

Foundations of Chemical Kinetics  
Lecture 21:  
Marcus electron-transfer theory

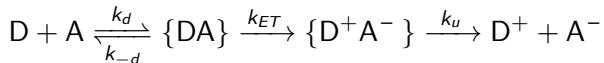
Marc R. Roussel

December 7, 2021

## Electron-transfer reactions

- E.g.:  $[\text{Fe}(\text{OH}_2)_6]^{2+} + [\text{Ru}(\text{bpy})_3]^{3+} \rightleftharpoons [\text{Ru}(\text{bpy})_3]^{2+} + [\text{Fe}(\text{OH}_2)_6]^{3+}$
- Two kinds of electron-transfer (ET) reactions:
  - Inner sphere ET: the coordination spheres of the ions rearrange, and a bridging ligand conveys the electron(s) from one to the other.
  - Outer sphere ET: no reorganization of the ligands (as in the example).  
A solvent molecule often acts as a transfer agent for the electron(s).
- Theory developed by Canadian Nobel Prize winner **Rudy Marcus**
- We initially focus on the simpler **outer sphere electron-transfer theory**.

## Mechanistic decomposition of an electron-transfer reaction

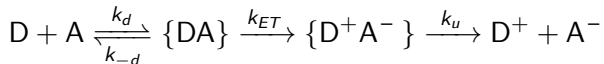


D: donor

A: acceptor

- $k_d$ ,  $k_{-d}$ ,  $k_u$  from theory of diffusion-influenced reactions

## Rate of reaction



- $v = k_u[\{D^+A^-\}]$
- Apply steady-state approximation to intermediates.
- SSA for  $\{D^+A^-\}$  gives  $k_u[\{D^+A^-\}] = k_{ET}[\{DA\}]$
- SSA for  $\{DA\}$  gives

$$[\{DA\}] = \frac{k_d[D][A]}{k_{-d} + k_{ET}}$$

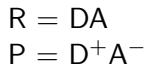
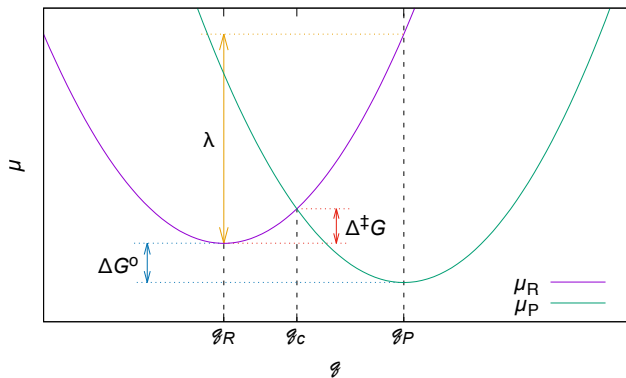
- Rate of reaction:

$$v = \frac{k_{ET}k_d[D][A]}{k_{-d} + k_{ET}}$$

- Second-order (observed) rate constant:

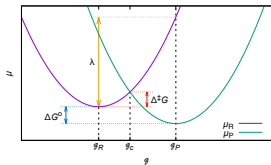
$$k_{\text{obs}} = \frac{k_{ET}k_d}{k_{-d} + k_{ET}}$$

# $k_{ET}$ from a free energy argument



$$\mu_i \approx \mu_i^\circ + \frac{1}{2}f(q - q_i)^2, \quad i = R, P$$

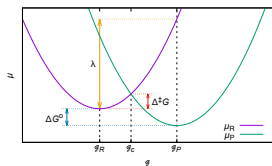
## $k_{ET}$ from a free energy argument (continued)



$$\mu_i \approx \mu_i^\circ + \frac{1}{2}f(q - q_i)^2, \quad i = R, P$$

- $f$  characterizes the shape of the parabolas.  
It's mathematically simpler (but not necessary) to assume a common  $f$ .
- $\Delta G^\circ = \mu_P^\circ - \mu_R^\circ$
- The two curves intersect at the transition state.
- The intersection point  $q_c$  (c for crossing) is obtained by solving the equation  $\mu_R = \mu_P$ .

# $k_{ET}$ from a free energy argument (continued)



$$\mu_R^\circ + \frac{1}{2}f(q_c - q_R)^2 = \mu_P^\circ + \frac{1}{2}f(q_c - q_P)^2$$

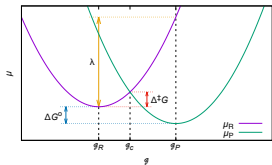
$$\therefore \frac{1}{2}f(q_c - q_R)^2 = \Delta G^\circ + \frac{1}{2}f(q_c - q_P)^2$$

$$\therefore -fq_c q_R + \frac{1}{2}fq_R^2 = \Delta G^\circ - fq_c q_P + \frac{1}{2}fq_P^2$$

$$\therefore fq_c (q_P - q_R) = \Delta G^\circ + \frac{1}{2}f (q_P^2 - q_R^2)$$

$$\therefore q_c = \frac{\Delta G^\circ}{f(q_P - q_R)} + \frac{q_P + q_R}{2}$$

## $k_{ET}$ from a free energy argument (continued)



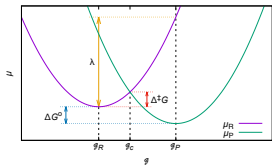
$$\lambda = \mu_R(q_P) - \mu_R^\circ$$

$$\therefore \lambda = \frac{1}{2} f (q_P - q_R)^2$$

- $\lambda$  is the **reorganization energy**, the energy required to reorganize both DA and the surrounding solvent to the configuration of  $\{D^+A^-\}$  at equilibrium.
- Efficient reaction requires this reorganization **before** electron transfer (Franck-Condon effect).



# $k_{ET}$ from a free energy argument (continued)



$$\lambda = \frac{1}{2} f (q_P - q_R)^2$$

$$\begin{aligned} \Delta^\ddagger G &= \mu_R(q_c) - \mu_R(q_R) = \frac{1}{2} f (q_c - q_R)^2 \\ &= \frac{1}{2} f \left( \frac{\Delta G^\circ}{f (q_P - q_R)} + \frac{q_P + q_R}{2} - q_R \right)^2 \\ &= \frac{1}{2} f \left( \frac{\Delta G^\circ}{f (q_P - q_R)} + \frac{q_P - q_R}{2} \right)^2 \\ &= \frac{1}{2f (q_P - q_R)^2} \left[ \Delta G^\circ + \frac{1}{2} f (q_P - q_R)^2 \right]^2 \end{aligned}$$

$$\therefore \Delta^\ddagger G = \frac{1}{4\lambda} (\Delta G^\circ + \lambda)^2$$

$k_{ET}$  from a free energy argument (continued)

$$\Delta^\ddagger G = \frac{1}{4\lambda} (\Delta G^\circ + \lambda)^2$$

- You have probably been told over and over again that kinetics and thermodynamics are independent.
- Here is an example where it is not:  $\Delta^\ddagger G$  depends on  $\Delta G^\circ$ .

$k_{ET}$  from a free energy argument (continued)

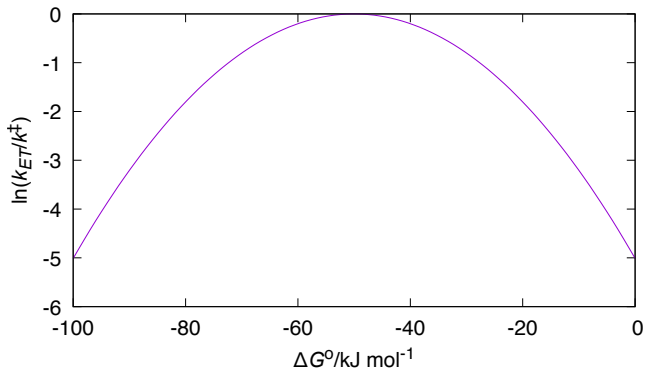
- We now borrow an idea from transition-state theory:

$$\begin{aligned}
 k_{ET} &= k^\ddagger K^\ddagger \\
 &= k^\ddagger \exp\left(\frac{-\Delta^\ddagger G}{k_B T}\right) \\
 \therefore k_{ET} &= k^\ddagger \exp\left(\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right)
 \end{aligned}$$

or  $\ln k_{ET} = \ln k^\ddagger - \frac{(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}$

- This equation makes a remarkable prediction:  
Because of the quadratic dependence on  $\Delta G^\circ$ , the rate constant should initially increase, and then decrease as  $\Delta G^\circ$  becomes more negative.

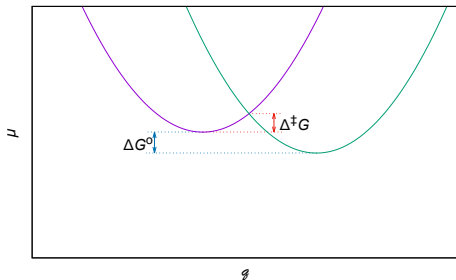
## Variation of $k_{ET}$ with $\Delta G^\circ$



$\lambda = 50 \text{ kJ mol}^{-1}$ ,  $T = 300 \text{ K}$

# Variation of $k_{ET}$ with $\Delta G^\circ$

Normal region



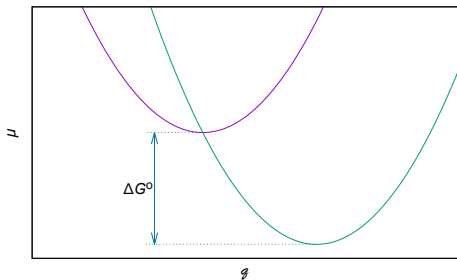
'Normal' region

$\Delta G^\circ$  more negative  $\implies \Delta^\ddagger G$  smaller

$\implies$  electron transfer faster

# Variation of $k_{ET}$ with $\Delta G^\circ$

Barrierless transfer

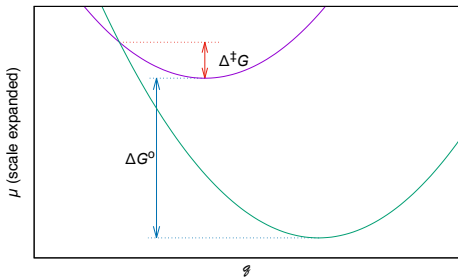


$$\Delta^\ddagger G = 0$$

Maximum rate of electron transfer

# Variation of $k_{ET}$ with $\Delta G^\circ$

Inverted region



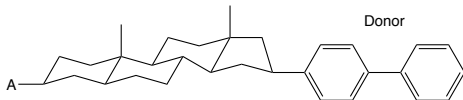
'Inverted' region

$\Delta G^\circ$  more negative  $\implies \Delta^\ddagger G$  larger

$\implies$  electron transfer slower

## Experiments of Closs and Miller

*Science*, **240**, 440 (1988)

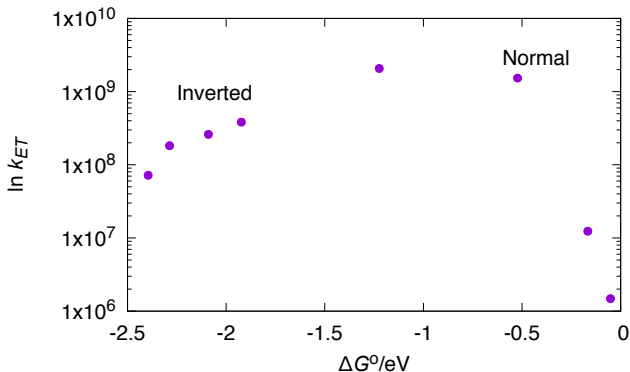


- Intramolecular electron transfer eliminates diffusive component
- Varying acceptor (A) varies  $\Delta G^\circ$
- $\lambda$  should be more-or-less constant



## Experiments of Closs and Miller: results

*Science*, **240**, 440 (1988)



- Not as symmetric as simple Marcus theory prediction
- Asymmetry due to involvement of vibrational modes of acceptor, which can be included in a more sophisticated model

## Refinement of the theory

- A more refined version of the theory gives

$$k_{ET} = \frac{2\pi}{\hbar} \frac{H_{DA}^2}{\sqrt{4\pi\lambda k_B T}} \exp\left(\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda k_B T}\right)$$

- New variable  $H_{DA}$  measures electronic coupling between donor and acceptor (direct overlap or mediated through ligand or solvent)

## Applications/further developments

- Inorganic redox chemistry
- Processes at electrode surfaces
- Redox enzymes