Chap. 21. Molecular Reaction Dynamics

Atomic/Molecular Encounters

What happens to atoms/molecules at the climax of reactions?

Extensive changes of electronic structures are taking place.

Energies are redistributed among the bonds.

Old bonds are being ripped apart, and new bonds are being formed.

The kinetics (rate) calculation from first principles is not possible.

Bimolecular processes (단순화)

Gas Phase vs. Solid or Liquid

Molecular Encounters

In solution, we cannot so easily speak of **collisions** because the relative migration of species is **diffusional**, and the solvent hinders their free flight.

The rate at which the potentially reactive species encounter each other in solution can be calculated and related to the **diffusivities** of the dissolved species.

21A. Collision Theory (Gas-Phase Reaction)

$$[\mathrm{A}] = \frac{n_A}{V} = \frac{\mathrm{N_A}}{N_A V}$$

molar concentration

∴ The rate of a gas phase reaction in which A is destroyed,

$$-\frac{d[\mathrm{A}]}{dt} = -\frac{1}{N_A V}\frac{d\mathrm{N_A}}{dt}$$

$A+B \rightarrow P$

The **collision rate** of A with B per volume is Z_{AB}. Therefore, the rate of change of the number of A molecules per unit vol., $(dN_A/dt)/V$, is Z_{AB} multiplied by the proportion of collisions that occur with a kinetic energy along the line of approach **in excess of some threshold value E_a.**

$$\frac{1}{V}\left(\frac{dN_A}{dt}\right) = -Z_{AB}\underline{\exp\left(-\frac{E_a}{RT}\right)}$$

$$\therefore -\frac{d[A]}{dt} = -\frac{1}{N_A V}\left(\frac{dN_A}{dt}\right) = \frac{Z_{AB}}{N_A}\exp\left(-\frac{E_a}{RT}\right)$$

Collision frequency density

$$Z_{AB} = \sigma\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}\left(\frac{N_A}{V}\right)\left(\frac{N_B}{V}\right) = \underline{\sigma}\left(\frac{8kT}{\underline{\pi\mu}}\right)^{\frac{1}{2}} N_A^2\underline{[A][B]} \qquad \textbf{(21A.3)}$$

(Justific. 21A.1)

where σ : collision cross-section, μ : reduced mass.

$z^{-1} = \tau$

Collision Time

$$\text{Collision frequency } z = \sigma\bar{c}_{rel}\tilde{N} \qquad \bar{c}_{rel} = \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \qquad \textbf{(1B.11a)}$$

$$-\frac{d[\mathrm{A}]}{dt}=\frac{\mathrm{Z_{AB}}}{N_A}\exp\left(-\frac{E_a}{RT}\right) \qquad \mathrm{Z_{AB}}=\sigma\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}\left(\frac{\mathrm{N_A}}{V}\right)\left(\frac{\mathrm{N_B}}{V}\right)$$

$$\therefore -\frac{d[\mathrm{A}]}{dt}=\sigma N_A\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}[\mathrm{A}][\mathrm{B}]\exp\left(-\frac{E_a}{RT}\right)$$

A+B → P

$$\text{Since } -\frac{d[\mathrm{A}]}{dt}=k_2[\mathrm{A}][\mathrm{B}],$$

(21A.8)

$$k_2=\sigma N_A\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}\exp\left(-\frac{E_a}{RT}\right)$$

Table 21A.1

Activation enthalpy (energy) and pre-exponential factor for gas-phase reactions.

Reaction	A / dm^{3}mol^{-1}s^{-1}		E_a / kJmol^{-1}	$P = \sigma^*/\sigma$
	Experimental	Theory		
$2NOCl \rightarrow 2NO + Cl_2$	9.4×10^9	5.9×10^{10}	102	0.16
$2NO_2 \rightarrow 2NO + O_2$	2.0×10^9	4.0×10^{10}	111	0.05
$2ClO \rightarrow Cl_2 + O_2$	6.3×10^7	2.5×10^{10}	0	2.5×10^{-3}
$K + Br_2 \rightarrow KBr + Br$	1.0×10^{12}	2.1×10^{10}	0	4.8
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.24×10^6	7.3×10^{11}	180	1.7×10^{-6}

1 eV/particle = 9.6484×10^4 joule/mole

= 2.306×10^4 cal/mole

Collision with sufficient energy is not the only criterion for reaction, and some other factor, such as the relative orientation of the colliding species, has taken into account.

The reactive cross-section $\sigma^* = P\sigma$

A+B → P

$$k_2 = \underset{\substack{\downarrow \\ \textbf{\textit{Steric Factor}}}}{P} \underbrace{\left\{ \sigma N_A \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} \right\}}_{\textbf{\textit{Encounter Rate}}} \underbrace{\left\{ \exp\left(-\frac{E_a}{RT} \right) \right\}}_{\textbf{\textit{Energy Criteria}}} \tag{21A.9}$$

P: Steric Factor: Local properties of the reaction = the orientations required of the species, and the details of how close they have to come in order to react, so-called **the steric factor**.

원자의 공간적/입체적 배치

21B. Reactions in Solution: Diffusion-Controlled or Activation-Controlled

- The molecular motion is **diffusional** in solution, not free flight. Still, the concepts of activation energy and steric requirements survive.
- Since a molecule migrates only slowly into the region of a possible reaction partner, it also migrates only slowly away from it. In other words, the members of the encounter pair **linger in each other's vicinity** for much longer than in a gas.

The activation energy of reaction is a much more complicated quantity in solution than in the gas: the encounter pair is **surrounded** by solvent, and its energy is determined by all the interactions.

오래 머물다

$A + B \rightarrow P$

$$\begin{tikzcd}
\mathrm{A} + \mathrm{B} \arrow[r, "k_{\mathrm{d}}"] & (\mathrm{AB}) \arrow[d] \\
& \text{encounter pair}
\end{tikzcd}$$

$$\frac{d[(\mathrm{AB})]}{dt} = k_{\mathrm{d}}[\mathrm{A}][\mathrm{B}]$$

k_{d}: determined by the diffusivity

21B.1(a)

The **encounter pair** can break up without reaction, or it can react to give products.

$$\mathrm{A} + \mathrm{B} \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (\mathrm{AB}) \xrightarrow{k_1} \text{Products P}$$

(page 889)

‘*d*’ signifies diffusion

$$\mathrm{A} + \mathrm{B} \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (\mathrm{AB}) \xrightarrow{k_1} \mathrm{P}$$

A+B → P

$$-\frac{d[\mathrm{A}]}{dt} = k_2[\mathrm{A}][\mathrm{B}]$$

Steady-State Approximation for (AB)

$$\frac{d[(\mathrm{AB})]}{dt} = k_\mathrm{d}[\mathrm{A}][\mathrm{B}] - k_{-\mathrm{d}}[(\mathrm{AB})] - k_1[(\mathrm{AB})] \underline{= 0}$$

$$[(\mathrm{AB})] = \left(\frac{k_\mathrm{d}}{k_{-\mathrm{d}} + k_1}\right)[\mathrm{A}][\mathrm{B}]$$

$\therefore$ The overall rate

$$\frac{d[(\mathrm{P})]}{dt} = k_1[(\mathrm{AB})] = \left(\frac{k_1 k_\mathrm{d}}{k_{-\mathrm{d}} + k_1}\right)[\mathrm{A}][\mathrm{B}] \qquad \textbf{(21B.1)}$$

$$\text{where } k_2 = \left(\frac{k_1 k_\mathrm{d}}{k_{-\mathrm{d}} + k_1}\right)$$

§ 20E.2. Consecutive Reactions

A couple of kinetic steps **can induce** ***mathematical complexity.***

$A+B \rightarrow P$

$$\frac{d[P]}{dt} = k_2[A][B] \qquad k_2 = \left(\frac{k_1 k_d}{k_{-d} + k_1}\right) \qquad A + B \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (AB) \xrightarrow{k_1} P$$

(i) $k_{-d} << k_1$

(21B.2a)

$k_2 \approx \dfrac{k_1 k_d}{k_1} = k_d$: In this limit, the rate of the reaction is determined by the rate at which the **species diffuse together** through the medium: the reaction is **diffusion-controlled**.

21B.1(a)

(ii) $k_1 << k_{-d}$

(21B.2b)

$k_2 = k_1\left(\dfrac{k_d}{k_{-d}}\right) = k_1 K$: In this case, the rate depends on the **accumulation of energy in the encounter pair** as a result of its interaction with the solvent molecules: the reaction is **activation-controlled**.

***K* = Equilibrium Constant**

***

§ 20E.5. Pre-Equilibrium

21B.1. Rate at which the Molecules Diffuse Together

Consider a static A molecule immersed in a solvent also containing B molecules. Consider a sphere of radius *r* surrounding the static molecule. What is the total flow of B molecules through its surface?

$$\hat{J} = 4\pi r^2 J$$

$\hat{J}$: total flow

J : flux (the amount of material passing through unit area per unit time)

From Fick's first law of diffusion,

-171030(월)

$$J = D_{\mathrm{B}} \frac{d[\mathrm{B}]}{dr}$$

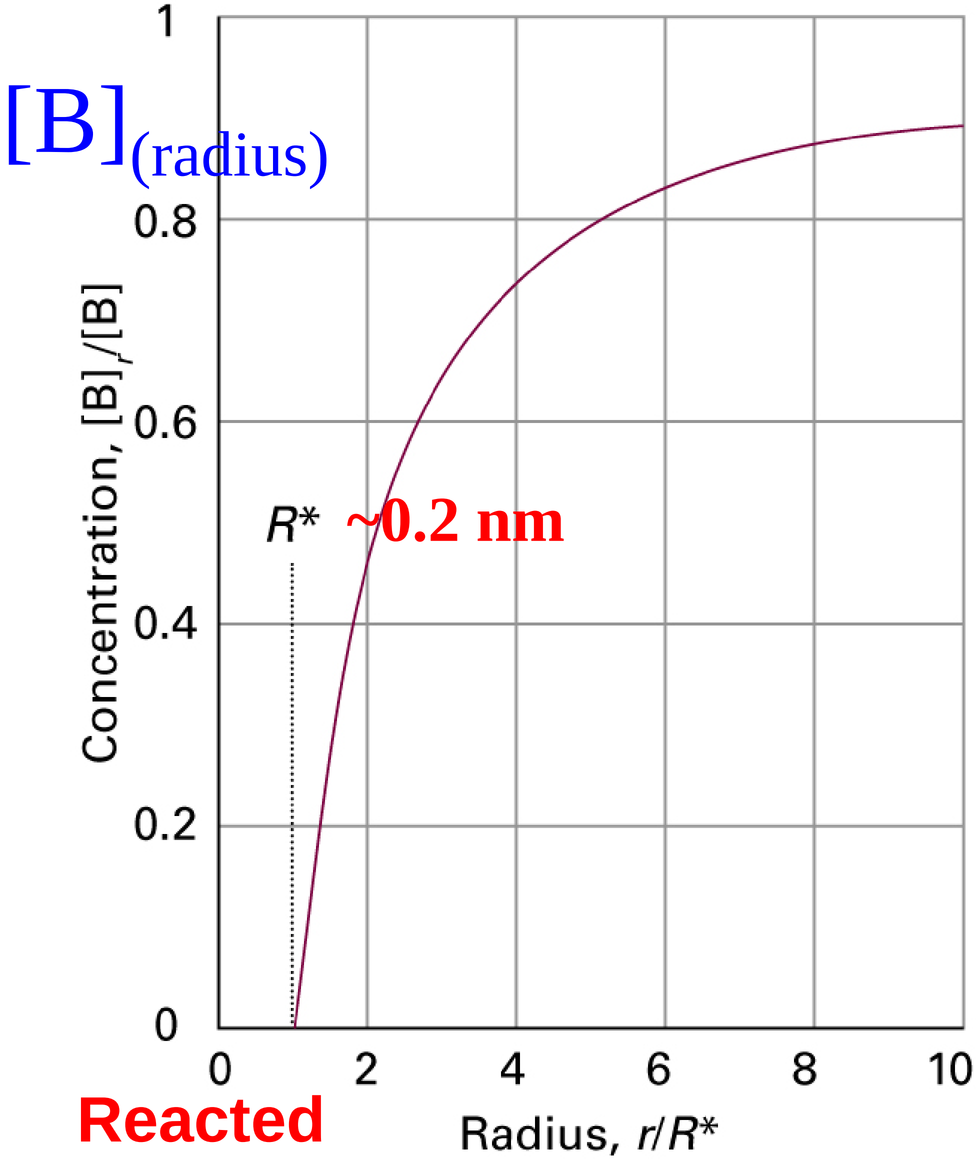
[B]: Concentration of B Molecules

= Number of Molecules / Volume

D_{B}: Diffusion Coefficient in the Medium

$$\therefore \hat{J} = 4\pi r^2 D_{\mathrm{B}} \frac{d[\mathrm{B}]}{dr}$$

A molecule waits. [과장]



$[B]_{(radius)}$

R^* ~0.2 nm

Reacted

$[B] = [B]_\infty$

Figure 21B.1

The concentration profile for reaction in solution when a molecule B diffuses towards another reactant molecule and **reacts if it reaches R^*.**

The overall concentration of B at any distance from A

(Justific. 21B.1)

1. When $r \sim \infty$, the concentration of B is the same as in the bulk solution [B].
2. The total flow through a shell is the same whatever its distance from A, because **no molecules are destroyed until A and B touch**: therefore $\hat{J}$ is constant independent of *r*.

$$\int_{[\mathrm{B}]_r}^{[\mathrm{B}]_\infty} d[\mathrm{B}] = \int_r^\infty \frac{\hat{J}\,dr}{4\pi r^2 D_\mathrm{B}} = \frac{\hat{J}}{4\pi D_\mathrm{B}} \int_r^\infty \frac{dr}{r^2}$$

$$\hat{J} = 4\pi r^2 D_\mathrm{B} \frac{d[\mathrm{B}]_r}{dr}$$

$$\therefore [\mathrm{B}]_r = [\mathrm{B}]_\infty - \frac{\hat{J}}{4\pi D_\mathrm{B} r}$$

At **critical distance *R****, A and B 'touch': reaction takes place, and B is removed. When $r = R^*$, $[\mathrm{B}]_{r\,=\,R^*} = 0$. When this condition is substituted into the last equation, we obtain an expression for the flow of B towards A:

$$\hat{J} = 4\pi R^* D_\mathrm{B} [B]_\infty$$

total flow

$$\hat{J} = 4\pi R^* D_B[B]$$

This flow is the average number of B molecules per unit time passing through any spherical surface centered on any A molecule.

Total Flow = Constant

The rate of reaction is equal to the average flow of B molecules to all the A molecules in the sample.

Number of A molecules in the sample of volume (V) = [A]V

$$[A] = \frac{N_A}{V}$$

$\therefore$ Global flow of all B to all A = $4\pi R^* D_B[A][B]V$

[숫자 / 시간]

A: static; B: mobile → unrealistic: This is easily remedied by replacing the diffusion coefficient D_B by

$$D = D_A + D_B.$$

$$\therefore \frac{d[(AB)]}{dt} = 4\pi R^* D[A][B]$$

$$\mathbf{k_d = 4\pi R^* D}$$

$$A + B \underset{k_{-d}}{\overset{k_d}{\leftrightarrow}} (AB) \xrightarrow{k_1} P$$

Diffusion-Controlled Rate Constant is:

$$k_{-d} << k_1 \qquad \mathbf{A+B \rightarrow P}$$

$$\mathbf{k_2 = k_d = 4\pi R^* D}$$

(ppt 21-9)

$$-\frac{d[A]}{dt} = k_2[A][B]$$

(21B.3)

21C. Activated Complex Theory
= Transition State Theory

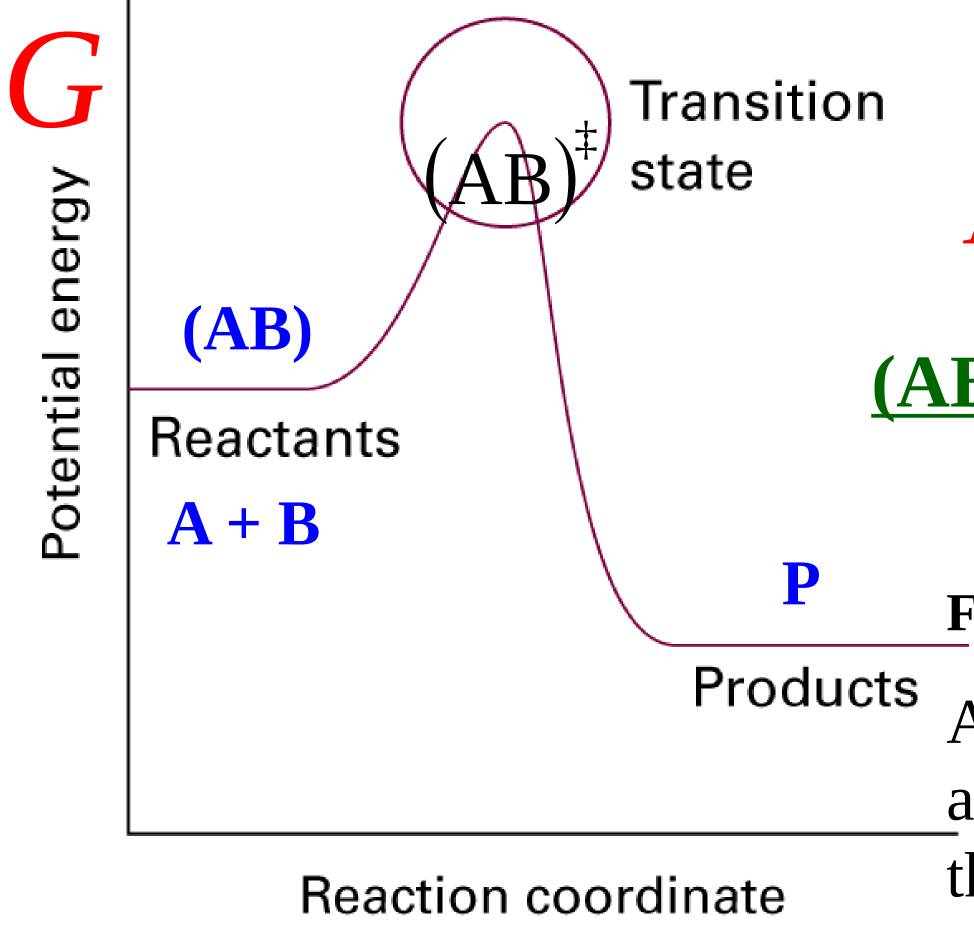
The reaction coordinate and the transition state

Reaction Coordinate: The **horizontal axis** of the diagram representing the course of the reaction.

Transition State of Reaction: A pair of reactants has been brought to the degree of closeness and distortion such that ***a small distortion* in an appropriate direction** will **send the system in the direction of products**. This ***crucial configuration*** is also called as the activated complex.

$k_1 << k_{-d}$ **ppt 21-10**

$$A + B \leftrightarrow (AB) \leftrightarrow (AB)^{\ddagger} \rightarrow P$$



High (10^{23}) Dimensional Space

‡

Activated Complex

$(AB)^{\ddagger}$ in equilibrium with (AB)

Figure 21C.2

A reaction profile. The horizontal axis is the reaction coordinate, and the vertical axis is potential energy. The activated complex is the region **near the potential maximum**, and the transition state corresponds to the maximum itself.

$$C \leftrightarrow C^{\ddagger} \leftrightarrow C$$

e.g., diffusion in a single crystal

21C. Formation and Decay of the Activated Complex

Activated Complex

Assume $(AB)^{\ddagger}$ in equilibrium with (AB)

$$(AB) \rightleftharpoons (AB)^{\ddagger} \xrightarrow{k^{\ddagger}} P$$

$$\frac{d[P]}{dt} = k^{\ddagger}\left[(AB)^{\ddagger}\right] \qquad \left[(AB)^{\ddagger}\right] = K[(AB)]$$

ppt 21-10

$$k_2 = k^{\ddagger}K$$

where $\left[(AB)^{\ddagger}\right]$ = concentration of activated complex

Pre-Equilibrium

sec. 20E.5

K: equilibrium constant **ppt 20-34**

---

ppt 21-9 and 21-10

- Steady-state approximation

- Activation-controlled

activation-controlled **(21B.2b)**

$$k_2 = k_1\left(\frac{k_d}{k_{-d}}\right) = k_1 K \qquad k_1 << k_{-d} \qquad \frac{d[P]}{dt} = k_2[A][B]$$

Sec. 21C.1(b).

Once the activated complex has been found, motion along the reaction coordinate corresponds to a distortion of some relevant bonds.

If the frequency of the **crucial vibration of the complex is $\nu^{\ddagger}$,** the frequency of passing through the transition state is also $\nu^{\ddagger}$. The rate of passage through the true transition state is proportional to the vibrational frequency $\nu^{\ddagger}$ along the reaction coordinate, and write

$$k^{\ddagger} \approx \nu^{\ddagger} \qquad \mathbf{(21C.5)}$$

$$\nu^{\ddagger} << 10^{13} \,/\, \mathrm{s}$$

$$h\nu^{\ddagger} << k_B T$$

21C.1(c). The Concentration of the Activated Complex

We assume that all distributions of energy compatible with a given total energy are equally likely.

Sec. 21C.1(a).

$\mathrm{A + B \leftrightarrow (AB) \leftrightarrow (AB)^\ddagger \rightarrow P}$

$$K=\frac{[(\mathrm{AB})^\ddagger]}{[\mathrm{A}][\mathrm{B}]}=RT\left(\frac{p^\ddagger}{p_\mathrm{A}p_\mathrm{B}}\right)$$

$$=\left(\frac{RT}{p^\circ}\right)\left\{\frac{\left(p^\ddagger/p^\circ\right)}{\left(p_\mathrm{A}/p^\circ\right)\left(p_\mathrm{B}/p^\circ\right)}\right\}=\left(\frac{RT}{p^\circ}\right)K^\ddagger$$

$$[(\mathrm{AB})^\ddagger]=\left(\frac{RT}{p^\circ}\right)K^\ddagger[\mathrm{A}][\mathrm{B}]$$

$$PV=nRT$$

$$[J]=\frac{n_j}{V_j}=\frac{p_j}{RT}$$

$$K=\frac{N_P}{N_R}=\frac{q_P}{q_R}\exp(-\beta\Delta E_0)$$

ppt 16-37

$K^\ddagger$: dimensionless **equilibrium constant** expressed in terms of pressure

$$K^\ddagger=\left\{\frac{N_\mathrm{A}q_\mathrm{m}^{\ddagger\circ}}{q_\mathrm{A,m}^\circ q_\mathrm{B,m}^\circ}\right\}\exp\left(-\frac{\Delta E_0^\ddagger}{RT}\right)$$

$$K_p=\frac{\left(\frac{q_C^0}{N}\right)^c\left(\frac{q_D^0}{N}\right)^d}{\left(\frac{q_A^0}{N}\right)^a\left(\frac{q_B^0}{N}\right)^b}e^{-\beta\Delta\varepsilon}$$

(21C.9)

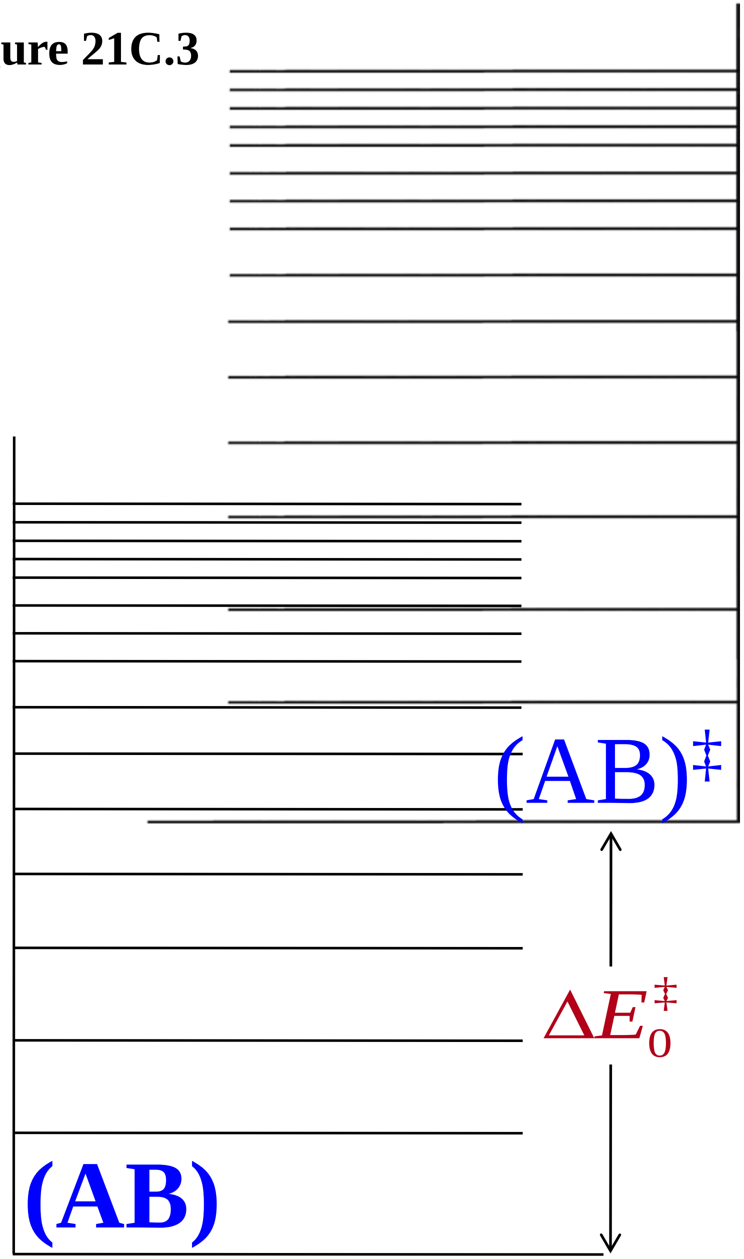
ppt 15-69

$q_\mathrm{m}^\ddagger$: molar **partition function** of the activated complex

$q_\mathrm{A,m}, q_\mathrm{B,m}$: the molar **partition function** for the reactant molecules

$\Delta E_0^\ddagger$: the energy separation of the complex and the reactants

Figure 21C.3



$\nu^{\ddagger} << 10^{13}$ / s

$h\nu^{\ddagger} << k_B T$

Many energy levels at the activated state.

No dip

at the top of the going-through barrier

Saddle Point

$\nu_{max} \sim 10^{13}$ / s

Phonon

Partition Function for Vibrational Mode at the Saddle Point

$$k^{\ddagger} \approx \nu^{\ddagger}$$

Harmonic approximation

$$\frac{1}{1-\exp(-h\nu^{\ddagger}/kT)}$$

where $\nu^{\ddagger}$: its frequency (the same frequency that determine $k^{\ddagger}$)

$$\frac{1}{1-\exp(-h\nu^{\ddagger}/kT)} \cong \frac{kT}{h\nu^{\ddagger}}$$

$$h\nu^{\ddagger} << k_B T$$

$$q^{\ddagger} = \left(\frac{kT}{h\nu^{\ddagger}}\right)\bar{q}^{\ddagger}$$

where $\bar{q}^{\ddagger}$: **partition function for all the other modes of the activated complex**

$$K^{\ddagger} = \frac{kT}{h\nu^{\ddagger}}\bar{K}^{\ddagger}$$

$$\text{where } \bar{K}^{\ddagger} = \left\{\frac{N_A \bar{q}_{\mathrm{m}}^{\ddagger\circ}}{q^{\circ}_{\mathrm{A,m}} q^{\circ}_{\mathrm{B,m}}}\right\}\exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

(21C.6)

The rate constant

$\kappa = 1$

(21C.10)

$$k_2 = k^{\ddagger}K = k^{\ddagger}\left(\frac{RT}{p^{\circ}}\right)K^{\ddagger} = \kappa\cancel{\nu^{\ddagger}}\left(\frac{RT}{p^{\circ}}\right)\left(\frac{kT}{h\cancel{\nu^{\ddagger}}}\right)\bar{K}^{\ddagger}$$

Unknown frequency $\nu^{\ddagger}$ cancels.

$$\bar{K}^{\ddagger} = \left\{\frac{N_A\bar{q}_{\mathrm{m}}^{\ddagger\circ}}{q^{\circ}_{\mathrm{A,m}}q^{\circ}_{\mathrm{B,m}}}\right\}\exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

(skip derivation)

(21C.10)

$$\therefore k_2 = \kappa\left(\frac{kT}{h}\right)\bar{K}$$

Eyring equation

Where $\bar{K} = \left(\frac{RT}{p^{\circ}}\right)\bar{K}^{\ddagger} = \left(\frac{RT}{p^{\circ}}\right)\left\{\frac{N_A\bar{q}_{\mathrm{m}}^{\ddagger\circ}}{q^{\circ}_{\mathrm{A,m}}q^{\circ}_{\mathrm{B,m}}}\right\}\exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$

ppt 15-69

How to use the Eyring equation:

The possibility of using the Eyring equation to calculate the rate of a reaction depends on **being able to calculate the partition function** for the species involved.

The reaction partition function can normally be calculated with confidence, either by using spectroscopic information about the energy levels or from the approximate expressions.

The real difficulty:

determination of the

(canonical) partition function

for the activated complex.

-171101(수)
-171106(월) 자율
-171108(수) 자율
-171113(월) Quiz 2
Chaps. 19B-21B (pp. 798-893)
-171206(수) Final Exam

21D. Collision of Structureless Particles

(skip)

A, B: structureless particles: The only contributions to their partition function are the translational terms.

from (15.19)

$$q^{\circ}_{\mathrm{A,m}} = q^{t\circ}_{\mathrm{A,m}} = \left(\frac{2\pi m_{\mathrm{A}} kT}{h^2}\right)^{\frac{3}{2}} V^{\circ}_{\mathrm{m}} = \tau_{\mathrm{A}} V^{\circ}_{\mathrm{m}} = \tau_{\mathrm{A}}\left(\frac{RT}{p^{\circ}}\right)$$

$$q^{\circ}_{\mathrm{B,m}} = \left(\frac{2\pi m_{\mathrm{B}} kT}{h^2}\right)^{\frac{3}{2}} V^{\circ}_{\mathrm{m}} = \tau_{\mathrm{B}}\left(\frac{RT}{p^{\circ}}\right)$$

21D. **(skip)**

The activated complex is a diatomic molecule of mass $m_{\mathrm{AB}} = m_{\mathrm{A}} + m_{\mathrm{B}}$ and moment of inertia I_{AB}. There is only one vibrational mode, but that corresponds to motion along the reaction coordinate, and so it does not appear in $\bar{q}^{\ddagger}$.

$$\bar{q}_{\mathrm{m}}^{\ddagger\circ} = \tau^{\ddagger}\left(\frac{2I_{\mathrm{AB}}kT}{\hbar^2}\right)V_{\mathrm{m}}^{\circ}, \quad \tau^{\ddagger} = \left(\frac{2\pi m_{\mathrm{AB}}kT}{h^2}\right)^{\frac{3}{2}}$$

$$I_{\mathrm{AB}} = \mu_{AB}R_{\mathrm{AB}}^2$$

μ_{AB}: the reduced mass, R_{AB}: the bond length of the diatomic

$$\therefore k_2 = \left(\frac{RT}{p^{\circ}}\right)\left[\frac{\kappa(kT/h)N_A\tau^{\ddagger}V_{\mathrm{m}}^{\circ}\left(2I_{\mathrm{AB}}kT/\hbar^2\right)}{\tau_{\mathrm{A}}\tau_{\mathrm{B}}\left(V_{\mathrm{m}}^{\circ}\right)^2}\right]\exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

$$= N_A\left(\frac{8kT}{\pi\mu_{\mathrm{AB}}}\right)^{\frac{1}{2}}\kappa\pi R_{\mathrm{AB}}^2\exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

↓

reactive cross-section σ^*

$$I_{\mathrm{AB}} = \mu_{\mathrm{AB}}R_{\mathrm{AB}}^2$$

Compare with k_2 derived from the collision theory:

$$k_2 = \sigma N_A \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} \exp\left(-\frac{\Delta E_\mathrm{a}}{RT}\right)$$

$$k_2 = N_A \left(\frac{8kT}{\pi\mu_\mathrm{AB}}\right)^{\frac{1}{2}} \kappa\pi R_\mathrm{AB}^2 \exp\left(-\frac{\Delta E_0^{\ddagger}}{RT}\right)$$

21C.2. Thermodynamic Aspects

$$K = \exp(-\beta\Delta G)$$

$$-RT\ln\bar{K}^{\ddagger} = \Delta G_{\mathrm{m}}^{\ddagger},$$

$$k_2 = \kappa\left(\frac{RT}{p^{\circ}}\right)\left(\frac{kT}{h}\right)\bar{K}^{\ddagger}$$

$\kappa = 1$

교재 = Definition

= *Never Ever*

$$k_2 = \kappa\left(\frac{kT}{h}\right)\left(\frac{RT}{p^{\circ}}\right)\exp\left(-\frac{\Delta G_{\mathrm{m}}^{\ddagger}}{RT}\right)$$

(21C.11)

$$\Delta G_{\mathrm{m}}^{\ddagger} = \Delta H_{\mathrm{m}}^{\ddagger} - T\Delta S_{\mathrm{m}}^{\ddagger}$$

$\Delta S_{\mathrm{m}}^{\ddagger}$: Entropy of activation

(21C.13)

$\Delta H_{\mathrm{m}}^{\ddagger}$: Enthalpy of activation

$$\therefore k_2 = \left(\frac{kT}{h}\right)\left(\frac{RT}{p^{\circ}}\right)\exp\left(\frac{\Delta S_{\mathrm{m}}^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_{\mathrm{m}}^{\ddagger}}{RT}\right)$$

(21C.15a)

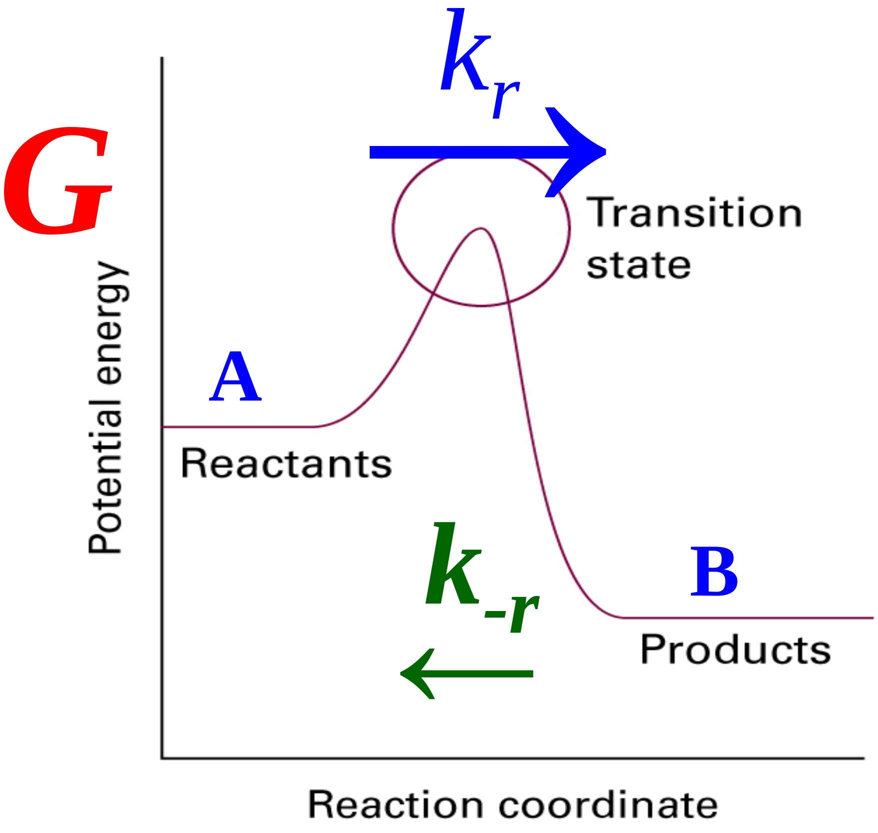
Reaction-Rate Constant

$A \rightarrow (A)^{\ddagger} \rightarrow B$

***

$$k_r = \nu_r \exp\left(\frac{\Delta S_{\mathrm{m}}^{\ddagger}}{R}\right)\exp\left(-\frac{\Delta H_{\mathrm{m}}^{\ddagger}}{RT}\right)$$

~(21C.15a)



$\nu^{\ddagger}_r \ll 10^{13}$ / s

activated state

$\nu_r \sim 10^{13}$ / s

phonon

$A \leftarrow (A)^{\ddagger} \leftarrow B$

David Turnbull (1915–2007)

J. W. Christian
"The Theory of Transformations"

$H + H_2 \rightarrow H_2 + H$

21D.3. Potential Energy Surfaces

Consider a collision between H atom and an H_2 molecule. The potential energy surface is the plot of the potential energy for all relative locations of the three hydrogen nuclei. Three parameters are required to define the nuclear separations:

H_A–H_B separation R_{AB}

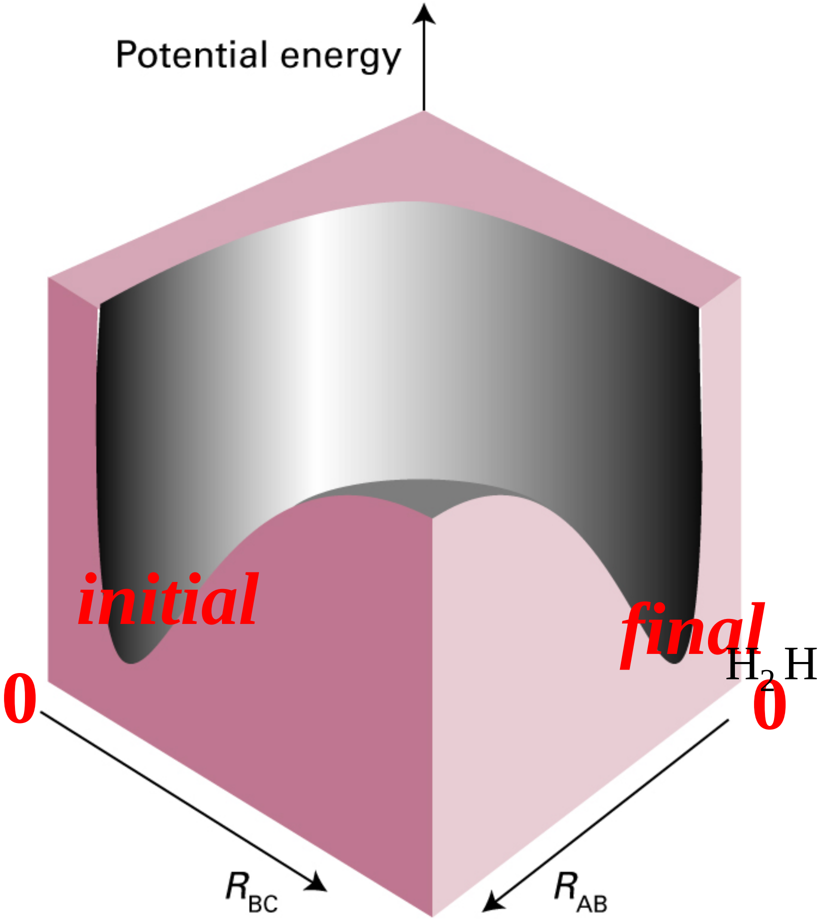
H_B–H_C separation R_{BC}

H_C–H_A separation R_{CA}

A	H	A-B	H_2
B-C	H_2	C	H

At the start of the encounter, R_{AB} is infinite and R_{BC} is the H_2 equilibrium bond length. At the end of a successful reactive encounter R_{AB} is equal to the bond length and R_{BC} is infinite.

$H + H_2 \rightarrow H_2 + H$

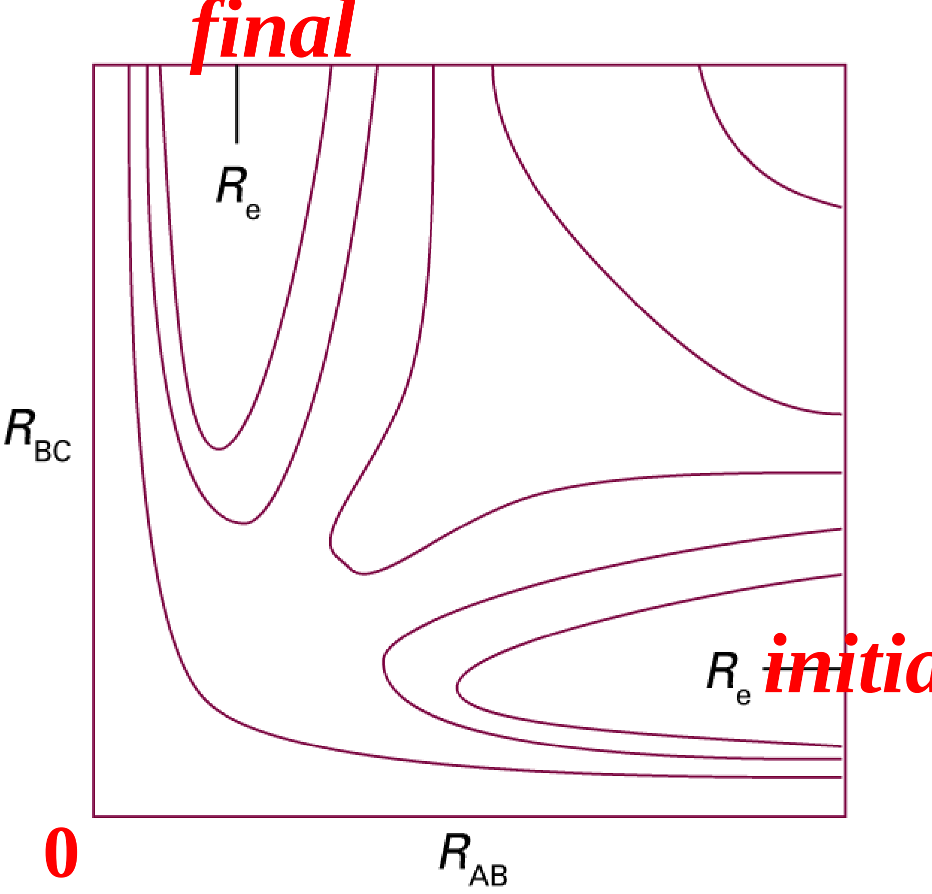


H_2 H + **Figure 21D.12**

The potential energy surface for the $H + H_2$ reaction when the atoms are constrained to be collinear.

$R_{AB} = \infty$ A section through the surface is the same as the H_2 potential energy curve.

$R_{BC} = \infty$ A section through the surface is the molecular potential energy curve of an isolated H_A–H_B molecule.



$H + H_2 \rightarrow H_2 + H$

Figure 21D.13

The contour diagram (with contour of equal potential energy).

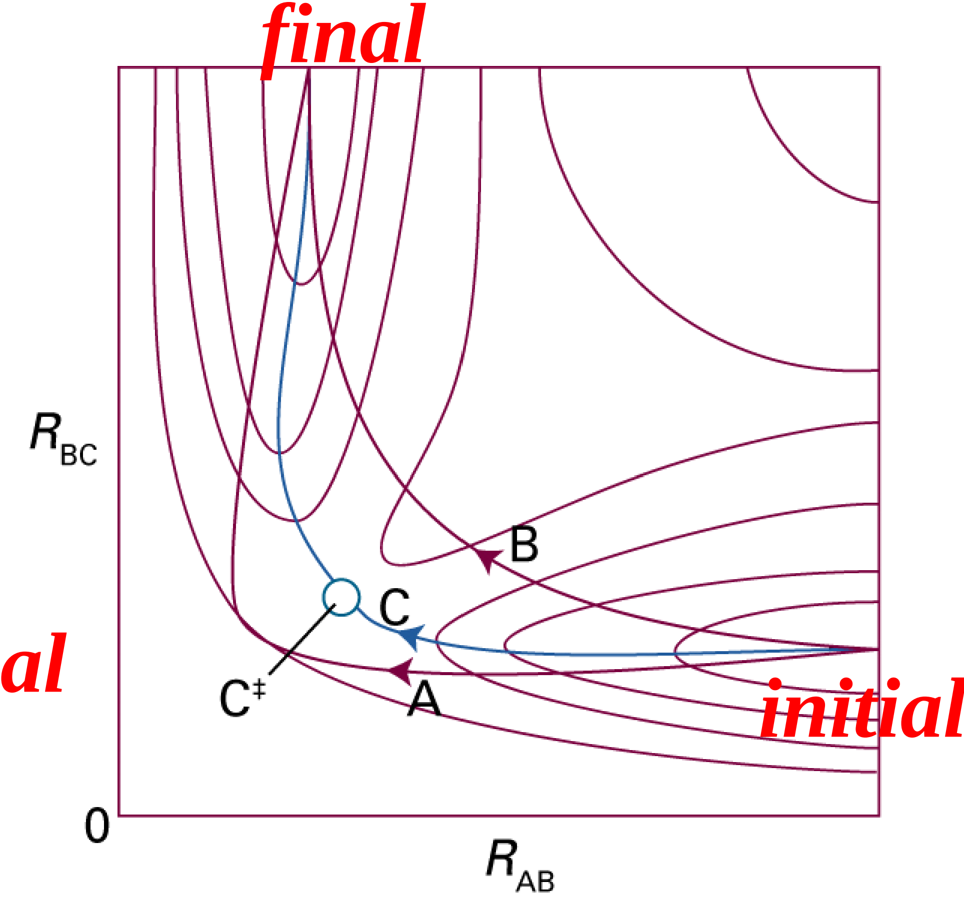


Figure 21D.14

Various trajectories through the potential energy surface:

A corresponds to a path in which R_{BC} is held constant as H_A approaches.

B corresponds to a path in which R_{BC} lengthens at an early stage during the approach of H_A.

C is the path along the floor of the potential valley.

$H + H_2 \rightarrow H_2 + H$

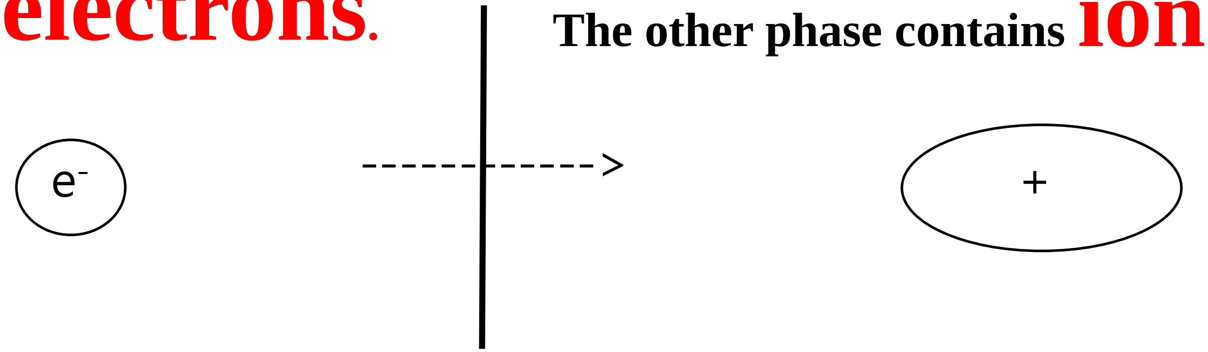
Consider the changes in potential energy as H_A approaches $H_B–H_C$. If the $H_B–H_C$ bond length is constant during the initial approach of H_A, the potential energy of the H_3 cluster would rise along the path marked A.

Path B: the $H_B–H_C$ bond length increases while H_A is still far away.

Path C: the path of least potential energy R_{BC} lengthening as H_A approaches and begins to form a bond with H_B. The $H_B–H_C$ bond relaxes at the diamond of the incoming atom, and although the potential energy rises, it climbs only as far as the saddle-shaped region of the surface, to the saddle point marked $C^{\ddagger}$.

21E. Electrochemistry

One phase contains electrons. **The other phase contains ions.**



Fundamental act in electrochemistry

"Passage of Current Caused by Chemical Changes"

Battery, Water Splitting, CO_2 Reduction, Fuel Cell, Quantum-Rod Solar Cells, Sensors,

Electro-Analysis, Electro-Synthesis, Electrodeposition, Corrosion, etc.

Electrochemistry is the Study of Phenomena at the Electrode/Electrolyte Interfaces.

Dynamics of Electron Transfer

Oxidation vs. Reduction

$$\vec{E} = -\nabla\phi$$

21E.1. Electron Transfer in Homogeneous System

Consider electron transfer from ***a donor species D*** to ***an acceptor species A*** in solution:

$$\mathrm{D} + \mathrm{A} \rightleftarrows \mathrm{D}^+ + \mathrm{A}^- \qquad v = k_r[\mathrm{D}][\mathrm{A}] \qquad (1)$$

(21E.1)

(skip---)

(1) Diffusion of D and A in Solution

(2) Complex Formation

$$\mathrm{D} + \mathrm{A} \underset{k_a'}{\overset{k_a}{\rightleftarrows}} \mathrm{DA} \qquad K_{DA} = \frac{k_a}{k_a'} \qquad (2)$$

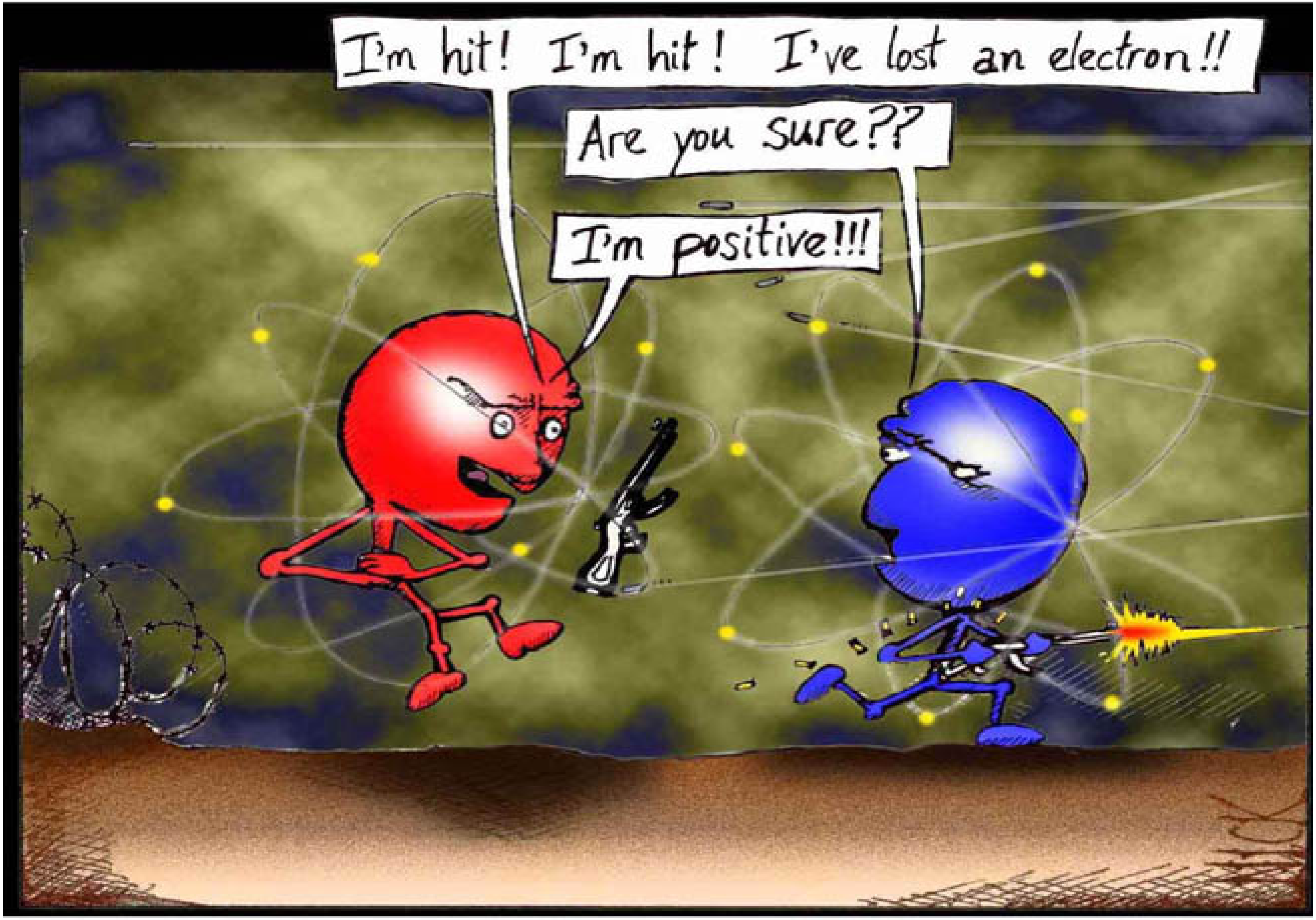
(3) Reversible Electron Transfer

$$\mathrm{DA} \underset{k_{et}'}{\overset{k_{et}}{\rightleftarrows}} \mathrm{D}^+\mathrm{A}^- \qquad (3)$$

(4) The Formation of Separated Ions

$$\mathrm{D}^+\mathrm{A}^- \xrightarrow{k_d} \mathrm{D}^+ + \mathrm{A}^- \qquad (4)$$

Oxidation and Reduction



Another casualty in the War of the Atoms.

-171115(수)

(skip---)

Justific. 21E.1

The rate constant for the overall electron transfer process

$$\frac{1}{k_{\mathrm{r}}}=\frac{1}{k_{\mathrm{a}}}+\frac{k_{\mathrm{a}}^{'}}{k_{\mathrm{a}}k_{\mathrm{et}}}\left(1+\frac{k_{et}^{'}}{k_{\mathrm{d}}}\right) \qquad (5) \qquad (21E.3)$$

The overall reaction rate = The rate of formation of separated ions

$$v=k_{\mathrm{r}}[\mathrm{D}][\mathrm{A}]=k_{\mathrm{d}}[\mathrm{D^{+}A^{-}}] \qquad (6)$$

Steady-state approximations for two intermediates: DA and D^+A^-

$$\frac{d[\mathrm{D^{+}A^{-}}]}{dt}=k_{\mathrm{et}}[\mathrm{DA}]-k_{\mathrm{et}}^{'}[\mathrm{D^{+}A^{-}}]-k_{\mathrm{d}}[\mathrm{D^{+}A^{-}}]=0$$

$$[\mathrm{DA}]=\frac{k_{\mathrm{et}}^{'}+k_{\mathrm{d}}}{k_{\mathrm{et}}}[\mathrm{D^{+}A^{-}}] \qquad (7)$$

(skip)

$$\frac{d[\mathrm{DA}]}{dt} = k_{\mathrm{a}}[\mathrm{D}][\mathrm{A}] - k_{\mathrm{a}}^{'}[\mathrm{DA}] - k_{\mathrm{et}}[\mathrm{DA}] + k_{\mathrm{et}}^{'}[\mathrm{D}^{+}\mathrm{A}^{-}]$$

$$= k_{\mathrm{a}}[\mathrm{D}][\mathrm{A}] - \left\{\frac{\left(k_{\mathrm{a}}^{'} + k_{\mathrm{et}}\right)\left(k_{\mathrm{et}}^{'} + k_{\mathrm{d}}\right)}{k_{\mathrm{et}}} - k_{\mathrm{et}}^{'}\right\}[\mathrm{D}^{+}\mathrm{A}^{-}] = 0$$

$$[\mathrm{D}^{+}\mathrm{A}^{-}] = \frac{k_{\mathrm{a}}k_{\mathrm{et}}}{k_{\mathrm{a}}^{'}k_{\mathrm{et}}^{'} + k_{\mathrm{a}}^{'}k_{\mathrm{d}} + k_{\mathrm{d}}k_{\mathrm{et}}}[\mathrm{D}][\mathrm{A}] \qquad (8)$$

$$\nu = k_{\mathrm{d}}[\mathrm{D}^{+}\mathrm{A}^{-}] = \frac{k_{\mathrm{d}}k_{\mathrm{a}}k_{\mathrm{et}}}{k_{\mathrm{a}}^{'}k_{\mathrm{et}}^{'} + k_{\mathrm{a}}^{'}k_{\mathrm{d}} + k_{\mathrm{d}}k_{\mathrm{et}}}[\mathrm{D}][\mathrm{A}] \qquad (9)$$

$$\therefore k_{\mathrm{r}} = \frac{k_{\mathrm{d}}k_{\mathrm{a}}k_{\mathrm{et}}}{k_{\mathrm{a}}^{'}k_{\mathrm{et}}^{'} + k_{\mathrm{a}}^{'}k_{\mathrm{d}} + k_{\mathrm{d}}k_{\mathrm{et}}}$$

$$\frac{1}{k_{\mathrm{r}}} = \frac{k_{\mathrm{a}}^{'}k_{\mathrm{et}}^{'} + k_{\mathrm{a}}^{'}k_{\mathrm{d}} + k_{\mathrm{d}}k_{\mathrm{et}}}{k_{\mathrm{d}}k_{\mathrm{a}}k_{\mathrm{et}}} = \frac{1}{k_{\mathrm{a}}} + \frac{k_{\mathrm{a}}^{'}}{k_{\mathrm{a}}k_{\mathrm{et}}}\left(1 + \frac{k_{\mathrm{et}}^{'}}{k_{\mathrm{d}}}\right) \qquad (10)$$

Assuming that the main decay route for D^+A^- is dissociation of the complex into separated ions, or $k_d \gg k'_{et}$:

$$\frac{1}{k_\mathrm{r}} \approx \frac{1}{k_\mathrm{a}}\left(1+\frac{k'_\mathrm{a}}{k_\mathrm{et}}\right) \tag{11}$$

(a) If $k_{et} \gg k'_a,\ k_r \approx k_a.$

The rate of product is controlled by diffusion of D and A in solution.

(b) If $k_{et} \gg k'_a,\ k_r = \left(\frac{k_a}{k'_a}\right)k_{et} = K_{DA}k_{et}.$

This process **controlled by the activation energy of electron transfer in the DA complex**.

(skip---)

Using the transition state theory,

$$k_{\mathrm{et}} = \kappa \nu^{\ddagger} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (12)$$

κ : transmission coefficient

$\nu^{\ddagger}$: vibrational frequency at the transition state

$\Delta G^{\ddagger}$: Gibbs free energy of activation

21E.(a) The rate of electron tunneling

The Frank-Condon principle

The nuclei do not have time to move when the system passes from the reactant to the product surface as a result of the transfer of an electron.

$\kappa \nu^{\ddagger}$: a measure of the probability that the system will convert from reactants (DA) to products ($D^{+}A^{-}$) at q^{*} by an electron transfer

(skip---)

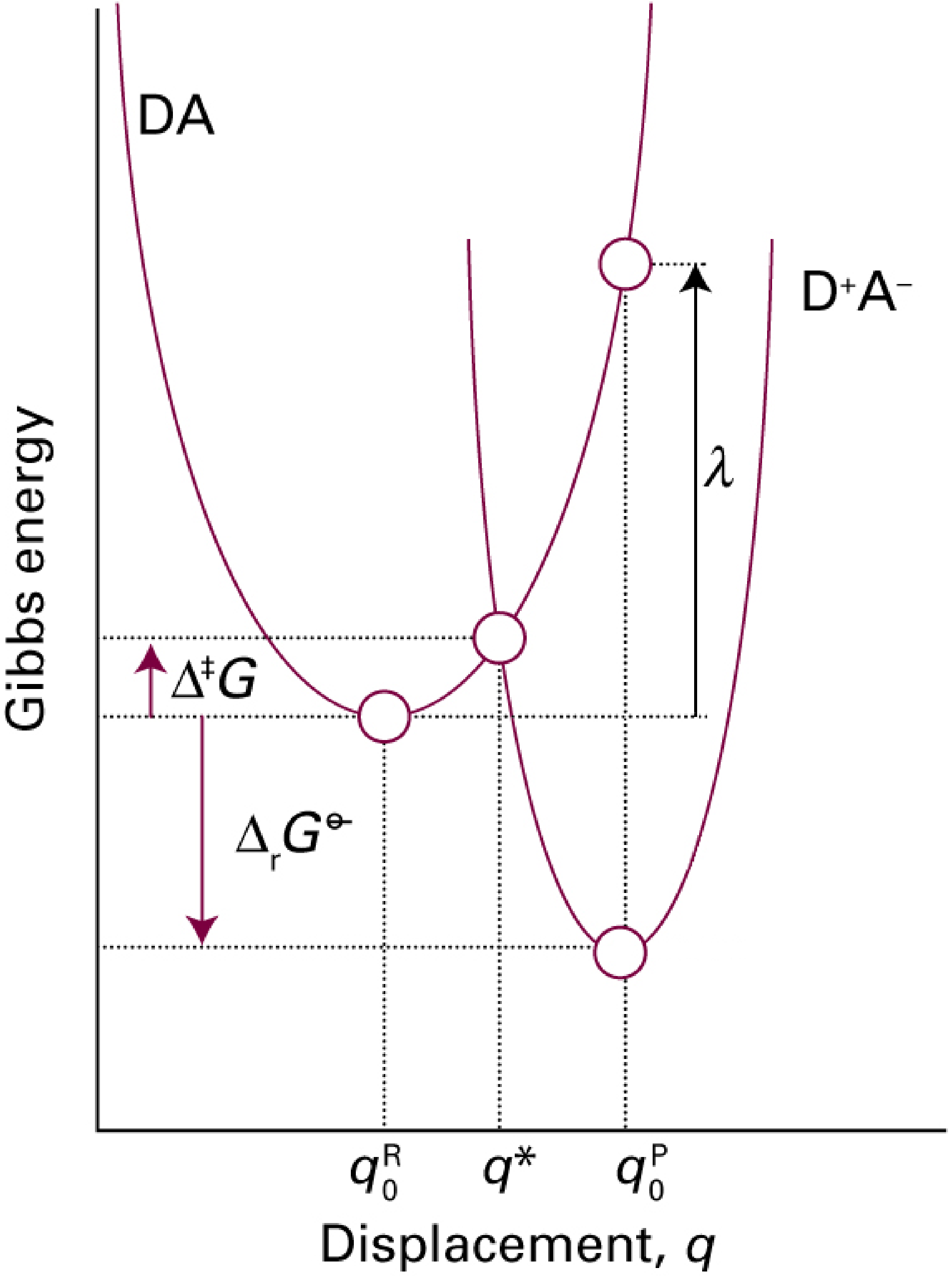


Figure 21E.3
The Gibbs energy surfaces of the **complexes DA and D^+A^-** involved in an electron transfer process are represented by parabolas characteristic of harmonic oscillators, with the displacement coordinate q corresponding to the changing geometries of the system. In the plot, q_0^R and q_0^P are the values of q at which the minima of the reactant and product parabolas occur, respectively. The parabolas intersect at $q=q^*$. The plots also portray the Gibbs energy of activation, $\Delta G^{\ddagger}$, the standard reaction Gibbs energy, ΔG°, and the reorganization energy, λ.

According to the theory for electron tunneling,

$$k_{\mathrm{et}} \propto e^{-\beta r} \tag{13}$$

where *b* depends on the medium through which the electron must travel from donor to acceptor, and *r* is the edge-to-edge distance.

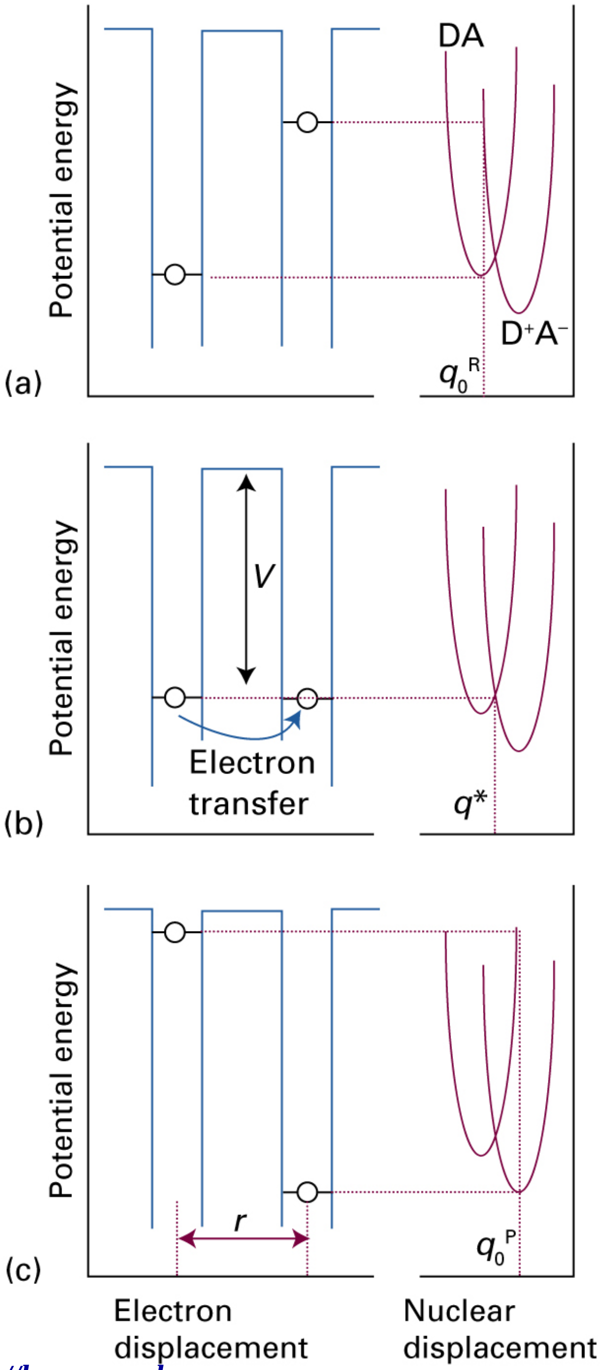


Figure 21E.2

Correspondence between the electronic energy levels (shown on the left) and the nuclear energy levels (shown on the right) for the DA and D^+A^- complexes involved in an electron transfer process. (a) At the nuclear configuration denoted by q_0^R, the electron to be transferred in DA is in an occupied energy level and the lowest unoccupied energy level of D^+A^- is of too high energy to be a good electron acceptor. (b) As the nuclei rearrange to a configuration represented by q^*, DA and D^+A^- become degenerate and electron transfer occurs by tunneling through the barrier of height V and width r, the edge-to-edge distance between donor and acceptor. (c) The system relaxes to the equilibrium nuclear configuration of D^+A^- denoted by q_0^P, in which the lowest unoccupied electronic level of DA is higher in energy than the highest occupied electronic level of D^+A^-.

(Adapted from R.A. Marcus and N. Sutin, *Biochim. Biophys. Acta* **1985**, *811*, 265.)

21E.1. The expression for the rate of electron transfer

(skip---)

The Gibbs energy of activation for electron transfer

$$\Delta G^{\ddagger} = \frac{\left(\Delta G^{0} + \lambda\right)^{2}}{4\lambda} \qquad (14)$$

ΔG^{0} : the standard reaction Gibbs energy for $\mathrm{DA} \rightarrow \mathrm{D^{+}A^{-}}$

λ : the reorganization energy, the energy change associated with molecules rearrangements that must take place so that DA can take on the equilibrium geometry of $\mathrm{D^{+}A^{-}}$

$\Delta G^{0} = -\lambda, \ \Delta G^{\ddagger} = 0$

The reaction is not slowed down by an activation barrier when the reorganization energy is equal to the standard reaction Gibbs energy.

From eqs. (12) and (13),

$$k_{\mathrm{et}} \propto e^{-\beta r} e^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (15)$$

Derivation of eq (14)

$$\mathrm{DA} = \mathrm{R}, \quad \mathrm{D^{+}A^{-}} = \mathrm{P}$$

The molar Gibbs energies, $G_{m,\mathrm{R}}(q)$ and $G_{m,\mathrm{R}}(q)$

$$G_{m,\mathrm{R}}(q) = \frac{1}{2} N_{\mathrm{A}} \mu \omega^{2} \left(q - q_{0}^{\mathrm{R}}\right)^{2} + G_{m,\mathrm{R}}\left(q_{0}^{\mathrm{R}}\right) \qquad \text{(a)}$$

$$G_{m,\mathrm{P}}(q) = \frac{1}{2} N_{\mathrm{A}} \mu \omega^{2} \left(q - q_{0}^{\mathrm{P}}\right)^{2} + G_{m,\mathrm{P}}\left(q_{0}^{\mathrm{P}}\right) \qquad \text{(b)}$$

$q_{0}^{\mathrm{R}}, q_{0}^{\mathrm{P}}$: the value of q at which the minima of the reactant and product parabolas occur, respectively

$$\Delta G^{0} = G_{m,\mathrm{P}}(q_0^{\mathrm{P}}) - G_{m,\mathrm{R}}(q_0^{\mathrm{R}}) \qquad \text{(c)}$$

$$q^{*} = q_0^{\mathrm{R}} + \alpha\left(q_0^{\mathrm{P}} - q_0^{\mathrm{R}}\right) \qquad \text{(d)}$$

where α is the parameter representing the fractional change in q.

$$\Delta G^{\ddagger} = G_{m,\mathrm{R}}(q^{*}) - G_{m,\mathrm{R}}(q_0^{\mathrm{R}}) \qquad \text{(e)}$$

From eqs. (a), (b), (d) and (e),

$$\Delta G^{\ddagger} = \frac{1}{2} N_{\mathrm{A}} \mu \omega^{2} \left(q^{*} - q_0^{\mathrm{R}}\right)^{2} = \frac{1}{2} N_{\mathrm{A}} \mu \omega^{2} \left\{\alpha\left(q_0^{\mathrm{P}} - q_0^{\mathrm{R}}\right)\right\}^{2} \qquad \text{(f)}$$

Since $\lambda = G_{m,\mathrm{R}}\left(q_0^{\mathrm{P}}\right) - G_{m,\mathrm{R}}\left(q_0^{\mathrm{R}}\right)$,

$$\lambda = \frac{1}{2} N_{\mathrm{A}} \mu \omega^{2} \left(q_0^{\mathrm{P}} - q_0^{\mathrm{R}}\right)^{2}. \qquad \text{(g)}$$

From eqs. (f) and (g),

$$\Delta G^{\ddagger} = \alpha^2 \lambda \tag{h}$$

Because $G_{m,\mathrm{R}}(q^*) = G_{m,\mathrm{P}}(q^*)$, combining eqs. (b), (c), (d), (g) and (h) gives

$$\alpha^2 \lambda = \frac{1}{2} N_{\mathrm{A}} \mu \omega^2 \left\{ (\alpha - 1)\left(q_0^{\mathrm{P}} - q_0^{\mathrm{R}} \right) \right\}^2 + \Delta G^0$$

$$= (\alpha - 1)^2 \lambda + \Delta G^0$$

$$\therefore \alpha = \frac{1}{2}\left(\frac{\Delta G^0}{\lambda} + 1 \right) \tag{i}$$

Combining eqs. (h) and (i),

$$\Delta G^{\ddagger} = \frac{\left(\Delta G^0 + \lambda \right)^2}{4\lambda}$$

21E. Experimental results

(skip---)

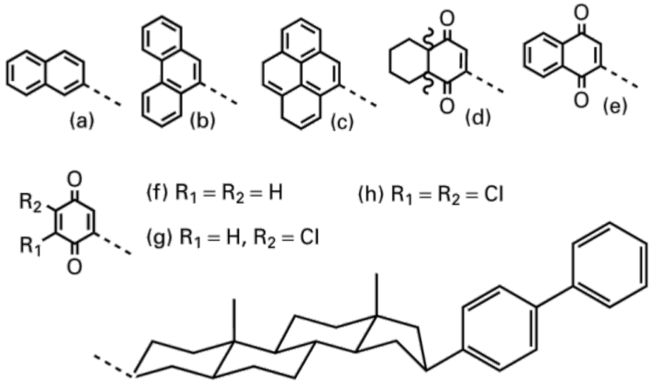
$$k_{et} \propto e^{-\beta r} e^{-\frac{\Delta G^{\ddagger}}{RT}} = e^{-\beta r} e^{-\left\{\frac{\left(\Delta G^{0}+\lambda\right)^{2}}{4\lambda RT}\right\}} \qquad (16)$$

Assuming that the edge-to-edge distance, the reorganization energy, and $\kappa v^{\ddagger}$ are constant,

$$\ln k_{et} = -\frac{RT}{4\lambda}\left(\frac{\Delta G^{0}}{RT}\right)^{2} - \frac{1}{2}\left(\frac{\Delta G^{0}}{RT}\right) + \text{constanat} \qquad (17)$$

A plot of $\ln k_{et}$ versus ΔG^{0} should be shaped like a downward parabola.

(skip)



1

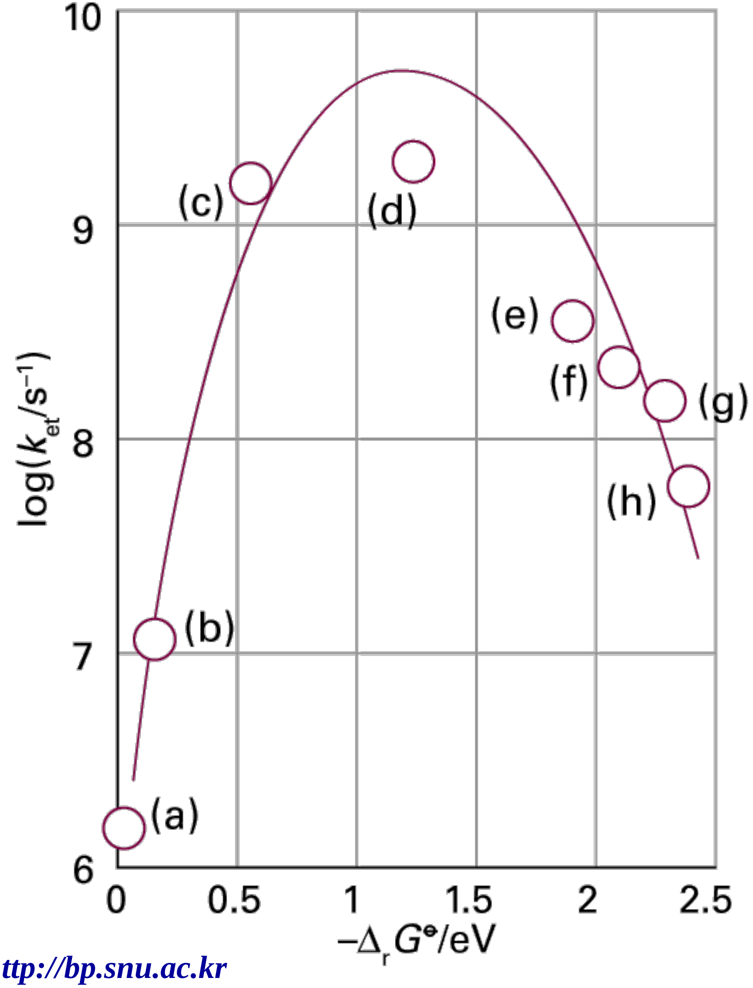


Figure 21E.5

Variation of $\log k_{et}$ with $-\Delta G^\ominus$ for a series of compounds with the structures given in **1**. Kinetic measurements were conducted in 2-methyltetrahydrofuran and at 296 K. The distance between donor (the reduced biphenyl group) and the acceptor is constant for all compounds in the series because the molecular linker remains the same. Each acceptor has a characteristic standard reduction potential, so it follows that the standard Gibbs energy for the electron transfer process is different for each compound in the series. The line is a fit to a version of eq 17 and the maximum of the parabola occurs at

$$-\Delta G^\ominus = \lambda = 1.2 eV = 1.2 \times 10^2 \, \mathrm{kJ mol^{-1}}.$$

(Reproduced with permission from J.R. Miller, L.T. Calcaterra, and G.L. Closs, *J. Amer. Chem. Soc.* **1984**, *106*, 3047.)

21F. Electron Transfer Processes at the Electrodes

21F.1. The Electrode (Metal) and Electrolyte (Solution) Interface

Formation of **electrical double layers** at the boundary between the solid and liquid phases creates **an electrical potential difference**, called the Galvani potential difference.

Models for the Electrode-Solution Interface

1. **Helmholtz Layer**

   The location of the sheet of ionic charge, which is called the **outer Helmholtz plane (OHP)**, is identified as the plane running through the solvated ions. Refinement of this model considers ions that have discarded their solvating molecules and have attached to the electrode surface by chemical bonds, forming the **inner Helmholtz plane (IHP)**.

$$\vec{D} = \varepsilon \vec{E}$$

$$\vec{E} = -\nabla\phi \qquad \nabla\cdot\vec{D} = 4\pi\rho$$

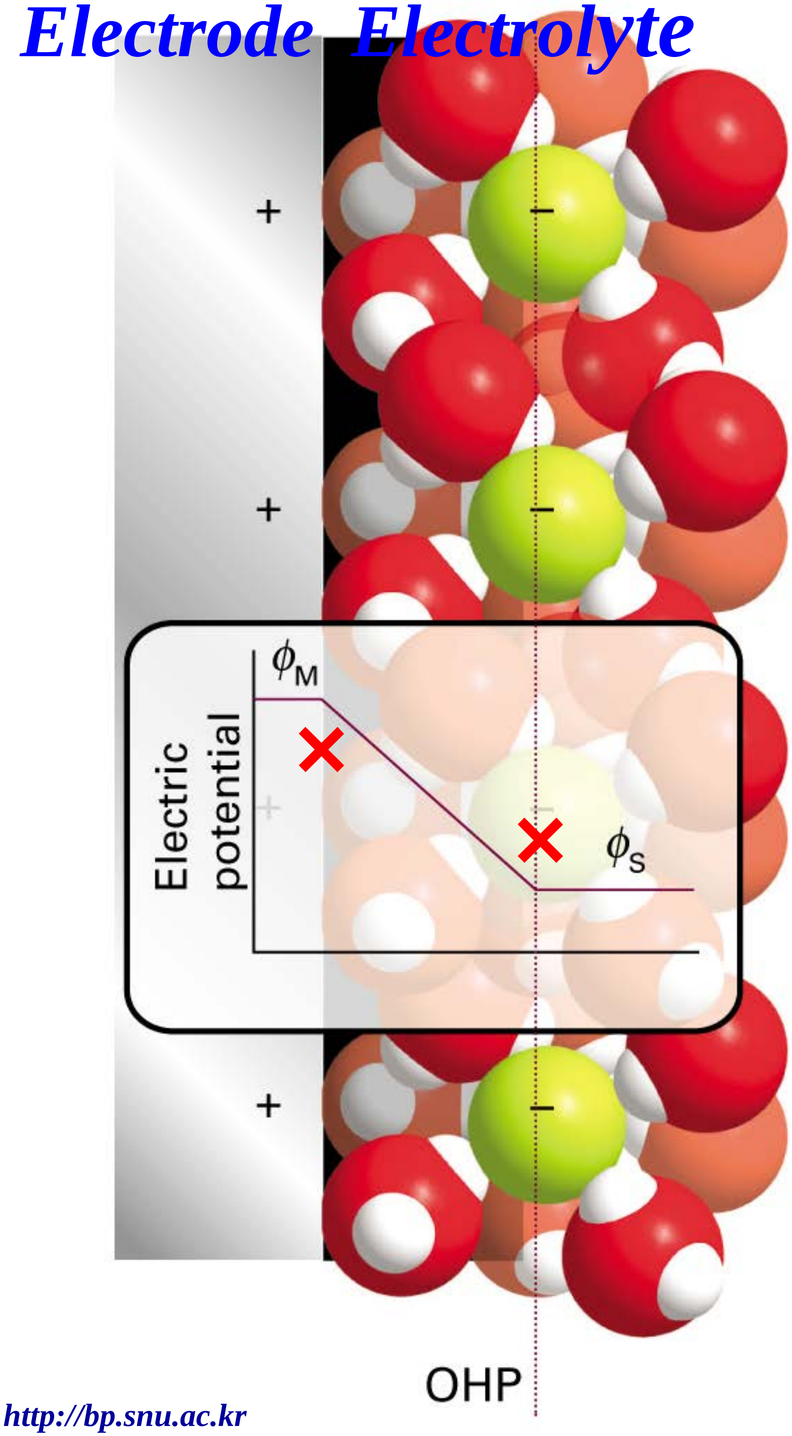


Figure 21F.31
A simple model of the electrode-solution interface treats it as two rigid planes of charge. One plane, the outer Helmholtz plane (OHP), is due to the ions with their solvating molecules and the other plane is that of the electrode itself. The plot shows the dependence of the electric potential with distance from the electrode surface according to this model. **Between the IHP and the OHP, the potential varies linearly**.

2. The Gouy-Chapman model of the diffuse double layer

The disordering effect of thermal motion is taken into account in the some way as the Debye-Huckel model describes the ionic atmosphere of an ion.

Diffuse Layer (~100 Å)

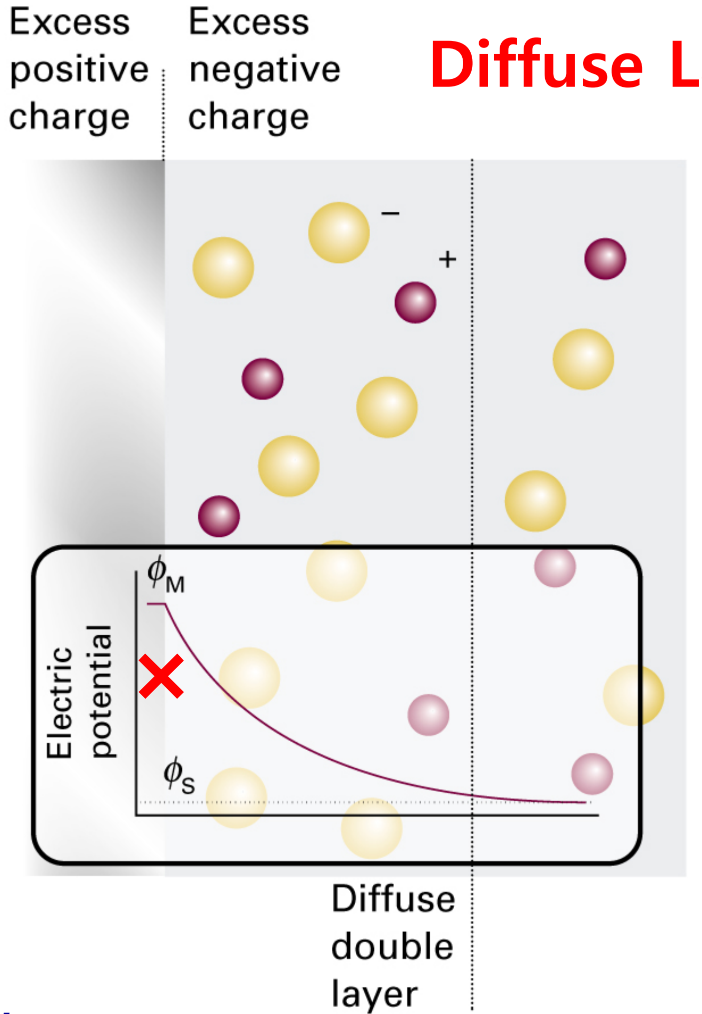
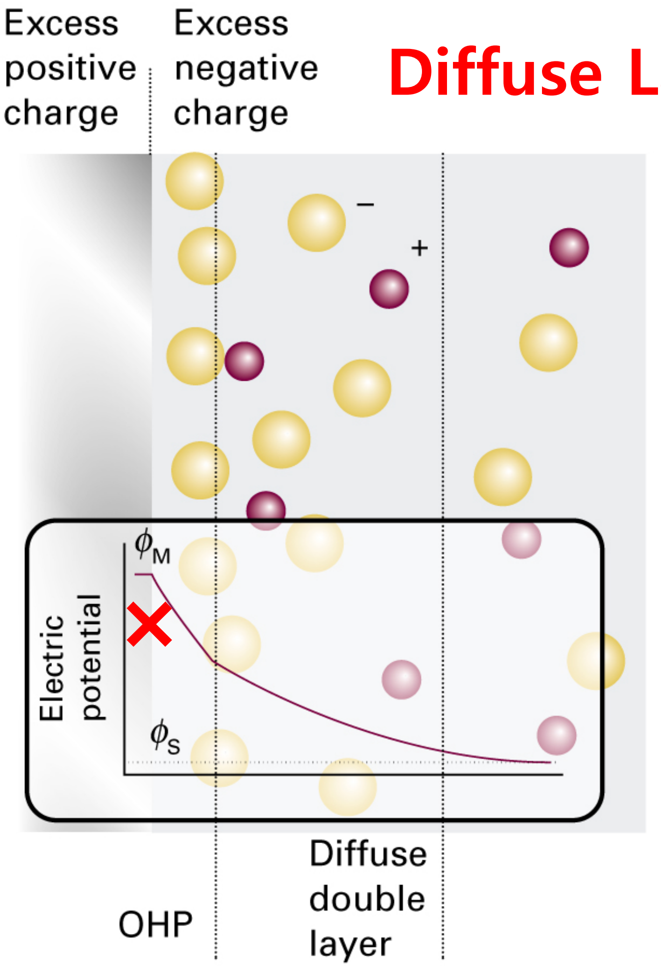


Figure 21F.2
The Gouy-Chapman model of the **electrical double layer** treats the outer region as an atmosphere of counter-charge, similar to the Debye-Huckel theory of ion atmosphere. The plot of electrical potential against distance from the electrode surface shows the meaning of the **diffuse double layer**.

3. The Stern model

The above two models are combined in the Stern model, in which the ions closest to the electrode are constrained into a rigid Helmholtz plane while outside that plane the ions are dispersed as in the Gouy-Chapman model.



Diffuse Layer (~100 Å)

Figure 21F.3
A representation of the Stern model of the electrode-solution interface. The model incorporates the ides of an **outer Helmholtz plane** near the electrode surface and of a **diffuse double layer** further away from the surface.

$$j = j_0 \left\{ e^{0.5e(E-E_0)/kT} - e^{-0.5e(E-E_0)/kT} \right\}$$

21F.2(a). The Butler-Volmer Equation

Consider a reaction at the electrode:

The current density *j* : the electric current flowing an electrode divided by the area of the electrode

$$j = j_0 \left\{ e^{(1-\alpha)f\eta} - e^{-\alpha f\eta} \right\} \qquad \textbf{(21F.1)}$$

$\alpha \sim 0.5$

$$f = \frac{F}{RT}$$

F : Faraday's constant

$$\eta = E' - E_0$$

the overpotential

E_0 : Electrode potential at equilibrium (no net flow of current)

E' : the electrode potential when a current is being drawn from the cell

α : the transfer coefficient α=0 (reactant-like) α=1 (product-like)

j_0 : Exchange-current density when the electrode is at equilibrium

Oxidation = Reduction

page 922

(skip)

$$f\eta << 1\left(\text{usu.}\,\eta < 0.01V\right)$$
$$j = j_0\left\{1 + (1-\alpha)f\eta + \cdots - (1 - \alpha f\eta + \cdots)\right\} \approx j_0 f\eta$$
$$\eta = \frac{RTj}{Fj_0}$$

This equation shows that the current density is proportional to the overpotential, so at low overpotentials the interface behaves like a conductor that obeys Ohm's law.

If η is large and positive $\left(\text{e.g.}\,\eta \geq 0.12V\right)$,

$$j = j_0\left\{e^{(1-\alpha)f\eta} - e^{-\alpha f\eta}\right\} \approx j_0 e^{(1-\alpha)f\eta}$$
$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

If η is large and negative $\left(\text{e.g.}\,\eta < -0.12V\right)$,

$$j \approx -j_0 e^{-\alpha f\eta}$$
$$\ln(-j) = \ln j_0 - \alpha f\eta$$

(skip)

Derivation of the Butler-Volmer equation

Electrode reaction: heterogeneous reaction

The flux of products: the amount of material produced over a region of the electrode surface in an interval of time divided by the area of the region and the duration of the interval

Product flux= k_r[species]

The rate of reduction of Ox and the rate of oxidation of Red

$$v_{\mathrm{Ox}} = k_{\mathrm{c}}[\mathrm{Ox}] \qquad (1)$$

$$v_{\mathrm{Red}} = k_{\mathrm{a}}[\mathrm{Red}] \qquad (2)$$

The net current density at the electrode is the difference between the current densities arising from the reduction of Ox and the oxidation of Red.

The current density *j* arising from the redox processes are the rate multiplied by the charge transferred per mole of reaction (*F*).

$$j_c = Fk_\mathrm{c}[\mathrm{Ox}] \quad \text{for Ox} + e^- \rightarrow \text{Red} \quad \text{Cathodic current density}$$

$$j_a = Fk_\mathrm{a}[\mathrm{Red}] \quad \text{for Red} \rightarrow \text{Ox} + e^- \quad \text{Anodic current density}$$

The net current

$$j = j_a - j_c = Fk_a[\mathrm{Red}] - Fk_c[\mathrm{Ox}] \qquad (3)$$

$$j_a > j_c \rightarrow j > 0 : \text{the current is anodic}$$

$$j_c > j_a \rightarrow j < 0 : \text{the current is cathodic}$$

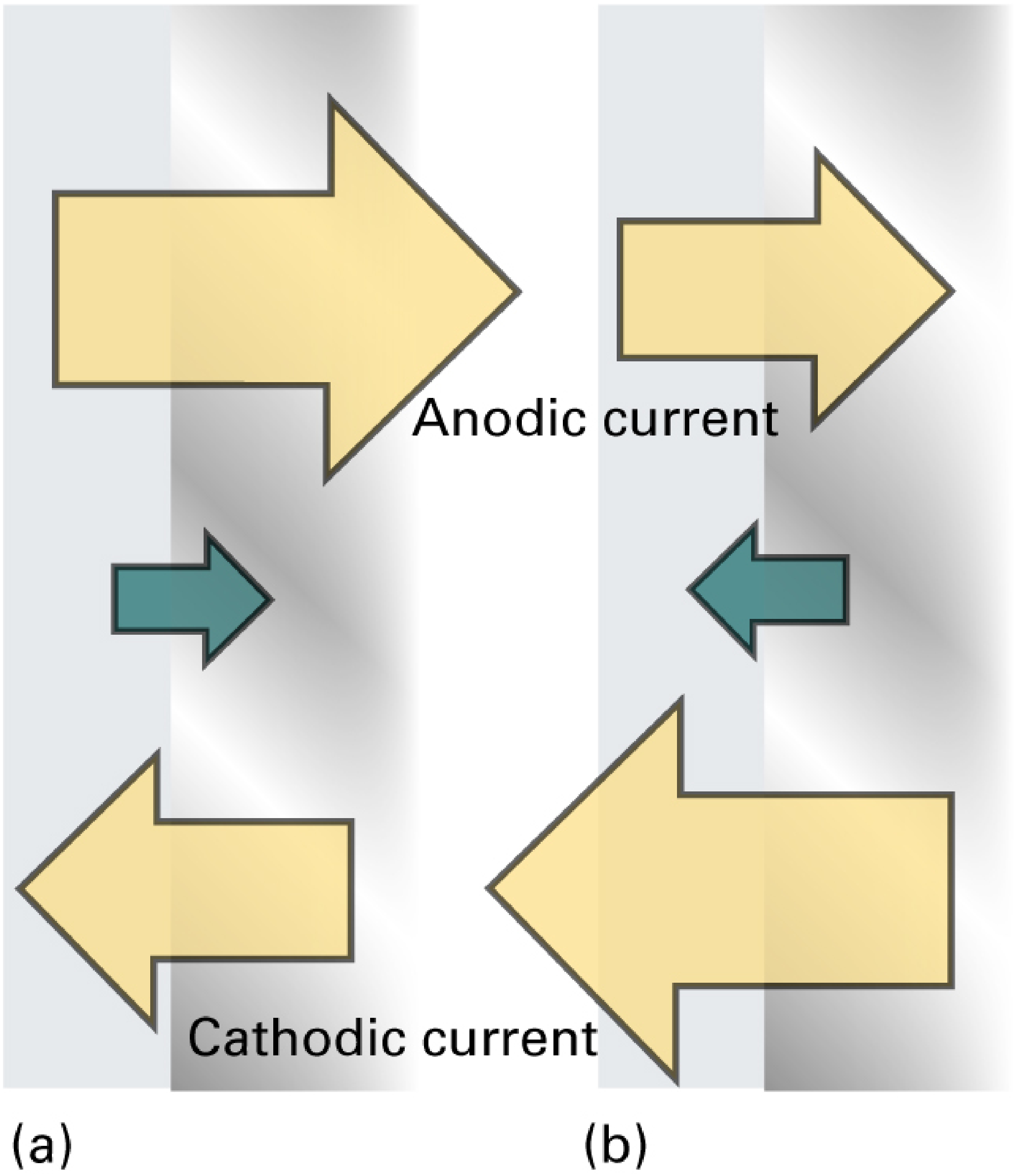


Figure 22. 36
The net current density is defined as the difference between the cathodic and anodic contributions. (a) When $j_a > j_c$, the net current is anodic, and there is a net oxidation of the species in solution. (b) When $j_c > j_a$, the net current is cathodic, and the net process is reduction.

According to the transition state theory

$$k_r = Be^{-\frac{\Delta G^{\ddagger}}{RT}} \qquad (4)$$

$\Delta G^{\ddagger}$: the activation Gibbs energy

B : a constant

Sunstituting eq4 into eq3

$$j = FB_a[\mathrm{Red}]e^{-\frac{\Delta G_a^{\ddagger}}{RT}} - FB_c[\mathrm{Ox}]e^{-\frac{\Delta G_c^{\ddagger}}{RT}} \qquad (5)$$

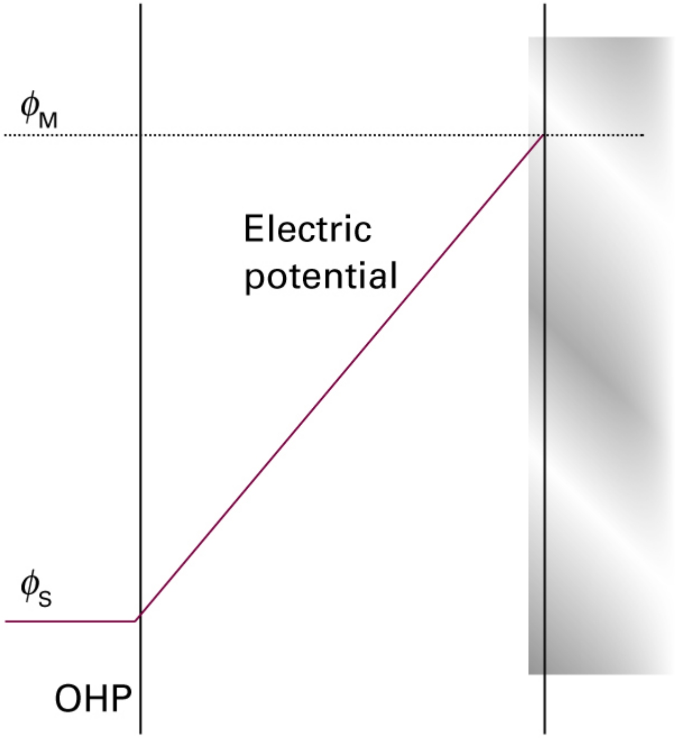


Figure 22.37
The potential ϕ varies between two plane parallel sheets of charge, and its effect on the Gibbs energy of the transition state depends on the extent to which the latter resembles the species at the inner or outer planes.

Consider the reduction rate $\mathrm{Ox} + e^- \rightarrow \mathrm{Red}$.

If the transition state of activated complex is product-like,

$$\Delta G_c^{\ddagger} = \Delta G_c^{\ddagger}(0) + F\Delta\phi \qquad (6)$$

$\Delta G_c^{\ddagger}(0)$: the activation Gibbs energy in the absence of a potential difference across the double layer

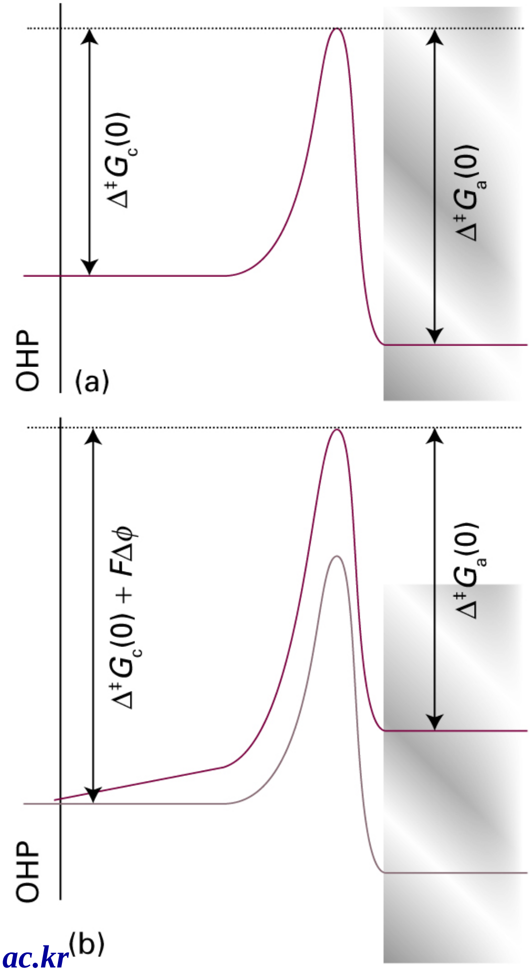


Figure 22.38
When the transition state resembles a species that has undergone reduction, the activation Gibbs energy for the anodic current is almost unchanged, but the full effect applies to the cathodic current. (a) Zero potential difference; (b) nonzero potential difference.

If the transition state is reactant-like,

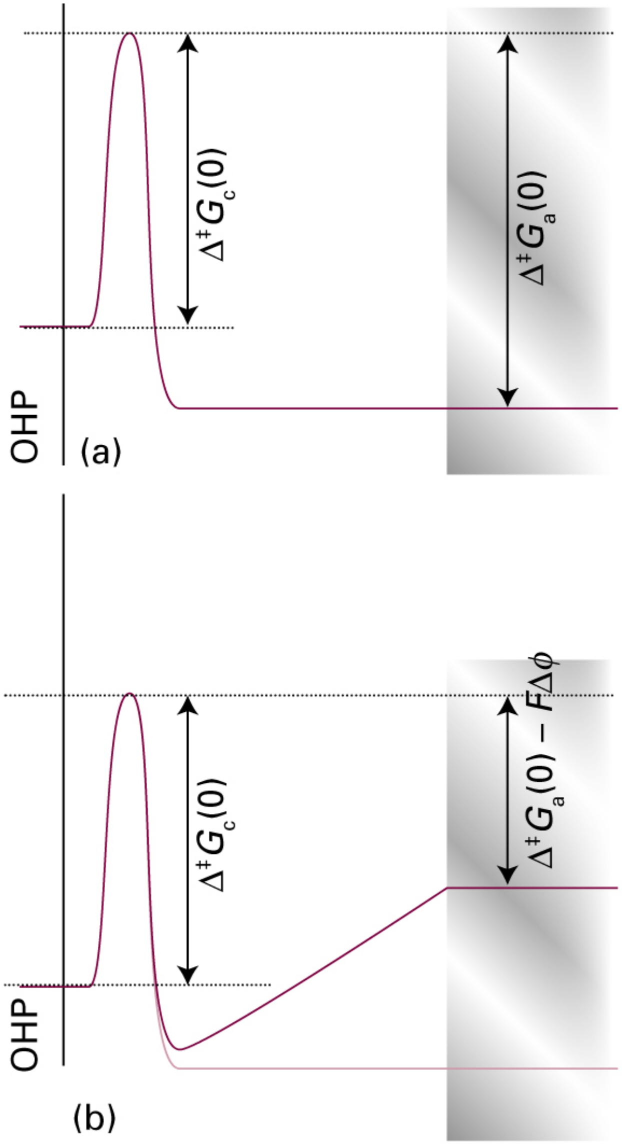


Figure 22.39
When the transition state resembles a species that has undergone oxidation, the activation Gibbs energy for the cathodic current is almost unchanged but the activation Gibbs energy for the anodic current is strongly affected. (a) Zero potential difference; (b) nonzero potential difference.

In a real system,

$$\Delta G_c^{\ddagger} = \Delta G_c^{\ddagger}(0) + \alpha F \Delta\phi \qquad (7)$$

$$0 < \alpha < 1 \left(\text{usu.}\ \alpha \approx 0.5\right)$$

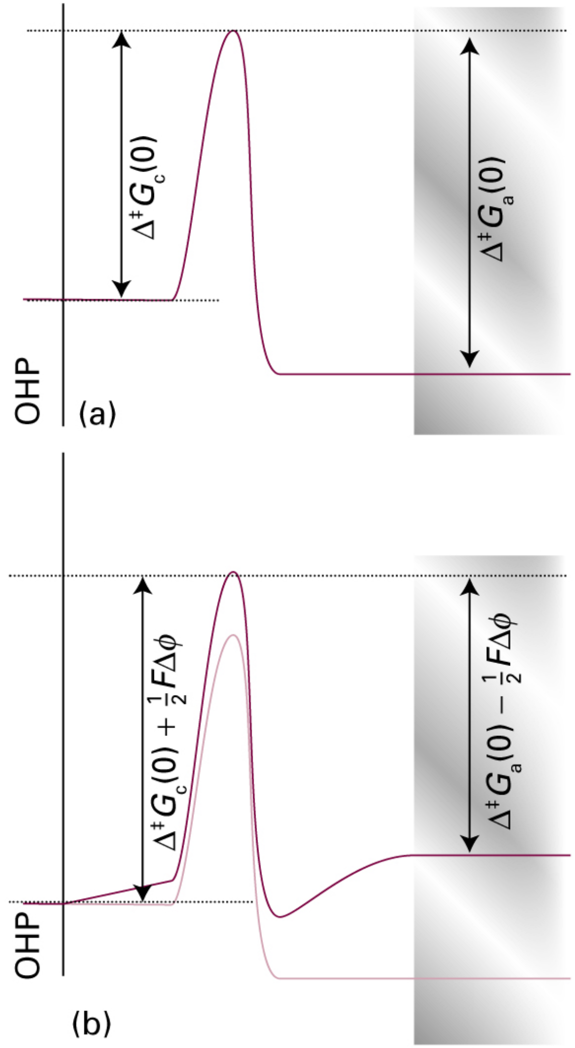


Figure 22.40
When the transition state is intermediate in its resemblance to reduced and oxidized species, as represented here by a peak located at an intermediate position as measured by α (with $0<\alpha<1$), both activation Gibbs energies are affected; here, $\alpha=0.5$. (a) Zero potential difference; (b) nonzero potential difference.

Consider **Red + e⁻ ⟶ Ox**. Red discards an electron to the electrode, so the extra work is zero if the transition state is reactant-like. The extra work is the full $-F\Delta\phi$ if it resembles the product. In general,

$$\Delta G_a^{\ddagger} = \Delta G_a^{\ddagger}(0) - (1-\alpha)F\Delta\phi \qquad (8)$$

Substituing eqs7 and 8 into eq5

$$\begin{aligned} j &= FB_a[\text{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}} e^{\frac{(1-\alpha)F\Delta\phi}{RT}} - FB_c[\text{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}} e^{\frac{\alpha F\Delta\phi}{RT}} \\ &= \underbrace{FB_a[\text{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}} e^{(1-\alpha)f\Delta\phi}}_{j_a} \underbrace{- FB_c[\text{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}} e^{-\alpha f\Delta\phi}}_{j_c} \end{aligned} \qquad (9)$$

If the cell is balanced against an external source, the Galvani potential difference $\Delta\phi$ can be identified as the (zero-current) electrode potential *E*.

$$\left.\begin{aligned} j_a &= FB_a[\text{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}} e^{(1-\alpha)fE} \\ j_c &= FB_c[\text{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}} e^{-\alpha fE} \end{aligned}\right\} = j_0$$

(skip)

When these equations apply, there is no net current at the electrode (as the cell is balanced), so the two current densities must be equal. Hence, we denote them both as j_0.

When the cell is producing current, the electrode potential changes from its zero-current value E to a new value E', and the difference is the electrode's overpotential $\eta = E' - E$. Hence, $\Delta\phi$ changes to $\Delta\phi = E + \eta$ and the two current densities become

$$\begin{aligned} j &= FB_a[\mathrm{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}}e^{(1-\alpha)F\Delta\phi} - FB_c[\mathrm{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}}e^{-\alpha F\Delta\phi} \\ &= FB_a[\mathrm{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}}e^{(1-\alpha)f(E+\eta)} - FB_c[\mathrm{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}}e^{-\alpha f(E+\eta)} \\ &= FB_a[\mathrm{Red}]e^{-\frac{\Delta G_a^{\ddagger}(0)}{RT}}e^{(1-\alpha)fE}e^{(1-\alpha)f\eta} - FB_c[\mathrm{Ox}]e^{-\frac{\Delta G_c^{\ddagger}(0)}{RT}}e^{-\alpha fE}e^{-\alpha f\eta} \\ &= j_0e^{(1-\alpha)f\eta} - j_0e^{-\alpha f\eta} = j_a - j_c \end{aligned}$$

$$j_a = j_0e^{(1-\alpha)f\eta}$$

$$j_c = j_0e^{-\alpha f\eta}$$

Problems from Chap. 21

- **D 21A.2**
- **D 21B.2**
- **D 21C.2**
- **D 21D.2**