_R(0,t)]}$$

plug in for k_f and k_b, and here $n=1$ (1e- process)

$$\boxed{i = FAk^o \Big[\underbrace{C_o(0,t)\exp[-\alpha f (E - E^o)]}_{\text{forward current}} - \underbrace{C_R(0,t)\, e^{(1-\alpha) f (E - E^o)}}_{\text{backwards current}}\Big]}$$

this is the Butler-Volmer formulation of electrode kinetics.

Very important → used in some form to treat all aspects of heterogeneous electron transfer.