3.6 Microscopic Theory of Charge Transfer

→ Marcus Theory

Goal: connect molecular structure and environment to electron transfer processes.

Pioneer Rudy Marcus (Caltech) Nobel Prize in Chemistry

1992 Nobel Prize in chemistry, 88 yrs old still active!

Outer sphere vs inner sphere

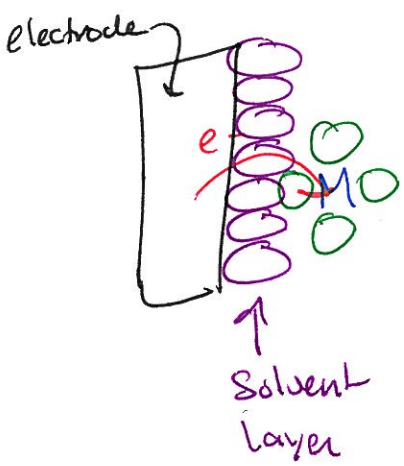
$$Co(NH_3)_6^{3+} + Cr(Bpy)_3^{2+} \rightarrow Co(NH_3)_6^{2+} + Cr(Bpy)_3^{3+}$$

outer sphere homogeneous

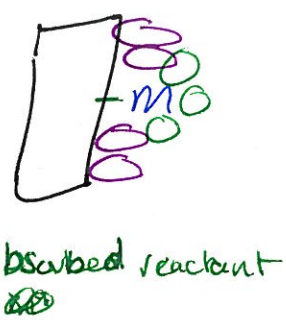
$$Co(NH_3)_5Cl^{2+} + Cr(H_2O)_6^{2+} \rightarrow (NH_3)_5Co\,Cl\,Cr(H_2O)_5^{4+}$$

inner sphere

outer sphere - not dependent on electrode material!



inner sphere - strong interaction between electrode and absorbed species



(another good example is I^-/I_3^- or H^+/H_2 vs. Fe^+/Fe or MV^{2+}/MV^{+})

3.6.1 → The Marcus Model

Consider homogeneous and heterogeneous charge transfer in the same context...

$$O + R' \rightarrow R + O'$$ electron exchange reaction

- e^- transfer rxn's are radiationless electronic rearrangements of reacting species.

Key concept: #1 — Requires ~~iso electronic~~ iso energetic e^- transfer

Key Concept #2 — Reactants and products do not change configurations on the timescale of the electron transfer:

i.e. Frank-Condon Principle → electrons move much faster than nuclei

Goal: obtain expression for the $\Delta G^{\ddagger}$ (free energy of activation) as a function of structural parameters of reactant.

Then calculate Rate constant (which is used in expressions of i-E)

$$k_f = K_{p,o} \nu_n \kappa_{el} \exp(-\Delta G_f^{\ddagger}/RT) \quad (1)$$

- $K_{p,o}$: precursor equilibrium constant, ratio of [reactant] in reactive position relative to bulk solution
- ν_n: nuclear frequency factor (s^{-1}), generally related to bond/solvent vibrations/motion
- κ_{el}: electronic transmission coefficient, probability of electron tunnelling 0 to 1

(1) can be used for a homogeneous or heterogeneous reaction

a. Consider heterogeneous e^- transfer from Electrode to molecule

$$\Rightarrow K_{P,O} = \frac{C_{O,surf}}{C_O^*}$$

$C_{O,surf}$ ← surface concentration of Reactants (mol/cm^2)

C_O^* ← bulk concentration of reactants (mol/cm^3)

↗ thus here, units of cm ⇒ k_f units of cm/s

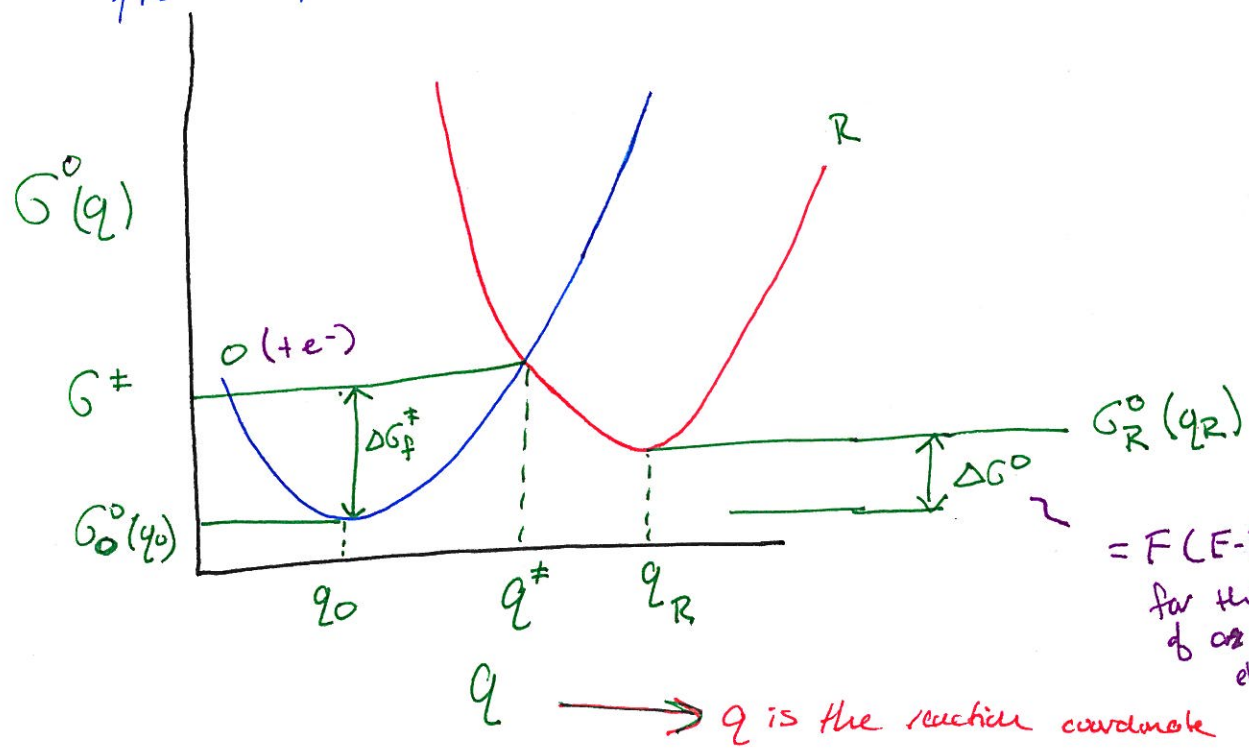
b. For Homogeneous electron transfer, precursor state has form of a reactive O − R' unit.

$$K_{P,O} = \frac{[OR']}{[O][R']}$$

→ units of $\frac{L}{mol}$

k_f units → $\frac{L}{mol\,s}$

Consider reaction takes place on a multidimensional free energy surface



$= F(E-E^o)$ for the case of heterogeneous electron transfer

q → q is the reaction coordinate

$$G_o^o(q) = \left(\frac{k}{2}\right)(q-q_o)^2$$

formula for parabola of reactant, O

$$G_R^o(q) = \left(\frac{k}{2}\right)(q-q_R)^2 + \Delta G^o$$

parabola for Reduced form R

k is a proportionality constant — $\boxed{\text{force constant for change in bond length}}$

an an example consider the example of $Ru(NH_3)_6^{3+/2+}$

O, Ru^{3+}

R, Ru^{2+}

transition state is where O and R have same bond length, $q^{\ddagger}$

In keeping with the Frank-Condon principle

e- transfer happens only at $q^{\ddagger}$

Not a rate constant!
~ spring constant
eee
$F = kx$

$$G_O^{\circ}(q^{\ddagger}) = \frac{k}{2}(q^{\ddagger} - q_O)^2$$

$$G_R^{\circ}(q^{\ddagger}) = \frac{k}{2}(q^{\ddagger} - q_R)^2 + \underbrace{\Delta G^{\circ}}_{= F(E - E^{\circ})}$$

for an electrode reaction

$\Rightarrow$ at $q^{\ddagger}$ $\quad G_O^{\circ} = G_R^{\circ}$

solve quadratic eqn. to yield:

$$\boxed{q^{\ddagger} = \frac{q_R + q_O}{2} + \frac{\Delta G^{\circ}}{k(q_R - q_O)}}$$

quadratic formula

$ax^2 + bx + c = 0$

$x^2 + \frac{b}{a}x = -\frac{c}{a}$

$x^2 + \frac{b}{a}x + \frac{b^2}{4a^2} = -\frac{c}{a} + \frac{b^2}{4a^2}$

$\left(x + \frac{b}{2a}\right)^2 = -\frac{c}{a} + \frac{b^2}{4a^2}$

$x = -\frac{b}{2a} \pm \sqrt{-\frac{c}{a} + \frac{b^2}{4a^2}}$

the free energy of activation for reduction of O is then given by:

$$\Delta G_f^{\ddagger} = G_O^{\circ}(q^{\ddagger}) - \underbrace{G_O^{\circ}(q_O)}_{= 0} = G_O^{\circ}(q^{\ddagger})$$

: as dictated by definition of parabola above

substituting for $q^{\ddagger}$ from above

$$\Delta G_f^{\ddagger} = G_O^{\circ}(q^{\ddagger}) = \frac{k}{2}(q^{\ddagger} - q_O)^2$$

$$= \frac{k}{2}\left[\frac{q_R + q_O}{2} - q_O + \frac{\Delta G^{\circ}}{k(q_R - q_O)}\right]^2$$

$=$

$$= \frac{k}{2}\left[\frac{q_R - q_0}{2} + \frac{2\Delta G^\circ}{k(q_R-q_0)^2}\,\frac{q_R-q_0}{2}\right]^2$$

$$= \frac{k\,(q_R-q_0)^2}{4\cdot 2}\left[1 + \frac{2\,\Delta G^\circ}{k(q_R-q_0)^2}\right]^2$$

we define λ, <u>the reorganization energy</u>,

as $\boxed{\lambda = \frac{k}{2}(q_R - q_0)^2}$

So that

$$\Delta G_f^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^\circ}{\lambda}\right)^2 = \frac{\lambda}{4}\left(1 + \frac{F(E-E^\circ)}{\lambda}\right)^2$$

homogeneous electron transfer — heterogeneous electron transfer

Q: What is the physical significance of λ?

λ represents the energy need to transform the nuclear configurations in the <u>reactants</u> and <u>solvent</u> to those of the product state.

$x - x_0$

$F = -(x - x_0)$

$= U = \frac{1}{2}k(x-x_0)^2$

analogy to potential energy of a <u>spring</u>...

There can be free energy contributions to actuation in addition...

→ work terms w_O and w_R

→ could be, for example, electrostatic components associated with ion pairing, ~~[illegible]~~ or bringing charged species to charged electrode surface.

Full expression is therefore:

$$\Delta G_f^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta G^{\circ} - w_O + w_R}{\lambda}\right)^2 \quad \ldots$$

So work terms are any additional energies that must be "paid" to bring reactants to product state.

Could skip discussion of work terms if necessary.

Move on the reorganization Energy, λ

$$\lambda = \lambda_i + \lambda_o$$

inner (bonds) — outer (solvent)

in principle,

$$\lambda_i = \sum_j \frac{1}{2} k_j \left(q_{o,j} - q_{R,j} \right)^2$$

Sum over all normal harmonic vibrational modes in the molecule.

λ_o is often calculated assuming solvent is a dielectric medium

→ related to electrostatic energy needed to re-arrange solvent

↳ (ie continuous, electrically polarizable)

$$\lambda_o = \frac{e^2}{8\pi\varepsilon_0} \left(\frac{1}{a_0} - \frac{1}{R} \right) \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s} \right)$$

fundamental charge

permittivity of free space

reactant sphere of radius a_0

distance from reactant to image charge in electrode $(2 \cdot x_0)$

optical dielectric

static dielectric

Predictions From Marcus Theory

$\alpha \rightarrow$ symmetry factor in Butler-Volmer kinetics

$$\alpha = \frac{1}{F}\frac{\partial G_f^{\ddagger}}{\partial E} = \frac{1}{F}\frac{\partial}{\partial E}\left[\left(\frac{\lambda}{4}\right)\left(1+\frac{F(E-E^{\circ})}{\lambda}\right)^2\right]$$

$$= \frac{1}{2} + \frac{F(E-E^{\circ})}{2\lambda}$$

i.e. when you change E, the electrode potential, what fraction of that goes into lowering the barrier for activation $\partial G_f^{\ddagger}$?

predicts that $\alpha \sim 1/2$ but also that there is a potential dependence, not in Butler-Volmer derivation.

We'll see in a bit how the potential dependence is very important.

B Marcus theory also provides relationships between the homogeneous "self-exchange" rates:

→ these can be directly measured by NMR

$$O + R \xrightarrow{k_{ex}} R + O$$

and the rates of electrode reactions:

$$O + e^- \xrightarrow{k_{el}} R$$

by $$\boxed{\left(\frac{k_{ex}}{A_{ex}}\right)^{1/2} = \frac{k^0}{A_{el}}}$$

A_{ex}, A_{el} are the preexponential factors

C. Qualitative predictions

at E^0, $\Delta G_f^{\ddagger} \Rightarrow \sim \frac{\lambda}{4}$, ($E - E_0$ term goes to $\emptyset$)

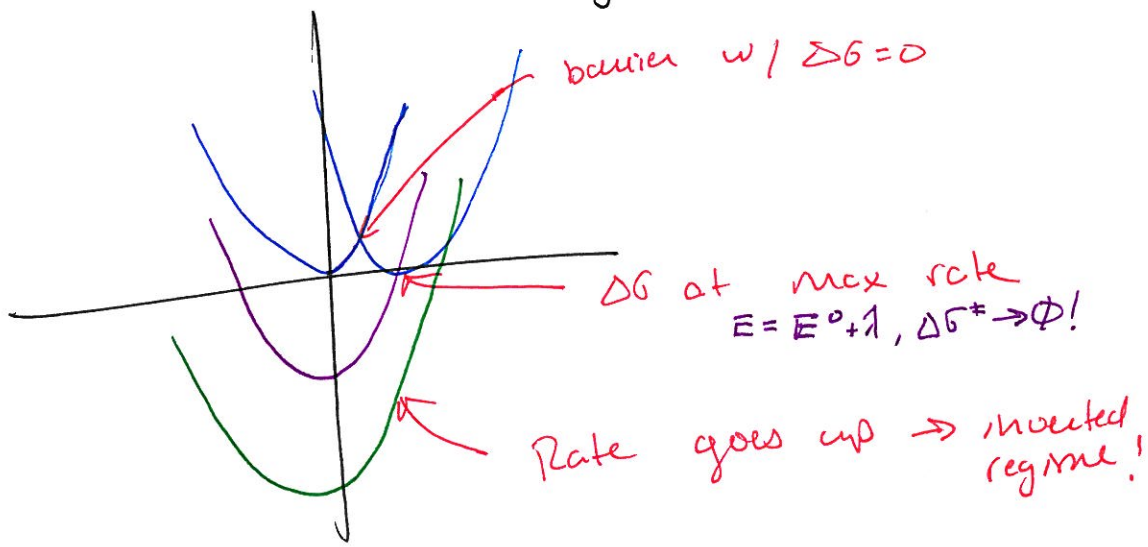
and $k_f = k_b = k^0$

less reorganization, larger k^0!

Solution is also important → small molecule = large changes in solution → slow rate

large molecules → small changes in solution → slow rate

D. the inverted Marcus Regime.



Physical explanation for this affect:

large, negative free energy means that products must accept liberated energy quickly in vibrational modes.

Can you observed (or do you expect to observe) this Marcus inverted regime using a metal electrode?

No! Due to continuous density of states in a metal electrode... (explained next!)
– i.e. there are electrons at many different energies! It is the sum of the microscopic rates

Can observe in a semiconducting electrode.

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