Chapter 22. Molecular Reaction Dynamics

Molecular encounters

In solution we cannot so easily speak of collisions because the relative migration of the species is diffusional and the solvent hinders their free flight, but the rate at which the potentially reactive species encounter each other in solution can be calculated and related to the diffusion constants of the dissolved species.

Collision theory

$$[\mathrm{A}] = \frac{n_\mathrm{A}}{V} = \frac{\mathrm{N}_\mathrm{A}}{N_A V}$$

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

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

The collision rate of A with B per unit vol. is Z_{AB}. Therefore the rate of change of the number of A molecules per unit vol., $\left(d\,\mathrm{N}_{\mathrm{A}}/dt\right)/V$, 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.

where σ : the collision cross-section, $\pi\left(R_{\mathrm{A}}+R_{\mathrm{B}}\right)^2$

μ : the reduced mass.

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

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

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

Table 1 Activation energies, pre-exponential factors 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}

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 $\sigma^* = P\sigma$

$$k_2 = \underset{\substack{\Bigg\downarrow \\ \text{Local prop.}}}{P}\underbrace{\left\{\sigma N_A\left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}}\right\}}_{\text{Transport prop.}}\underbrace{\left\{\exp\left(-\frac{E_\mathrm{a}}{RT}\right)\right\}}_{\text{Energy criterion}}$$

P: 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.

$$\mathrm{K} + \mathrm{Br}_2 \longrightarrow \mathrm{KBr} + \mathrm{Br}$$

$$P = 4.8$$

$$\sigma^* \cong 4.8\sigma$$

‘harpoon mechanism’

When two molecules are close enough, an electron flips across to the Br_2. In place of two neutral species there are now two ions, and so there is a Coulombic attraction between them. Under this influence the ions move together, the reaction takes place.

Calculation of *P* values for K + Br_2

The calculation depends on estimating the distance between K atom and Br_2 molecules at which it is energetically favorable for the electron to leap from one to another.

Ionization energy from K atom = $I(\mathrm{K})$

Electron affinity of Br_2 molecule = $E_A(\mathrm{Br}_2)$

Coulombic interaction between two ions $= -\dfrac{e^2}{4\pi\varepsilon_0 R}$

where *R*: the separation distance.

The total change of energy

$$\Delta E = I(\mathrm{K}) - E_{\mathrm{A}}(\mathrm{Br}_2) - \frac{e^2}{4\pi\varepsilon_0 R}$$

usually $I(\mathrm{K}) > E_{\mathrm{A}}(\mathrm{Br_2})$ $\Rightarrow$ ΔE becomes negative only when R has decreased to less than some critical value R^* given by

$$\frac{e^2}{4\pi\varepsilon_0 R^*} = I(\mathrm{K}) - E_{\mathrm{A}}(\mathrm{Br_2})$$

the reactive cross-section $\sigma^* = \pi R^{*^2}$

$$\therefore P = \frac{\sigma^*}{\sigma} = \frac{R^{*^2}}{d^2} \approx \left\{ \frac{e^2}{4\pi\varepsilon_0 d\left[I(\mathrm{K}) - E_{\mathrm{A}}(\mathrm{Br_2})\right]} \right\}^2$$

where $d = R(\mathrm{K}) + R(\mathrm{Br_2})$

For $\mathrm{K} + \mathrm{Br_2} \rightarrow \mathrm{KBr} + \mathrm{Br}$,

$$I(\mathrm{K}) = 420 \text{ kJ/mol}, \ E_{\mathrm{A}}(\mathrm{Br_2}) < 300 \text{ kJ/mol}, \ d \approx 310 \text{ pm}$$

$\therefore$ $P < 12$, which is consistent with the experimental value of 4.8.

Reactions in solution: diffusion control

- The molecular motion is diffusional, in place of free flight, but 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, and so their chance of undergoing reaction is greatly enhanced.

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

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

$$\frac{d\left[(\mathrm{AB})\right]}{dt} = k_d\,[\mathrm{A}][\mathrm{B}]$$

k_d: determined by the diffusion constants

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

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

the steady-state approximation for (AB)

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

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

$\therefore$ the overall rate

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

where $k_2 = \dfrac{k_1 k_d}{k_{-d} + k_1}$.

(i) $k_{-d} \ll k_1$

$k_2 \approx \dfrac{k_1 k_d}{k_1} = k_d$: 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.

(ii) $k_1 \ll k_{-d}$

$k_2 = k_1 \left(\dfrac{k_d}{k_{-d}} \right) = k_1 K$: 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.

Calculation of the 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)

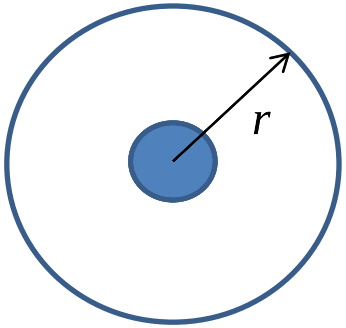
From Fick's first law of diffusion,

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

[B]: the molar concentration of the B molecules

D_{B}: their diffusion constant in the medium

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



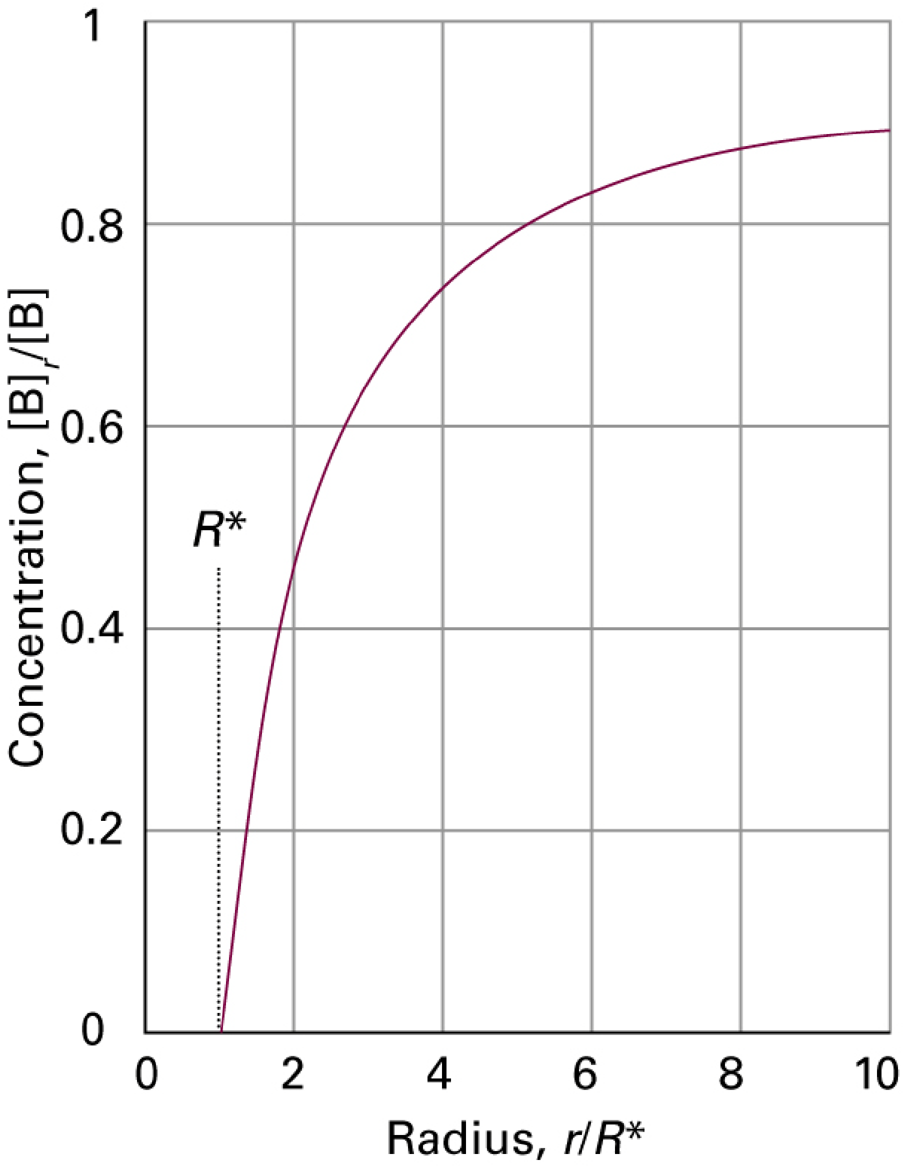


Figure 1

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

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 a constant independent of *r*.

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

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

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

At critical distance R^*, A and B 'touch', reaction takes place, and B is removed: that is, 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:

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

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

The rate of the diffusion-controlled 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 $V = N_A[\mathrm{A}]V$

$\therefore$ Global flow of all B to all A = $4\pi R^* D_\mathrm{B} N_A[\mathrm{A}][\mathrm{B}]V$.

A: static; B: mobile → unrealistic: This is easily remedied by replacing the diffusion coefficient D_B by $D = D_\mathrm{A}+D_\mathrm{B}$.

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

Then the diffusion-controlled rate coefficient can be identified as

$$\boldsymbol{k_2 = k_\mathrm{d} = 4\pi R^* D N_A}$$

Strokes-Einstein relation

$$D_{\mathrm{A}} = \frac{kT}{6\pi\eta R_{\mathrm{A}}}$$

$$D_{\mathrm{B}} = \frac{kT}{6\pi\eta R_{\mathrm{B}}}$$

$$R_{\mathrm{A}} \approx R_{\mathrm{B}} \approx \frac{1}{2}R^*$$

R_{A}, R_{B}: the effective hydrodynamic radii of A and B

$$k_2 \cong 4\cancel{\pi}\cancel{R^*}\left(\frac{2kT}{6\cancel{\pi}\eta\left(\cancel{R^*}/2\right)}\right)N_A$$

$$\approx 8kTN_A/3\eta = \frac{8RT}{3\eta}$$

$$k_2 = k_d = 4\pi R^* D N_A$$

$$= 4\pi R^*(D_{\mathrm{A}}+D_{\mathrm{B}})N_A$$

1. Note that the radii have cancelled, and so in this approximation k_2 is independent of the species involved in the reaction.

2. Temperature-dependence of diffusion-controlled reaction

$$\eta \approx A \exp\left(\frac{E_\mathrm{a}}{RT}\right)$$

$$k_2 \approx \frac{8RT}{3A} \exp\left(-\frac{E_\mathrm{a}}{RT}\right)$$

3. The diffusion-controlled reactions between ions

$$k_2 = 4\pi p R^* D N_A$$

$$p = \left(\frac{z_\mathrm{A} z_\mathrm{B} e^2}{4\pi\varepsilon_\mathrm{r}\varepsilon_\mathrm{o} R^* kT}\right)\left(\frac{1}{\exp\left(z_\mathrm{A} z_\mathrm{B} e^2 / 4\pi\varepsilon_r\varepsilon_o R^* kT\right) - 1}\right)$$

Activated Complex Theory (ACT)

The reaction coordinate and the transition state

the reaction coordinate: The horizontal axis of the diagram representing the course of the reaction

the transition coordinate: 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 called the transition state of the reaction.

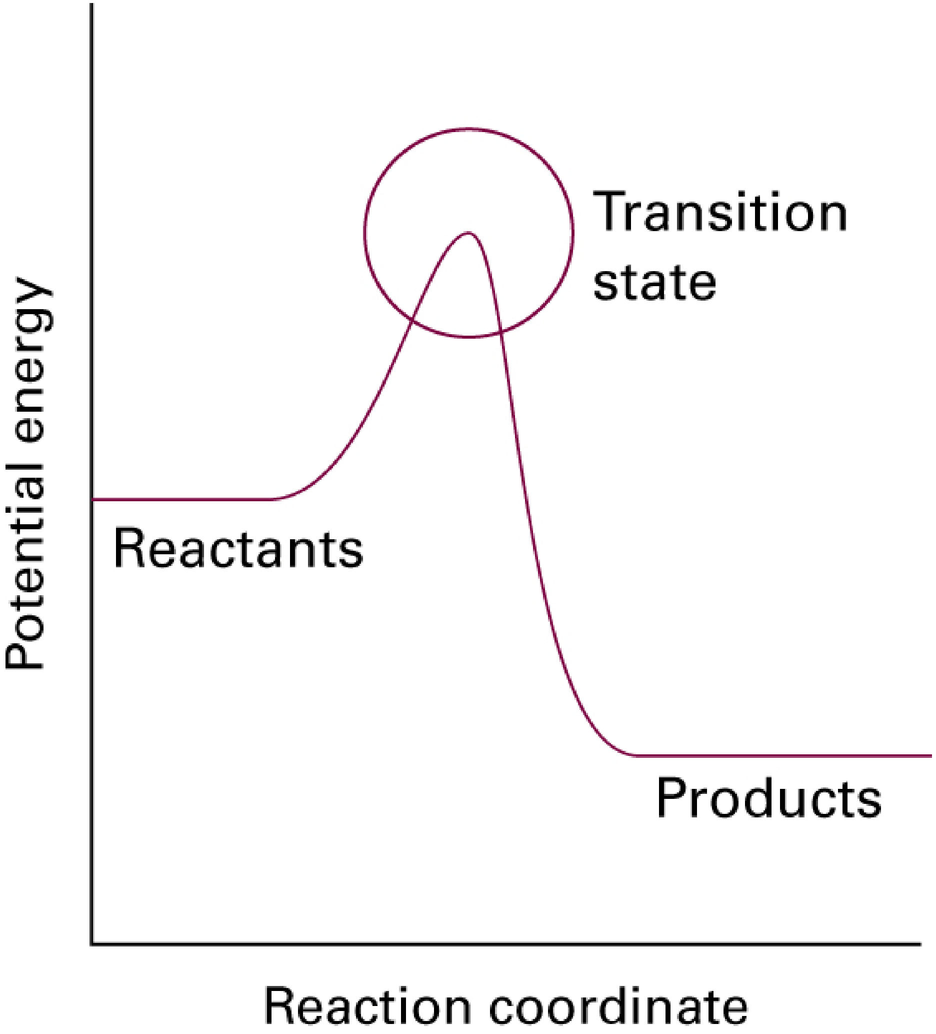


Figure 2

A reaction profile (for an exothermic reaction). 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.

Formation and decay of the activated complex

$$\mathrm{A} + \mathrm{B} \rightleftharpoons (\mathrm{AB})^{\ddagger} \xrightarrow{k^{\ddagger}} P$$

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

where $\left[(\mathrm{AB})^{\ddagger}\right]$: the concentration of activated complex.

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

K: some constant of proportionality

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

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

$$k^{\ddagger} = \kappa\nu^{\ddagger}$$

κ : the transition coefficient usually unity

Estimation of the concentration of the activated complex

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

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

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

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

$$PV = nRT$$

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

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

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

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

$q_{\mathrm{m}}^{\ddagger}$: the 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

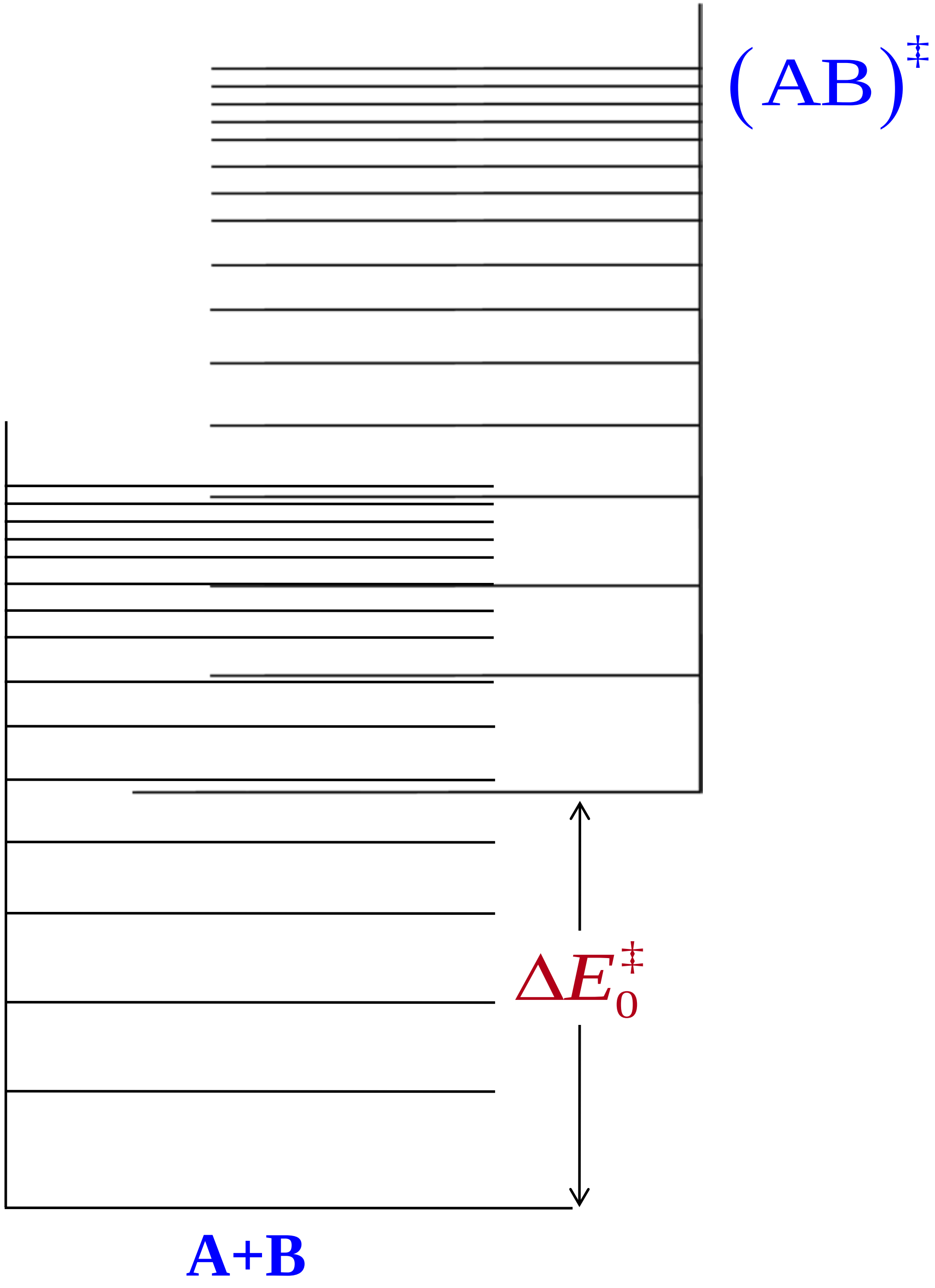


Figure 3

Energy levels of reactants and the activated complex.

The partition function for this vibrational mode

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

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

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

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

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

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

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

The rate constant

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

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

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

Eyring equation

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

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 lies in the determination of the partition function for the activated complex.

Example of the calculation of a rate constant:

$$\mathrm{A} + \mathrm{B} \rightleftharpoons (\mathrm{AB})^{\ddagger} \longrightarrow \mathrm{P}$$

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

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

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

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 $\bar{q}^{\ddagger}$.

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

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

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

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

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

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

$\downarrow$

reactive cross-section σ^*

Compare with k_2 derived from the collision theory:

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

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

Thermodynamic aspects

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

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

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

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

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

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

Setting $\Delta H_m^{\ddagger} = E_\mathrm{a} - 2RT$ for a bimolecular gas reaction*,

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

$$= \underbrace{\left(\frac{kTe^2}{h}\right)\left(\frac{RT}{p^\circ}\right)\exp\left(\frac{\Delta S_\mathrm{m}^{\ddagger}}{R}\right)}_{A\text{: frequency factor}}\exp\left(-\frac{E_\mathrm{a}}{RT}\right)$$

$$A = \left(\frac{kTe^2}{h}\right)\left(\frac{RT}{p^\circ}\right)\exp\left(\frac{\Delta S_m^{\ddagger}}{R}\right)$$

or $\Delta S_\mathrm{m}^{\ddagger} = R\ln\left[\dfrac{hAp^\circ}{N_A(ekT)^2}\right]$

$$k_2 = Be^{\frac{\Delta S^{\ddagger\ddagger}}{R}} e^{-\frac{\Delta H}{RT}}, \quad \text{where } B = \frac{kT}{h}\frac{RT}{p^\circ} \longrightarrow V_\circ$$

$$\Delta H^{\ddagger\ddagger} = \Delta U - RT \quad \text{for bimolecular gaseous reaction}$$

$$\therefore k_2 = eBe^{\frac{\Delta S^{\ddagger\ddagger}}{R}} e^{-\frac{\Delta U}{RT}}$$

Since $\Delta A^{\ddagger\ddagger\ddagger} = \Delta U - T\Delta S$,

$$k_2 = eBe^{-\frac{\Delta A^{\ddagger}}{RT}}$$

Since the activation energy is defined as

$$E_{\mathrm{a}} = RT^2 \left(\frac{\partial \ln k}{\partial T} \right)_V \qquad k_2 = eBe^{-\frac{\Delta A^{\ddagger}}{RT}}$$

$$= RT^2 \left(\frac{\partial \ln(Be)}{\partial T} \right)_V - T^2 \left(\frac{\partial \left(\Delta A^{\ddagger} / T \right)}{\partial T} \right)_V$$

$$= RT + \cancel{T}^2 \frac{\Delta U^{\ddagger}}{\cancel{T}^2} = RT + \Delta U^{?} \qquad \because \frac{d(\Delta A / T)}{dT} = \frac{-\Delta U}{T^2}$$

For a bimolecular gaseous reaction,

$$E_{\mathrm{a}} = RT + \Delta U^{\ddagger\ddagger\ddagger} = RT + \Delta H \;\; + RT = \Delta H \;\; + 2RT$$

or $\Delta H^{\ddagger} = E_{\mathrm{a}} - 2RT$

Reactions between ions

The application of activated complex theory to reactions in solution is very complicated because of the involvement of the solvent in the activated complex. We shall accept this difficulty, but avoid coming to a dead spot by using the thermodynamic approach to k_2.

$$k_2[\mathrm{A}][\mathrm{B}] = k^{\ddagger}\left[(\mathrm{AB})^{\ddagger}\right]$$

$$K = \frac{a_{(\mathrm{AB})^{\ddagger\ddagger}}}{a_{\mathrm{A}}a_{\mathrm{B}}} = \frac{\gamma_{(\mathrm{AB})}\left[(\mathrm{AB})^{\ddagger}\right]}{\gamma_{\mathrm{A}}[\mathrm{A}]\gamma_{\mathrm{B}}[\mathrm{B}]} = K_{\gamma}\frac{\left[(\mathrm{AB})^{\ddagger}\right]}{[\mathrm{A}][\mathrm{B}]}$$

γ: the activity coefficients

$$\therefore k_2 = k^{\ddagger\ddagger}\frac{K}{K_{\gamma}} = k\ \ K\left[\frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{\gamma_{(\mathrm{AB})^{\ddagger\ddagger}}}\right] = k_2^{\circ}\left[\frac{\gamma_{\mathrm{A}}\gamma_{\mathrm{B}}}{\gamma_{(\mathrm{AB})}}\right]$$

k_2°: the rate coefficient when all activity coefficients are unity

Relating the activity coefficients to the ionic strength of the solution using the Debye–Hückel Limiting Law:

$$\log \gamma_i = -Az_i^2 I^{\frac{1}{2}}$$

A: constant

$I = \frac{1}{2}\sum_j m_j z_j^2$: the ionic strength

m_j: the molarity

z_i: the number of charge

$$\therefore \log k_2 = \log k_2^{\circ} - A\left[z_{\mathrm{A}}^2 + z_{\mathrm{B}}^2 - \left(z_{\mathrm{A}} + z_{\mathrm{B}} \right)^2 \right] I^{\frac{1}{2}}$$

$$= \log k_2^{\circ} + 2Az_{\mathrm{A}} z_{\mathrm{B}} I^{\frac{1}{2}}$$

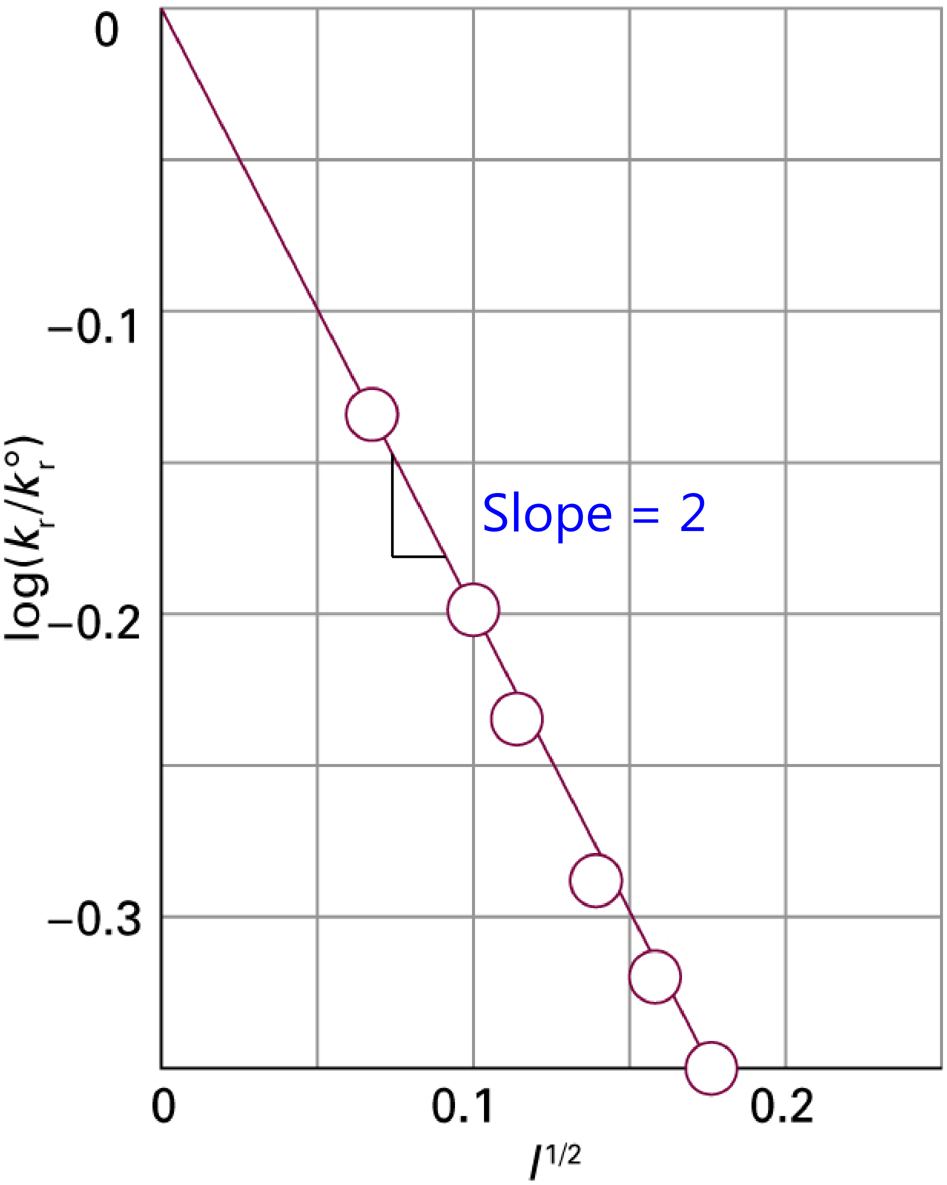


Figure 4

The experimental ionic strength dependence of the rate constant of a hydrolysis reaction: the slope gives information about the charge types involved in the activated complex of the rate-determining step.

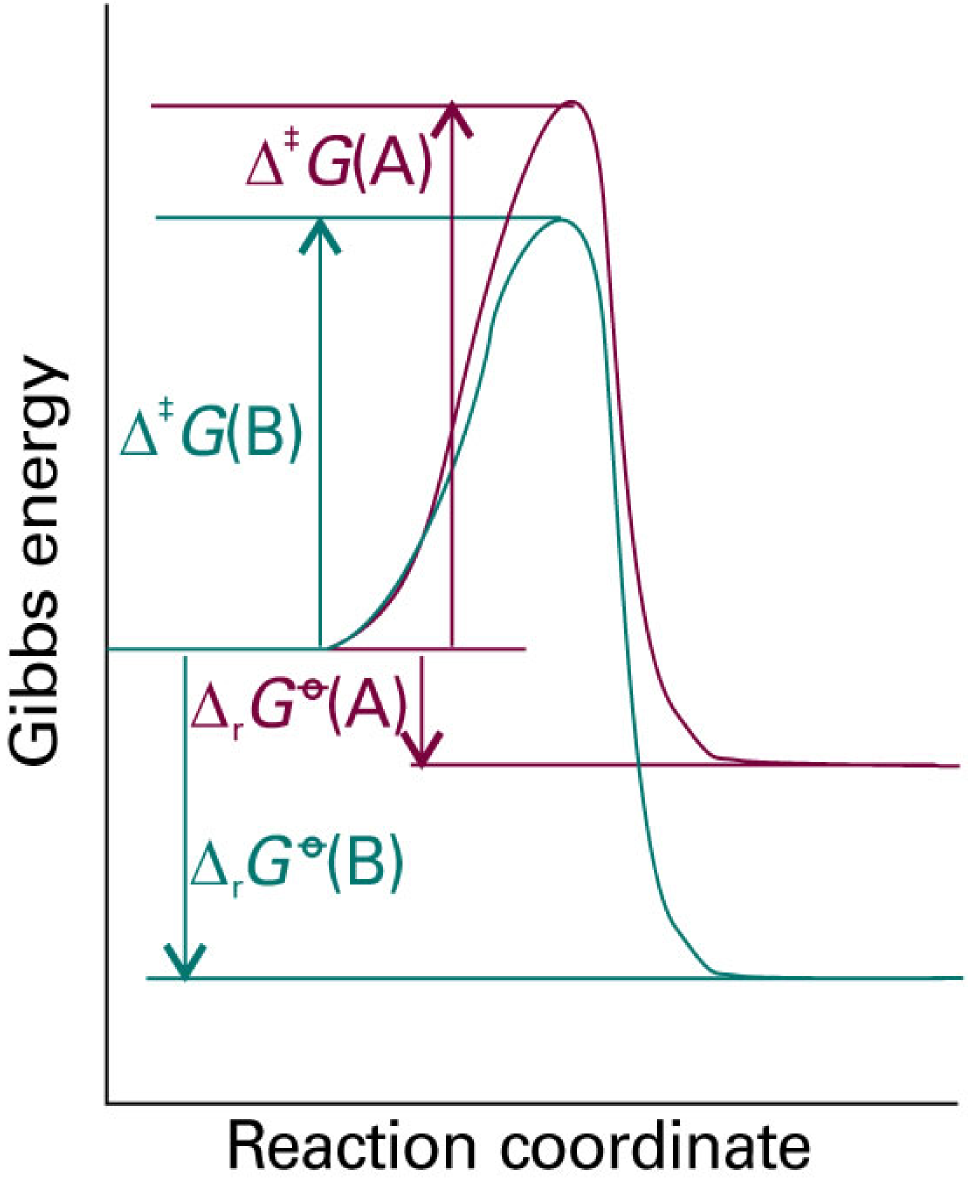


Figure 5

For a related series of reactions, as the magnitude of the standard reaction Gibbs energy increases, so the activation barrier decreases. The approximate linear correlation between $\Delta G^{\ddagger}$ and ΔG^{0} is the origin of linear free energy relation (LFER).

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. Two parameters are required to define the nuclear separations: one is the H_A–H_B separation R_{AB}, and the other is the H_B–H_C separation R_{BC}.

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.

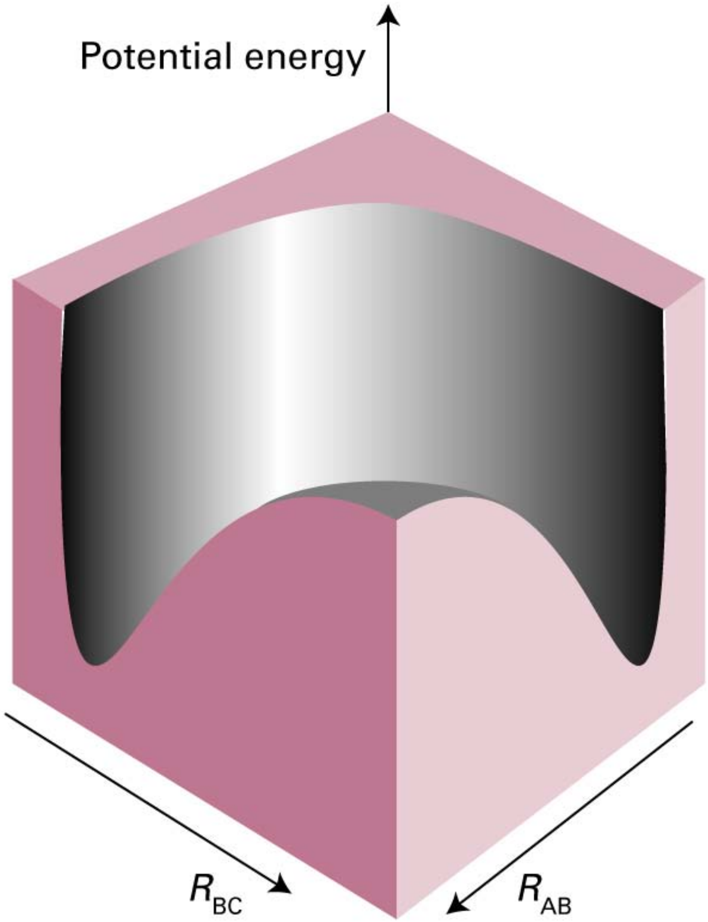


Figure 6

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.

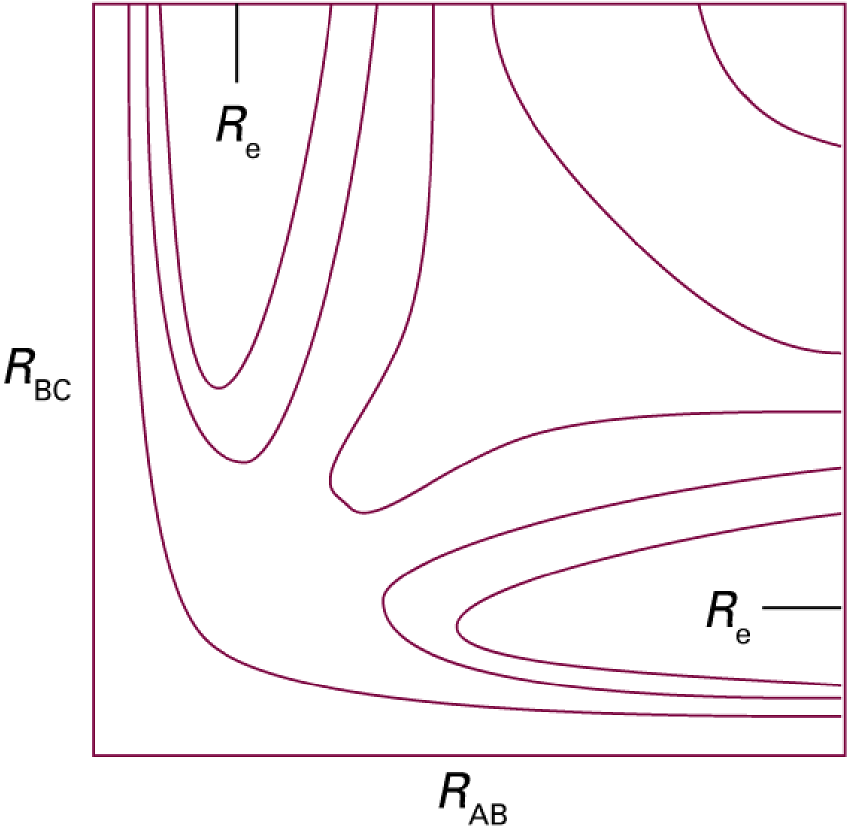


Figure 7

The contour diagram (with contour of equal potential energy) corresponding to the surface in Fig. 6. R_e marks the equilibrium bond length of an H_2 molecule (strictly, it relates to the arrangement when the third atom is at infinity).

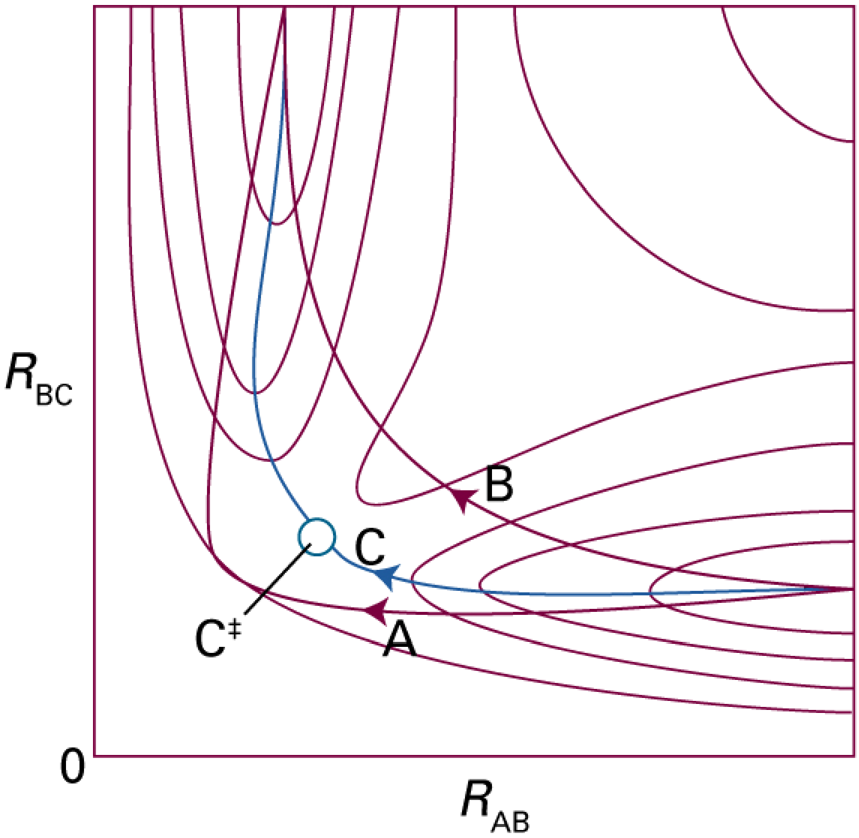


Figure 8

Various trajectories through the potential energy surface shown in Fig. 7. **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.

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 in Fig. 8.

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 $C^{\ddagger}$.

The Dynamics of Electron transfer

Electron transfer in homogeneous system

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

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{D}^{+} + \mathrm{A}^{-} \qquad v = k_{\mathrm{r}}[\mathrm{D}][\mathrm{A}] \qquad (1)$$

(1) Diffusion of D and A in solution

(2) Complex formation

$$\mathrm{D} + \mathrm{A} \underset{k_{\mathrm{a}}'}{\overset{k_{\mathrm{a}}}{\rightleftharpoons}} \mathrm{DA} \qquad k_{\mathrm{DA}} = \frac{k_{\mathrm{a}}}{k_{\mathrm{a}}'} \qquad (2)$$

(3) Reversible electron transfer

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

(4) The formation of separated ions

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

The rate constant for the overall electron transfer process

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

Let the overall reaction rate = the rate of formation of separated ions

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

Steady-state approximation

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

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

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

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

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

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

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

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

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

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

(a) If $k_{\mathrm{et}} \gg k_{\mathrm{a}}'$, $k_{\mathrm{r}} \approx k_{\mathrm{a}}$.

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

(b) If $k_{\mathrm{et}} \ll k_{\mathrm{a}}'$, $k_{\mathrm{r}} = \left(\frac{k_{\mathrm{a}}}{k_{\mathrm{a}}'}\right)k_{\mathrm{et}} = k_{\mathrm{DA}}k_{\mathrm{et}}$.

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

Using the transition state theory,

$$k_{\mathrm{et}} = \kappa v^{\ddagger} e^{-\frac{\Delta G^{\ddagger}}{RT}} \tag{12}$$

κ: transmission coefficient

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

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

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.

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

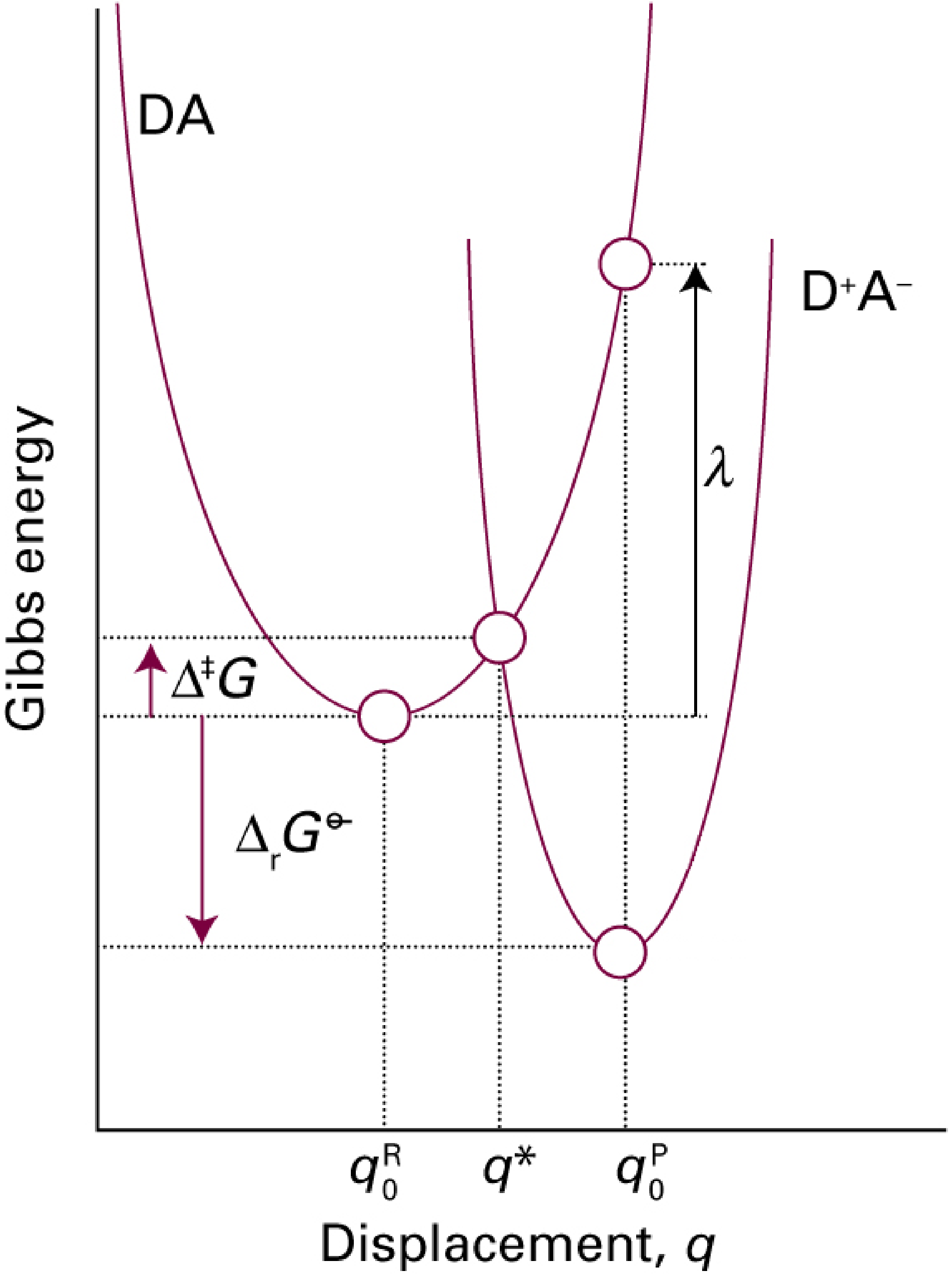


Figure 22.9
The Gibbs energy surfaces of the complexes DA and D^+A^- involved in an electron transfer process are represented by parabolas characteristic of harmonic oscillators, with the displacement coordinate q corresponding to the changing geometries of the system. In the plot, q_0^R and q_0^P are 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, $\Delta G^{\ominus}$, and the reorganization energy, λ.

According to the theory for electron tunneling,

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

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

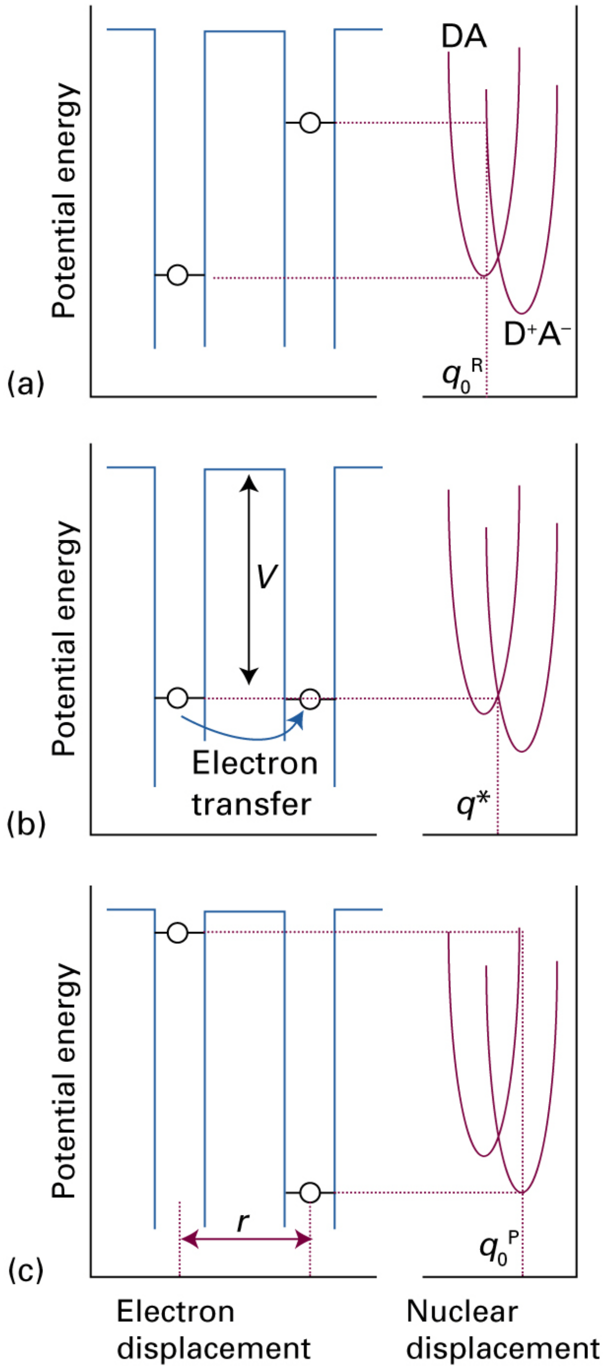
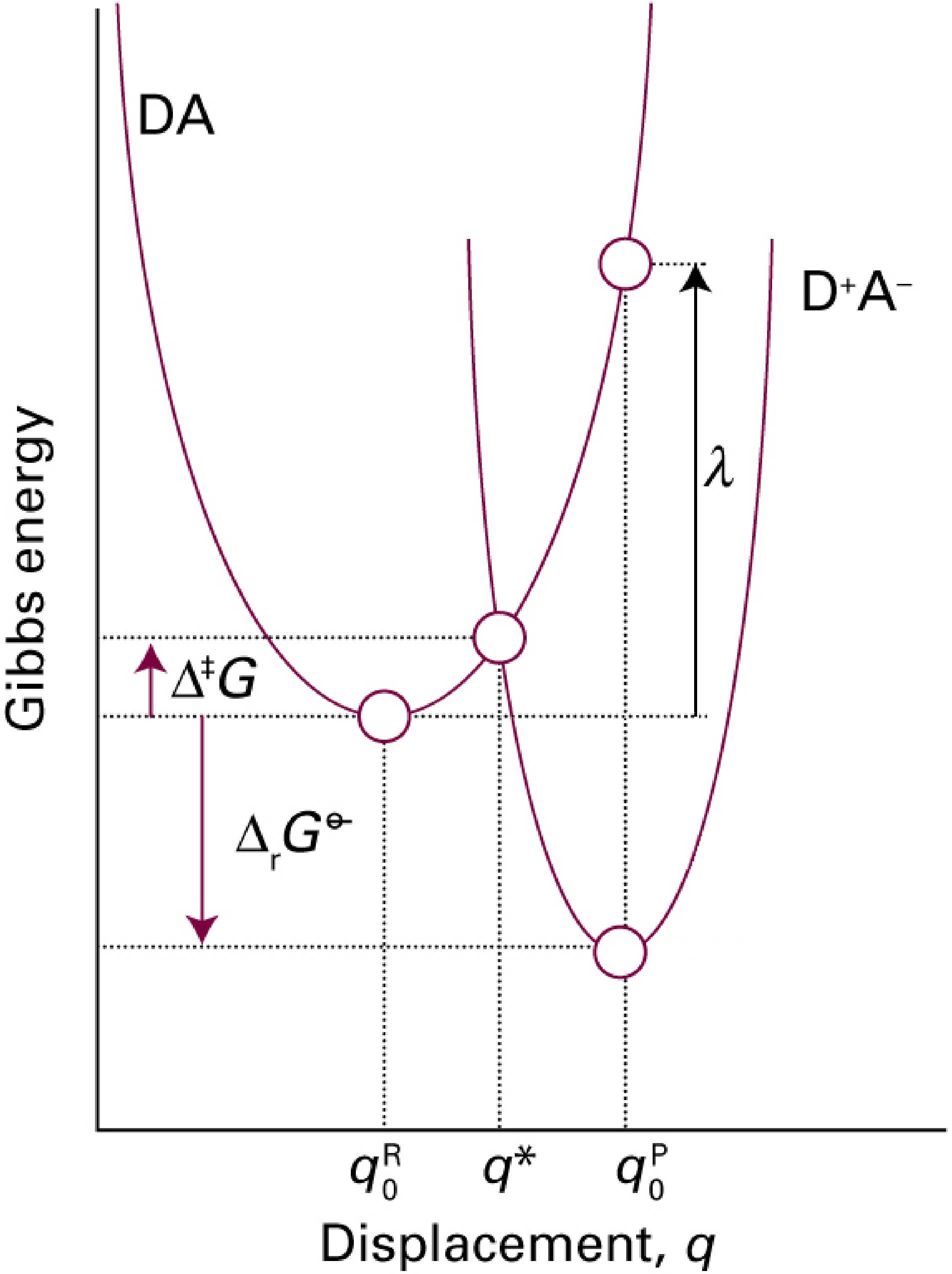


Figure 22.10

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.)



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The expression for the rate of electron transfer

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),

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

Derivation of eq (14)

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

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

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

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

q_{0}^{R}, q_{0}^{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),

$$\Delta G^{\ddagger} = \alpha^2 \lambda \qquad \text{(h)}$$

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

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

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

Combining eqs. (h) and (i),

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

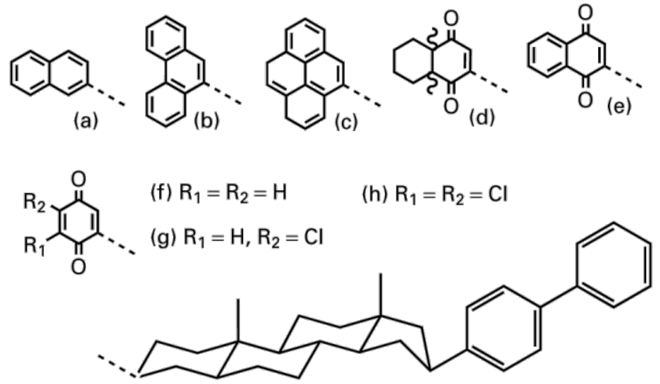
Experimental results

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

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

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

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



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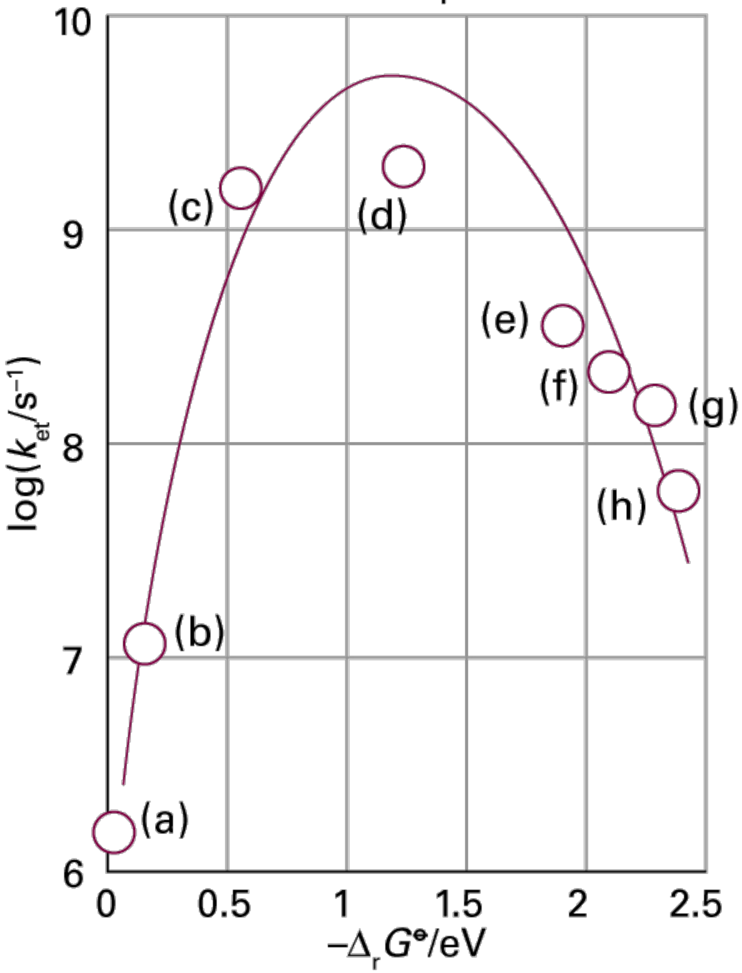

Figure 22.11

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 $-\Delta G^{\ominus} = \lambda = 1.2\,\mathrm{eV} = 1.2 \times 10^2\,\mathrm{kJ\,mol^{-1}}$. (Reproduced with permission from J.R. Miller, L.T. Calcaterra, and G.L. Closs, *J. Amer. Chem. Soc.* **1984**, *106*, 3047.)

Electron Transfer Processes at Electrodes

The electrode-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 model**
   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).

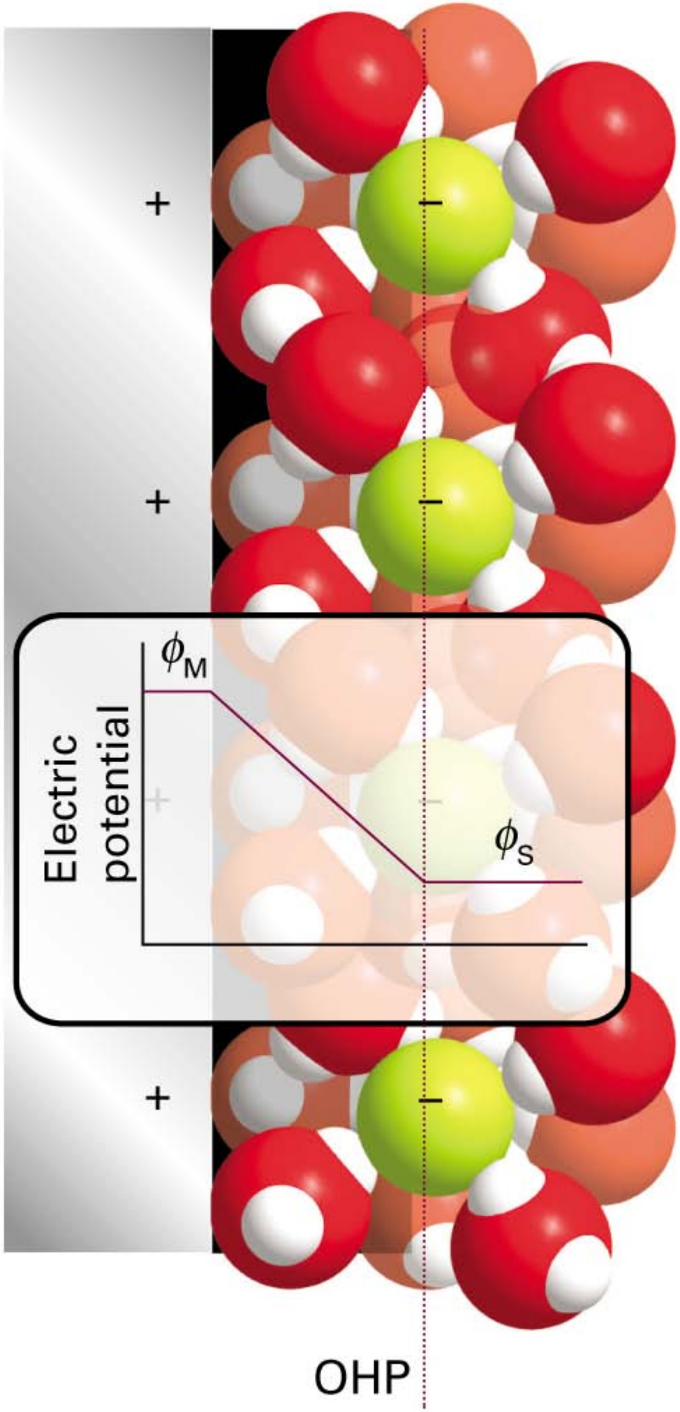

Figure 22. 12
A simple model of the electrode-solution interface treats it as two rigid planes of charge. One plane, the outer Helmholtz plane (OHP), is due to the ions with their solvating molecules and the other plane is that of the electrode itself. The plot shows the dependence of the electric potential with distance from the electrode surface according to this model. Between the electrode surface and the OHP, the potential varies linearly from ϕ_M, the value in the metal, to ϕ_S, the value in the bulk of the solution.

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.

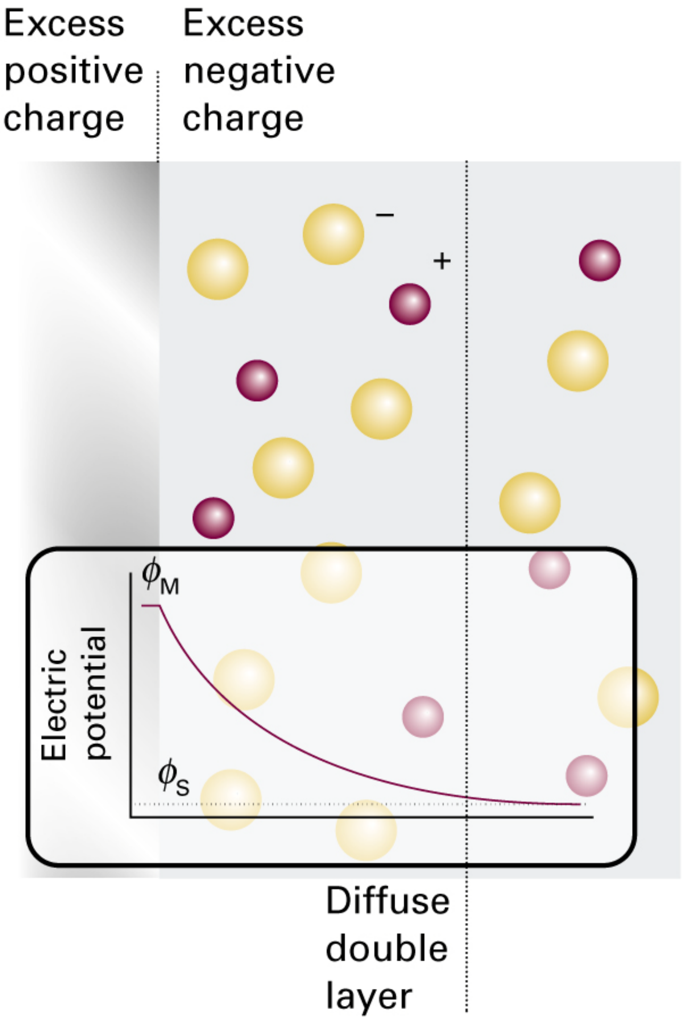

Figure 22. 13
The Gouy-Chapman model of the electrical double layer treats the outer region as an atmosphere of counter-charge, similar to the Debye-Huckel theory of ion atmosphere. The plot of electrical potential against distance from the electrode surface shows the meaning of the diffuse double layer.

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.

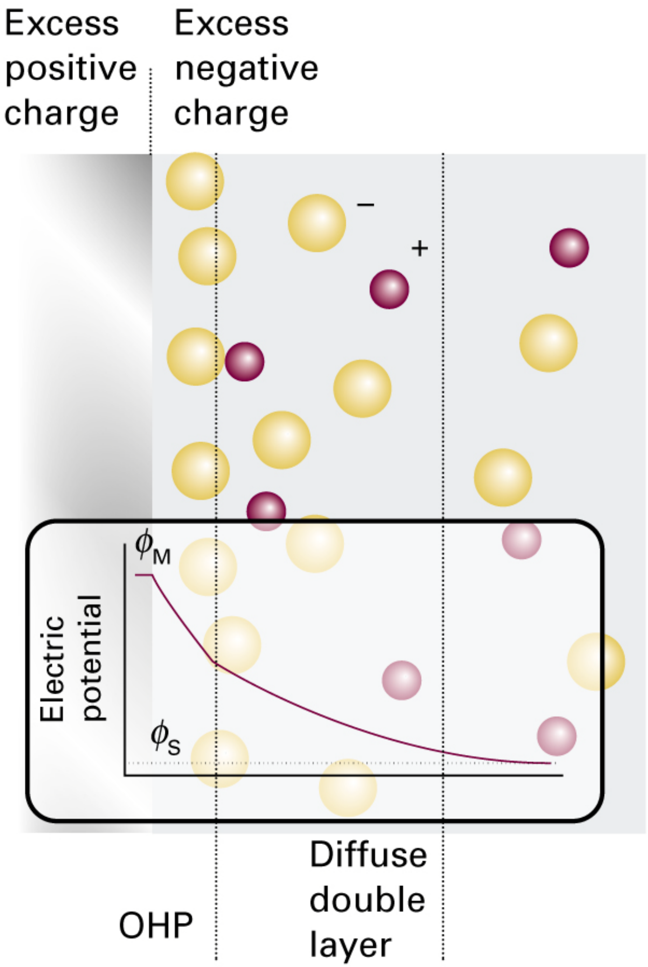

Figure 22. 14
A representation of the Stern model of the electrode-solution interface. The model incorporates the ides of an outer Helmholtz plane near the electrode surface and of a diffuse double layer further away from the surface.

The Butler-Volmer Equation

Consider a reaction at the electrode in which an ion is reduced by the transfer of a single electron.

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

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

$f = \dfrac{F}{RT}$ F : Faraday's constant

$\eta = E' - E$ the overpotential

E : the 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 : the exchange-current density when the electrode is at equilibrium

$f\eta \ll 1$ (usu. $\eta < 0.01\,V$)

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

$$\eta = \frac{RTj}{Fj_0}$$

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 (e.g. $\eta \geq 0.12\,V$),

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

$$\ln j = \ln j_0 + (1-\alpha)f\eta$$

If η is large and negative (e.g., $\eta < -0.12\,V$),

$$j \approx -j_0 e^{-\alpha f\eta}$$

$$\ln(-j) = \ln j_0 - \alpha f\eta$$

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*).

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

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

The net current

$$j = j_\mathrm{a} - j_\mathrm{c} = Fk_\mathrm{a}[\mathrm{Red}] - Fk_\mathrm{c}[\mathrm{Ox}] \qquad (3)$$

$$j_\mathrm{a} > j_\mathrm{c} \rightarrow j > 0\text{: the current is anodic}$$

$$j_\mathrm{c} > j_\mathrm{a} \rightarrow j < 0\text{: the current is cathodic}$$

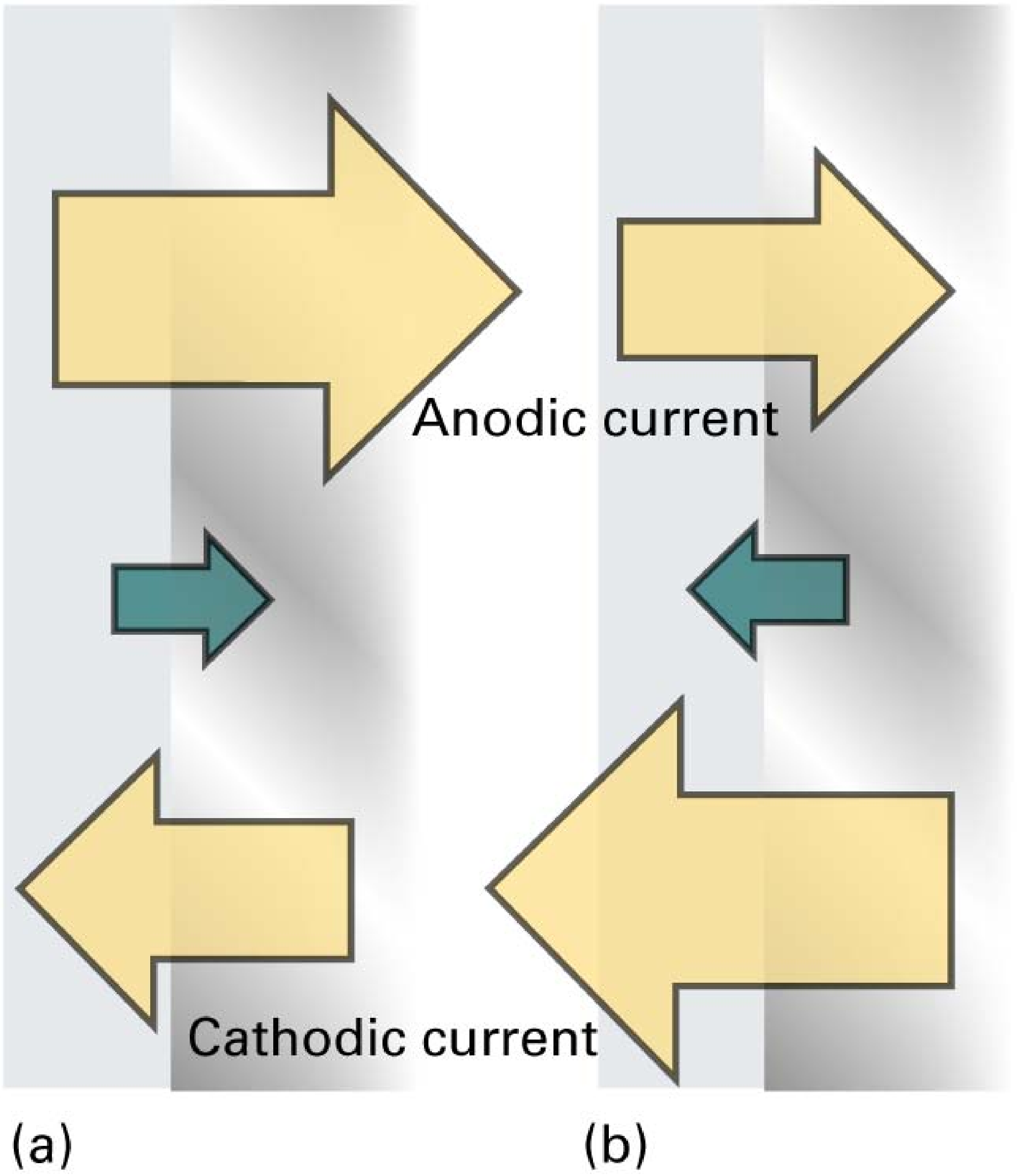

Figure 22. 15

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 eq 4 into eq 3

$$j = FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}}{RT}} - FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}}{RT}} \qquad (5)$$

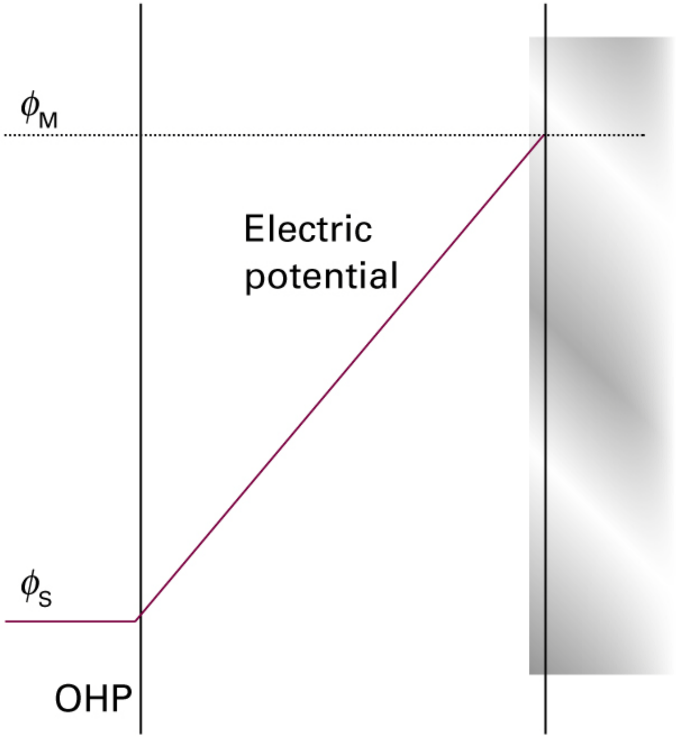

Figure 22.16
The potential ϕ varies between two plane parallel sheets of charge, and its effect on the Gibbs energy of the transition state depends on the extent to which the latter resembles the species at the inner or outer planes.

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

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

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

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

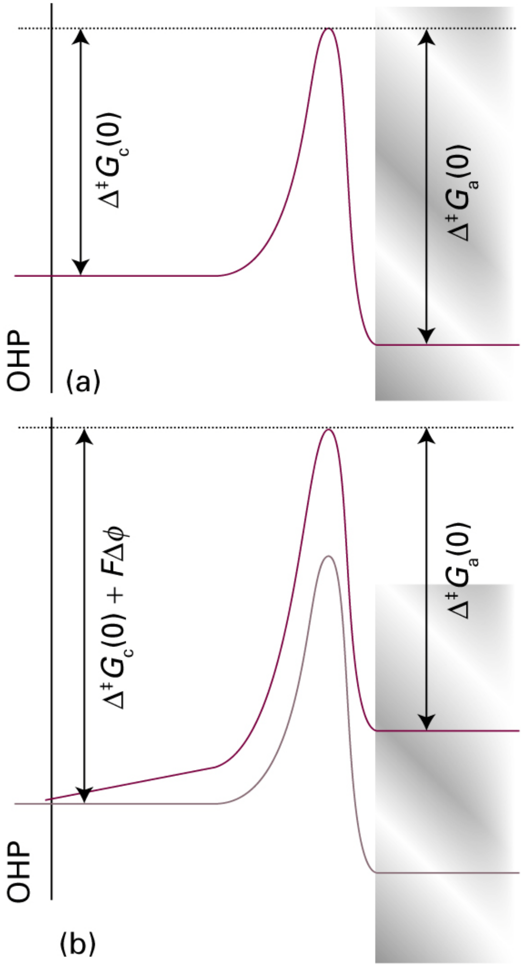

Figure 22.17

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,

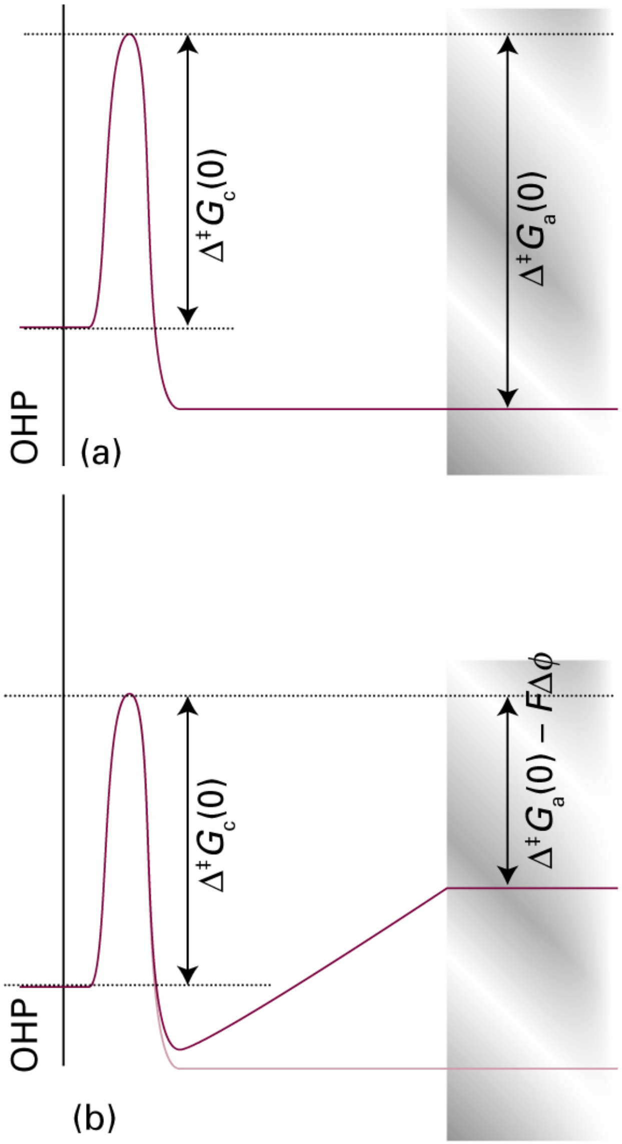

Figure 22.18
When the transition state resembles a species that has undergone oxidation, the activation Gibbs energy for the cathodic current is almost unchanged but the activation Gibbs energy for the anodic current is strongly affected. (a) Zero potential difference; (b) nonzero potential difference.

In a real system,

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

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

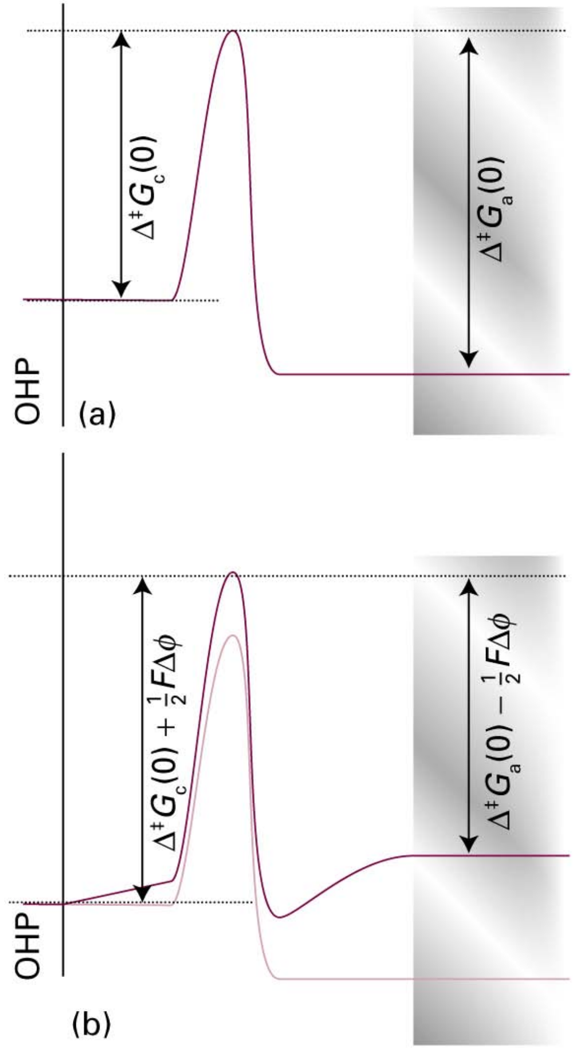

Figure 22.19
When the transition state is intermediate in its resemblance to reduced and oxidized species, as represented here by a peak located at an intermediate position as measured by α (with $0<\alpha<1$), both activation Gibbs energies are affected; here, $\alpha=0.5$. (a) Zero potential difference; (b) nonzero potential difference.

Consider **Red + e^- $\longrightarrow$ 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,

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

Substituting eqs 7 and 8 into eq 5

$$\begin{aligned} j &= FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}(0)}{RT}} e^{\frac{(1-\alpha)F\Delta\phi}{RT}} - FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}(0)}{RT}} e^{-\frac{\alpha F\Delta\phi}{RT}} \\ &= \underbrace{FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}(0)}{RT}} e^{(1-\alpha)f\Delta\phi}}_{j_a} - \underbrace{FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}(0)}{RT}} e^{-\alpha f\Delta\phi}}_{j_c} \end{aligned} \qquad (9)$$

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.

$$\left.\begin{aligned} j_{\mathrm{a}} &= FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger}(0)}{RT}} e^{(1-\alpha)fE} \\ j_{\mathrm{c}} &= FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}^{\ddagger}(0)}{RT}} e^{-\alpha fE} \end{aligned}\right\} = j_0$$

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

$$\begin{aligned}
j &= FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}(0)}{RT}}e^{(1-\alpha)f\Delta\phi} - FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}(0)}{RT}}e^{-\alpha f\Delta\phi} \\
&= FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}(0)}{RT}}e^{(1-\alpha)f(E+\eta)} - FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}(0)}{RT}}e^{-\alpha f(E+\eta)} \\
&= FB_{\mathrm{a}}[\mathrm{Red}]e^{-\frac{\Delta G_{\mathrm{a}}^{\ddagger\ddagger}(0)}{RT}}e^{(1-\alpha)fE}e^{(1-\alpha)f\eta} - FB_{\mathrm{c}}[\mathrm{Ox}]e^{-\frac{\Delta G_{\mathrm{c}}(0)}{RT}}e^{-\alpha fE}e^{-\alpha f\eta} \\
&= j_0 e^{(1-\alpha)f\eta} - j_0 e^{-\alpha f\eta} = j_{\mathrm{a}} - j_{\mathrm{c}}
\end{aligned}$$

$$\boldsymbol{j_a = j_0 e^{(1-\alpha)f\eta}}$$

$$\boldsymbol{j_c = j_0 e^{-\alpha f\eta}}$$