

- The properties of sound waves are related to the nature of molecular motion.
- The velocity of sound propagation is related to average molecular speed.
- The absorption of sound depends on viscosity and thermal conductivity.
- Hydrodynamics will be used to explore this further.
 - Hydrodynamics, like thermodynamics, deals with macroscopic variables.
 - In the context of the propagation of sound, some variables of interest include:
 - mass velocity (which is the same as local average velocity $u(x, t)$).
 - pressure
 - energy density.

- Hydrodynamics deals with time dependent processes.
- Thermodynamics deals with equilibrium conditions.
- Consider the Boltzmann equation, which describes the time dependence of the velocity distribution $\tilde{f}(\mathbf{v}, t)$ for homogeneous systems:

$$\left[\frac{d\tilde{f}(\mathbf{v}_1, t)}{dt} \right]_{\mathbf{v}_1} = 2\pi n \int_{\chi} \int_{\mathbf{v}_2} v \sigma(v, \chi) \times$$

$$\left[\tilde{f}(\mathbf{v}_1 + \Delta\mathbf{v}_1, t) \tilde{f}(\mathbf{v}_2 + \Delta\mathbf{v}_2, t) - \tilde{f}(\mathbf{v}_1, t) \tilde{f}(\mathbf{v}_2, t) \right] d\mathbf{v}_2 \sin \chi d\chi$$

- Now consider an inhomogeneous system.
 - This requires the more general form $\tilde{f}(\mathbf{r}, \mathbf{v}, t)$ which includes the spatial dependence.

- The local density is given by the integration of $\tilde{f}(\mathbf{r}, \mathbf{v}, t)$ over all velocities:

$$\rho(\mathbf{r}, t) = Nm \int \tilde{f}(\mathbf{r}, \mathbf{v}, t) d\mathbf{v}$$

- Now the equations of hydrodynamics will be obtained by combining the laws of thermodynamics with the conservation of mass, momentum, and energy required by the conservation laws of mechanics.
 - But the system is not at equilibrium, so the assumptions of non-equilibrium thermodynamics must be considered.
 - Assume that each volume element is small relative to the size of the system, but contains a sufficient number of molecules that it can be assumed to be at local equilibrium.

- These assumptions are valid for the propagation of sound.
 - Consider high frequency sound at 20000 Hz.
 - The wavelength is 1.6 cm.
 - Compared to this $1\ \mu\text{m}$ is negligible, yet a cube that is $1\ \mu\text{m}$ on each side, contains 2.7×10^7 molecules at standard temperature and pressure (STP).
- Long range variation is associated with the dissipative processes of viscosity, diffusion, and thermal conduction.
- Equilibrium thermodynamics can be applied to local conditions if local equilibrium is attained rapidly.
 - This is valid if it is assumed that the slower processes do not perturb significantly the local equilibrium.
- On the basis of this, the one-dimensional hydrodynamic equations will be derived.

- Since the system is one-dimension, flows, pressure, density gradients, and dissipative processes occur only in the x direction.
- All local variables are functions only of x and time such as mass velocity $u(x, t)$ and density $\rho(x, t)$.
- Consider a volume element with cross section area A where A is perpendicular to the x axis and thickness dx .
- The density varies with time at rate $[\partial\rho(x, t)/\partial t]$.
 - Since mass is conserved, a change in density occurs by a net mass flow into or out of the volume element.
 - The rate of mass flow across a unit area is ρu where u is positive if it is in the positive x direction.
- Thus the net flow into $A dx$ is:

$$A [\rho(x, t)u(x, t) - \rho(x + dx, t)u(x + dx, t)]$$

- Thus:

$$\left[\frac{\partial \rho(x, t)}{\partial t} \right]_x = \lim_{dx \rightarrow 0} \frac{[\rho(x, t)u(x, t) - \rho(x + dx, t)u(x + dx, t)]}{dx}$$

$$= - \left\{ \frac{\partial [\rho(x, t)u(x, t)]}{\partial x} \right\}_t$$

- This may be rewritten as:

$$\left(\frac{\partial \rho}{\partial t} \right)_x + \left[\frac{\partial(\rho u)}{\partial x} \right]_t = 0$$

- This is the one-dimensional continuity equation, also known as the mass conservation equation.
- Since mass is conserved, density may only change as the result of a flow of mass.

- Consider the conservation of linear momentum in the x direction.
- In order for the gas within volume element $A dx$ to be accelerated (i.e. change velocity), there must be a difference in forces on the surfaces of the volume element perpendicular to the x direction.
- The net force difference is:

$$A [p(x, t) - p(x + dx, t)]$$

- The acceleration is in accordance with Newton's Second Law ($\mathbf{F} = m\mathbf{a}$).
- The mass in volume $A dx$ is $\rho A dx$.
- The acceleration of the moving mass of gas is du/dt .

- Therefore:

$$F_x(x, t) = \lim_{dx \rightarrow 0} A[p(x, t) - p(x + dx, t)]$$

$$= -A dx \left[\frac{dp(x, t)}{dx} \right]_t = \rho A dx \frac{du}{dt}$$

- Dividing through $A dx$ gives:

$$\left(\frac{\partial p}{\partial x} \right)_t + \rho \frac{du}{dt} = 0$$

which is the one-dimensional equation of motion for conservation of momentum.

- The next step is to expand du/dt in terms of partial derivatives.

- This gives:

$$\frac{du}{dt} = \left(\frac{\partial u}{\partial t} \right)_x + \left(\frac{\partial u}{\partial x} \right)_t \frac{\partial x}{\partial t} = \left(\frac{\partial u}{\partial t} \right)_x + u \left(\frac{\partial u}{\partial x} \right)_t$$

- Therefore:

$$\left(\frac{\partial p}{\partial x} \right)_t + \rho \left(\frac{\partial u}{\partial t} \right)_x + \rho u \left(\frac{\partial u}{\partial x} \right)_t = 0$$

- The term $u(\partial u / \partial t)_x$ is sufficiently small to be neglected.
- At this point, there is still no dissipation because there is no loss to viscosity and the net force produces the change in velocity.

- Conservation of energy is given by the first Law of Thermodynamics:

$$dU = \vec{d}q + \vec{d}w$$

- Recall that the sign convention is positive with respect to energy being put *into* the system:
 - q is positive when heat is absorbed by the system.
 - w is positive when work is done on the system.
- It is assumed that the compression of gas associated with propagation of a sound wave is adiabatic and reversible and that there is no dissipation.
 - Thus: $\vec{d}q = 0$; $\vec{d}w = -pdV$
- Assuming the gas is ideal:

$$dU = C_V dT = -pdV$$

- Since $\rho = m/V$:

$$dV = d\left(\frac{m}{\rho}\right) = -\left(\frac{m}{\rho^2}\right) d\rho$$

and the First Law becomes:

$$C_V dT = \frac{mp}{\rho^2} d\rho$$

- If C_V is the molar heat capacity, then m may be replaced by the molar mass M .
- Consider the case of a periodic wave.
 - Consider a gas initially at rest with pressure p_0 , density ρ_0 , and temperature T_0 .

- The plane travelling wave can be described in terms of excess pressure \mathcal{P} which is described by a standard wave equation:

$$\mathcal{P}(x, t) = p(x, t) - p_0 = \mathcal{P}_0 e^{i(\omega t - kx)}$$

where

- \mathcal{P} is the amplitude of the pressure variation due to the plane wave.
- $\omega = 2\pi\nu$ is the angular frequency of the wave.
- $k = 2\pi/\lambda$ is the wave vector.
- Thus, excess density is given by:

$$\mathcal{R}(x, t) = \rho(x, t) - \rho_0 = \mathcal{R}_0 e^{i(\omega t - kx)}$$

- The excess temperature is given by:

$$\mathcal{T}(x, t) = T(x, t) - T_0 = \mathcal{T}_0 e^{i(\omega t - kx)}$$

- The mass velocity is given by: $u(x, t) = u_0 e^{i(\omega t - kx)}$
- Recall the continuity equation:

$$\left(\frac{\partial \rho}{\partial t} \right)_x + \left[\frac{\partial(\rho u)}{\partial x} \right]_t = 0$$

into which the wave equations will be substituted.

- The first term becomes:

$$\left(\frac{\partial \rho}{\partial t} \right)_x = \left(\frac{\partial \mathcal{R}}{\partial t} \right)_x = i\omega \mathcal{R}$$

- The second term becomes:

$$\left[\frac{\partial(\rho u)}{\partial x} \right]_t = \rho \left(\frac{\partial u}{\partial x} \right)_t + u \left(\frac{\partial \rho}{\partial x} \right)_t = (\rho_0 + \mathcal{R}) \left(\frac{\partial u}{\partial x} \right)_t + u \left(\frac{\partial \mathcal{R}}{\partial x} \right)_t$$

- If it is assumed that the perturbations due to the sound wave are small, then only first order deviations need be considered.
- Thus:

$$\left[\frac{\partial(\rho u)}{\partial x} \right]_t = \rho_0 \left(\frac{\partial u}{\partial x} \right)_t = -ik\rho_0 u$$

- The continuity equation becomes:

$$\left(\frac{\partial \mathcal{R}}{\partial x} \right)_t + \rho_0 \left(\frac{\partial u}{\partial x} \right)_t = 0 \text{ or } i\omega \mathcal{R} - ik\rho_0 u = 0$$

- Similarly, the equation of motion becomes:

$$\left(\frac{\partial \mathcal{P}}{\partial x}\right)_t + \rho_0 \left(\frac{\partial u}{\partial t}\right)_x = 0 \text{ or } i\omega \rho_0 u - ik\mathcal{P} = 0$$

- Note that the term $\rho u (\partial u / \partial x)$ is a second order perturbation and drops out.
- As long as the sound wave is causing only minor perturbations, dT and $d\rho$ may be replaced by \mathcal{T} and \mathcal{R} .
- Therefore:

$$C_V \mathcal{T} = \frac{M p_0}{\rho_0^2} \mathcal{R}$$

- An additional equation is needed to connect the four variables \mathcal{P} , \mathcal{R} , \mathcal{T} and u .
 - The equation of state is used.

- The equation of state may be written as:

$$p = p(\rho, T), \quad dp = \left(\frac{\partial p}{\partial \rho} \right)_T d\rho + \left(\frac{\partial p}{\partial T} \right)_\rho dT$$

- If the perturbation is small, then $dp = \mathcal{P}$, $d\rho = \mathcal{R}$ and $dT = \mathcal{T}$.
- Therefore:

$$\mathcal{P} = \left(\frac{\partial p}{\partial \rho} \right)_T \mathcal{R} + \left(\frac{\partial p}{\partial T} \right)_\rho \mathcal{T}$$

or

$$\mathcal{P} - \left(\frac{\partial p}{\partial \rho} \right)_T \mathcal{R} - \left(\frac{\partial p}{\partial T} \right)_\rho \mathcal{T} = 0$$

- The four simultaneous equations are:

$$iku - \frac{i\omega}{\rho_0} \mathcal{R} = 0$$

$$i\omega u - \frac{ik}{\rho_0} \mathcal{P} = 0$$

$$-\frac{Mp_0}{\rho_0^2} \mathcal{R} + C_v \mathcal{T} = 0$$

$$\mathcal{P} - \left(\frac{\partial p}{\partial \rho} \right)_T \mathcal{R} - \left(\frac{\partial p}{\partial T} \right)_\rho \mathcal{T} = 0$$

- These equations may be solved by determining the determinant of the corresponding matrix.

- The determinant of the matrix is:

$$ik \left\{ \frac{-ik}{\rho_0} \left[\frac{Mp_0}{\rho_0^2} \left(\frac{\partial p}{\partial T} \right)_\rho + C_V \left(\frac{\partial p}{\partial \rho} \right)_T \right] \right\} - i\omega \left(-\frac{i\omega C_V}{\rho_0} \right) = 0$$

- For a travelling wave of the form $Ae^{i(\omega t - kx)}$ the velocity of propagation is $c = \omega/k$.
 - In this case, this is the speed of sound.
- Rearranging the equation for the determinant gives:

$$ik \left\{ \frac{-ik}{\rho_0} \left[\frac{Mp_0}{\rho_0^2} \left(\frac{\partial p}{\partial T} \right)_\rho + C_V \left(\frac{\partial p}{\partial \rho} \right)_T \right] \right\} = i\omega \left(-\frac{i\omega C_V}{\rho_0} \right)$$

- Now, ω^2/k^2 may be isolated.

- This gives:

$$\frac{\omega^2}{k^2} = \left[\frac{Mp_0}{\rho_0^2} \left(\frac{\partial p}{\partial T} \right)_\rho + C_V \left(\frac{\partial p}{\partial \rho} \right)_T \right] \left[\frac{1}{C_V} \right]$$

or

$$c^2 = \frac{\omega^2}{k^2} = \left[\left(\frac{\partial p}{\partial \rho} \right)_T + \frac{Mp_0}{C_V \rho_0^2} \left(\frac{\partial p}{\partial T} \right)_\rho \right]$$

- To eliminate pressure from the equation, the ideal gas equation of state may be used:

$$p = \frac{\rho RT}{M}$$

- Therefore:

$$\left(\frac{\partial p}{\partial \rho}\right)_T = \frac{RT}{M} = \frac{p_0}{\rho_0}$$

and

$$\left(\frac{\partial p}{\partial T}\right)_\rho = \frac{\rho_0 R}{M}$$

- This gives:

$$c^2 = \frac{p_0}{\rho_0} + \frac{M p_0}{C_V \rho_0^2} \frac{\rho_0 R}{M}$$

$$c^2 = \frac{p_0}{\rho_0} \left(1 + \frac{R}{C_V}\right) = \frac{p_0}{\rho_0} \left(\frac{C_V + R}{C_V}\right) = \frac{p_0}{\rho_0} \gamma$$

where $\gamma = C_p/C_V$.

- Thus $c = (\gamma RT/M)^{1/2}$.

- So far, it has been assumed that the gas is ideal and that there is no dissipation.
- If the gas is not assumed to be ideal, then

$$c^2 = \left(\frac{\partial p}{\partial \rho} \right)_S = \frac{1}{\rho \kappa_S}$$

- Recall that

$$\kappa_S = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_S$$

and that S denotes constant entropy (which is the condition for adiabaticity).

- This still does not take in account the dissipation.
- Dissipation is the result of molecular collisions.

- When a sound wave is propagated by mass flow, energy is transferred by collisions from translation into internal vibrations and rotations.
- This causes attenuation of the amplitude of the sound wave because this process is irreversible.
 - Even if the energy of vibration and rotation were to be transferred back to translation, it would be in random directions.
- Lower frequency sound has the time between crests of the sound wave for the internal degrees of freedom to equilibrate.
- Higher frequency sounds carry better because the time between crests is short compared to the time required for energy transfer.
- The dissipation due to viscosity is relatively negligible.

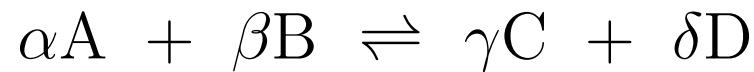
Chemical Kinetics

- Chemical kinetics is the study of how fast reactions take place.
 - Important to fundamental knowledge
 - Important in industrial chemistry
 - Important in biochemistry.
- Chemical kinetics studies often involve measurement of phenomenological rates.
 - This allows the testing for possible microscopic processes that make up the mechanism of the reaction.
 - A reaction mechanism describes how a reaction takes place.
 - The mechanism involves fundamental chemical processes, such as molecular collisions.
 - The nature of molecular collisions is important.

- Some major concepts in kinetics are:
 - rate
 - order
 - molecularity
- Also examined are:
 - the microscopic theory of bimolecular collisions.
 - interactions between reactive molecules.
 - dynamics of reactive collisions and associated thermodynamics.
 - activated complex theory.
 - specific types of reactions.
 - combinations of elemental processes that make up a mechanism.
 - effects of medium, phase, catalysts, and temperature.

General Concepts of Kinetics

- What is a rate of reaction?
- Consider the general reaction:



where:

- α, β, γ and δ are stoichiometric coefficients.
- Therefore, the disappearance of α moles of A is accompanied by:
 - the disappearance of β moles of B.
 - the appearance of γ moles of C.
 - the appearance of δ moles of D.
- A chemical reaction equation may be written more generally as:

$$\sum_i \nu_i X_i = 0$$

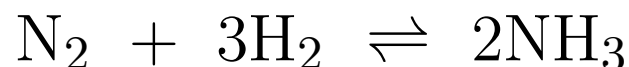
- ν_i are the stoichiometric coefficients and are positive for products and negative for reactants.
- Historically, the rate of reaction has been defined as $d[X_i]/dt$, but this is ambiguous if the ν_i 's are different.
- IUPAC has defined the rate of reaction as:

$$\dot{\xi} \equiv \frac{1}{\nu_i} \frac{dn_i}{dt}$$

where

- n_i is the amount (moles) of substance X_i in the system.
- ξ is the extent of reaction in moles.
- $\dot{\xi}$ is the rate of reaction in moles per unit time.

- Consider the reaction:



- The rate of reaction per unit volume is:

$$\frac{\dot{\xi}}{V} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt} = -\frac{d[\text{N}_2]}{dt} = -\frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

- Reaction rates are determined experimentally.
 - Such experiments involve measuring as a function of time properties related to the concentration of one or more chemical species involved in the reaction.
 - A number of chemical or physical methods may be used.
 - Different methods have different advantages or disadvantages.

- Chemical methods offer the advantage of high accuracy and specificity.
 - Disadvantages include:
 - Time required
 - Disturbance of the system.
 - Chemical methods can be used if quenching is possible.
 - Quenching can be achieved by rapid cooling if the chemical reaction under consideration is strongly temperature dependent.
 - It may also be accomplished by removing a reactant or catalyst by adding something that consumes the reactant or catalyst.
 - In the case of a photolytic reaction, a catalyst may be removed.

- Physical methods, such as monitoring an optical property, are rapid and can be used in real time.
- These include:
 - Index of refraction (polarimetry)
 - Optical absorption (spectroscopy)
 - Emission spectroscopy (chemiluminescence).
- Other physical properties include:
 - pressure
 - volume
- Properties that affect reaction rates need to be controlled.
 - temperature
 - pressure
 - concentrations

- Homogeneous reactions occur in one phase.
- Heterogeneous reactions occur at the interface between phases.
 - Rates of heterogeneous reactions depend on the presence of the surface.
 - A critical step in the mechanism occurs on the substance.
 - Rate of diffusion to the surface affects the rate of reaction.
- Reactions may have multiple routes, some of which may be homogeneous or heterogeneous.
 - Whether a heterogeneous route exists may be assessed by varying the surface to volume ratio of the surface.
 - Homogeneous reaction rates are independent of the surface area.

- Heterogeneous reaction rates are dependent on the surface area.
- Temperature dependence is different for homogeneous and heterogeneous reactions.
 - Homogeneous reaction rates vary exponentially with temperature.
 - Heterogeneous reactions tend to be controlled by diffusion which has $T^{1/2}$ temperature dependence.
- Catalysts can affect both homogeneous and heterogeneous reactions.
 - A catalyst can affect the rate of a chemical reaction but not the position of the equilibrium.
 - Surface catalysts act as a substrate upon which the reactants interact more readily.

- In homogeneous catalysis, the catalyst participates directly in the elementary processes that make up one or more steps of the reactions mechanism.
- Most reaction rates are affected by concentration.
- Many reactions have rate expressions of the form:

$$\frac{d[A]}{dt} = k[A]^{\alpha}[B]^{\beta}[C]^{\gamma} \dots$$

where α , β and γ are constants and k is the reaction rate coefficient.

- α , β , and γ are the orders of the reactions with respect to particular reactants or products and are usually small integers or ratios of small integers.
- The above is also referred to as empirical or experimental rate expression.

- The overall reactions order is the sum of the orders with respect to all species in the rate expression.
- Species not present in the stoichiometric reaction equation may appear in the rate expression.
- Species appearing in the stoichiometric reaction equation may not appear in the rate expression.
- It is possible for a reaction to have negative order.

First Order Reactions

- A reaction with a first order reaction expression has a rate that is directly proportional to the concentration of a single species.

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

where k is the rate coefficient.

- This rate expression can be integrated analytically to yield:

$$[A] = [A]_0 e^{-kt}$$

where $[A]_0$ is the concentration of A at the beginning of the experiment.

- This may be rewritten in the form of a straight line.

$$\ln[A] = \ln[A]_0 - kt$$

- Thus a plot of $\ln[A]$ against time should yield a straight line of slope $-k$.
- This is consistent with:

$$-\frac{d[A]}{[A]} = kt$$

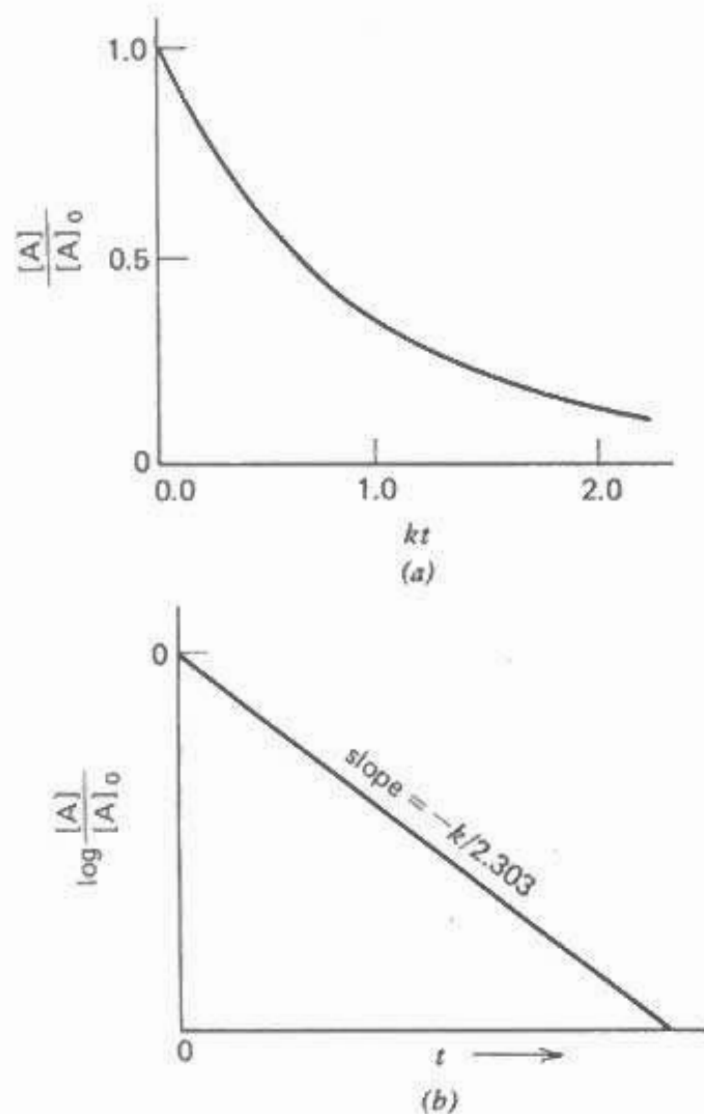


Figure 30.1 Concentration of A versus time for a first-order rate equation, according to Eqs. 30.5 and 30.6. (a) gives the exponential decay curve, (b) gives the logarithmic plot used to obtain the rate coefficient k .

- Much of the foundation of modern kinetics was laid in the late nineteenth century.
 - In the context of the computational tools of that era, it was more convenient to work in base 10 logarithms.
 - A plot of $\log[A]$ against time would yield a straight line of slope $-k/2.303$.
- A half-life is defined as the time interval required for the concentration of $[A]$ to reach half of its initial concentration.
- For a first order reaction, the half-life is a function only of the rate coefficient.

$$t_{1/2} = \frac{\ln 2}{k}$$

Second Order Reactions

- There are two types of second order reactions:
 - Second order in one species
 - First order in each of two species.
- A reaction that is second order in one species is:

$$-\frac{d[A]}{dt} = k[A]^2$$

- This may be integrated analytically to give:

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

- This means that a plot of $1/[A]$ against time will be linear with slope k and intercept $1/[A]_0$.

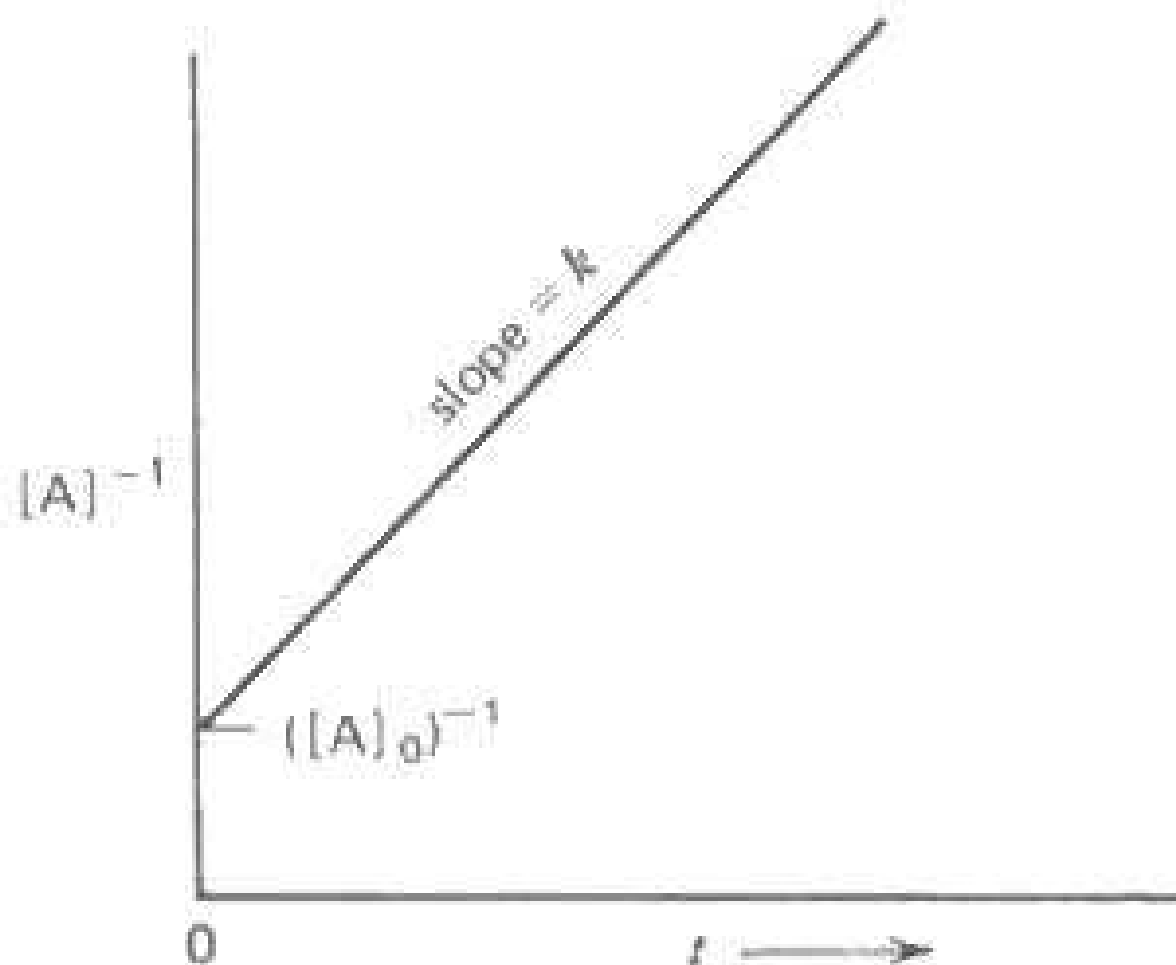


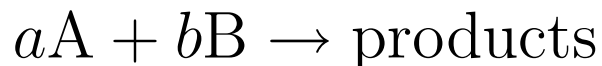
Figure 30.2 Straight-line plot giving k for a second-order reaction of the type according to Eq. 30.11.

- The other type of second order reaction is:

$$\text{rate} = k[\text{A}][\text{B}]$$

which is first order in each of two species.

- To integrate this equation analytically, the stoichiometry must be taken into consideration.
 - Suppose it is of the form:



- Then the rate expression is:

$$-\frac{1}{a} \frac{d[\text{A}]}{dt} = -\frac{1}{b} \frac{d[\text{B}]}{dt} = k[\text{A}][\text{B}]$$

- Define x by:

$$[A] = [A]_0 - ax, \quad [B] = [B]_0 - bx$$

- Thus the rate expression is:

$$\frac{dx}{dt} = -\frac{1}{a} \frac{d[A]}{dt} = k([A]_0 - ax)([B]_0 - bx)$$

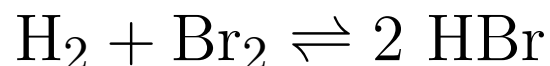
- This may be integrated by partial fractions to give:

$$\frac{1}{b[A]_0 - a[B]_0} \ln \left\{ \frac{[B]_0([A]_0 - ax)}{[A]_0([B]_0 - bx)} \right\} = kt$$

- This may be rearranged to:

$$\frac{[A]}{[B]} = \frac{[A]_0}{[B]_0} e^{(b[A]_0 - a[B]_0)t}$$

- A plot of $[A]/[B]$ against t will give a straight line with slope proportional k (Figure 30.3).
- Generally, if an empirical rate expression is known, the rate coefficient k may be found.
 - Rate expressions are determined by trial and error.
- Some rate expressions can be quite complicated.
 - Consider the reaction:



- The rate expression found experimentally is:

$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k'[\text{HBr}]/[\text{Br}_2]}$$

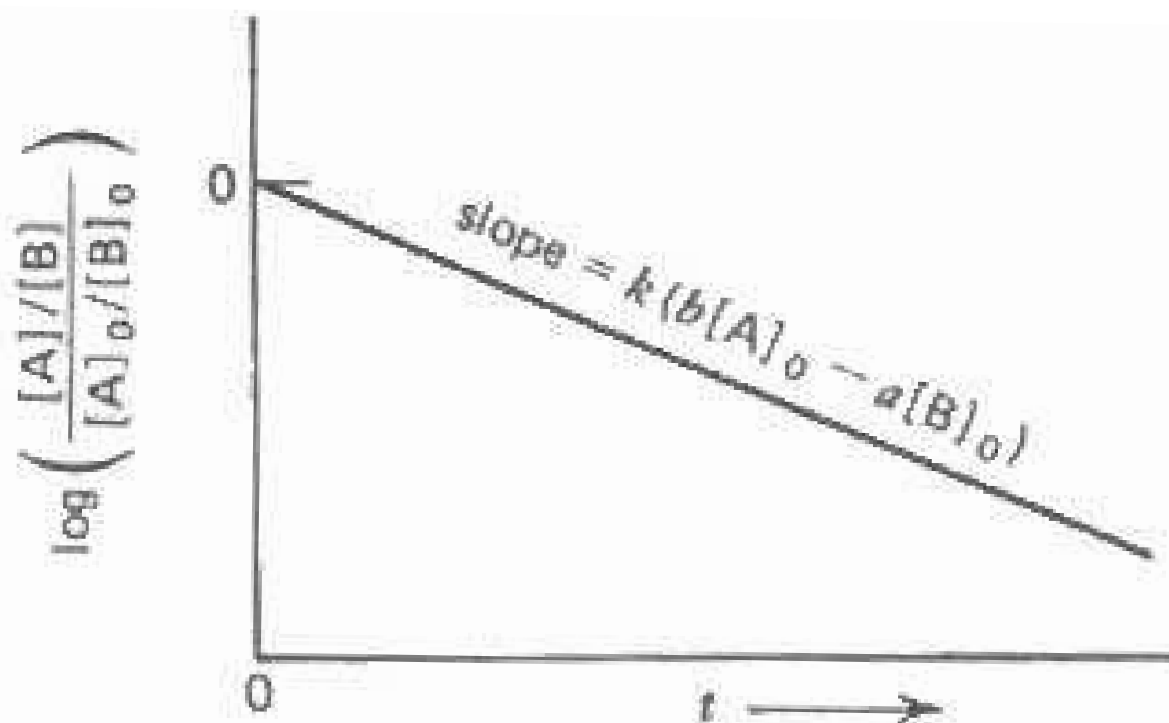


Figure 30.3 Straight-line plot giving k for a second-order reaction of the type



according to Eq. 30.18.

- There is no relation between the stoichiometric coefficients of a reaction and the reaction order with respect to the concentrations of various chemical species.
- Overall stoichiometry does not determine the reaction order.
- It is the mechanism that determines the reaction order and the rate expression.
 - The mechanism of a chemical reaction consists of the sequence of molecular processes by which the reaction occurs and is made up of elementary processes.
 - An elementary process transforms one or more chemical species into different chemical species.
 - The chemical species or “molecule” involved may include molecules, atoms, ions, free radicals, or electrons.

- Elementary reactions involve single collisions of reactants.
- The only exception is a unimolecular reaction, which often can occur only after a series of collisions or absorption of radiation has delivered energy to the molecule.
- Molecularity describes the number of molecules taking part in the elementary process.
 - If one molecule is involved, it is unimolecular.
 - If two molecules are involved, it is bimolecular.
 - If three molecules are involved, it is termolecular.

Molecularity, order, and stoichiometry can be different from one another.

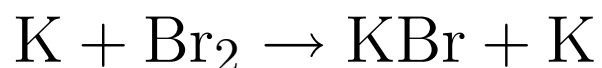
- Molecularity and order are the same only for elementary reactions.

- Chemical kinetics is related to the fundamental concepts of molecular dynamics.
- An understanding of chemical kinetic processes involves an understanding of elementary reactions and the details of the colliding molecules including:
 - Forces between molecules
 - Scattering caused by these forces.
 - Reaction cross section and its dependence on:
 - relative kinetic energy
 - internal energy (quantum states)
 - orientation of reactants and products.
- Thus an elementary process may be viewed as a transport process.
 - In a chemical reaction the colliding species lose their identity.

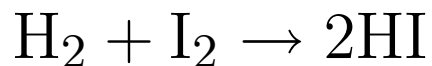
- The dynamics of a chemical reaction involves the details of how the reaction occurs.
 - It considers whether or not there is a relatively long-lived association between molecules, that is whether a “complex” is formed.
 - It also considers the timescale for a bond rearrangement relative to a rotational or vibrational period.
 - Another factor considered is whether there is localization of energy in particular degrees of freedom.
- Reaction dynamics has the task of:
 - From the molecular structure, predicting the kinds of reactions products expected.
 - Predicting the reaction probability and rate coefficient

- Reaction dynamics also predicts the energy required for the reaction to occur.
- Elementary reactions may be tested theoretically or experimentally.
 - Theoretical studies use information about interaction potentials, either determined *a priori* or extracted from macroscopic data.
 - Experimental studies use molecular beams and spectroscopic techniques.
- Most chemical reactions involve multiple elementary processes in a series of steps.
- The complete sequence of elementary reactions gives the mechanism for the overall reaction.
- There are many types of mechanisms.

- Consider the reaction between K and Br₂.
- Crossed beam experiments indicate that it proceeds as a single step:

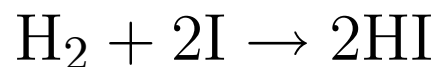
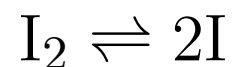


- The probability of reaction is quite large and corresponds to a single molecular collision.
- Consider the reactions

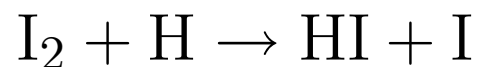
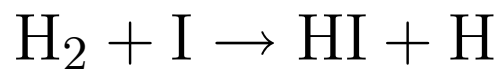
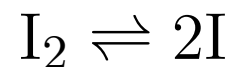


- Kinetic studies suggest that the overall reaction is second order with reaction rate first order in each of H₂ and I₂.
- However the reaction does not proceed by an elementary reaction corresponding to the stoichiometric equation.

- The mechanism has been established to be:

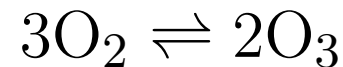


- At higher temperature a second mechanism is taking place simultaneously:

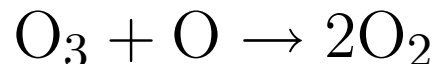
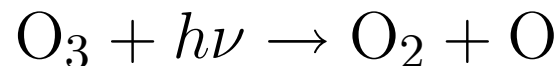
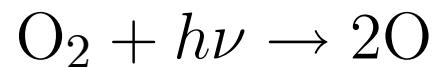


- Both mechanisms give rise to the same rate expression.
- There is no unique mechanism corresponding to an empirical rate law.

- Ozone destruction is associated with thinning of the ozone layer over Antarctica.
 - Competing with the destruction of ozone is its formation:
 - The overall reaction is:

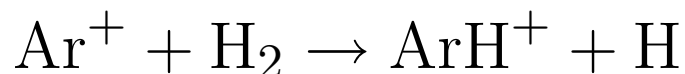
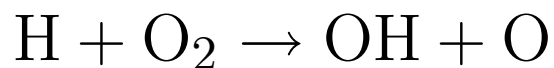


- Some of the reactions involved in the mechanism are:

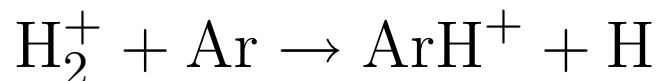


- Elucidation of mechanisms is non-trivial.
- Most mechanisms are guessed rather than deduced.
- If a mechanism is hypothesized, then experiments may be designed to test the mechanism.
- A hypothesized mechanism needs to be plausible, based on the energetics of the mechanism and what is known about the elementary processes.
- Most mechanisms consist of bimolecular processes.
- Bimolecular reactions may be classified according to the nature of the reactant species:
 - Neutral - Neutral
 - Ion - Neutral
 - Neutralization reactions

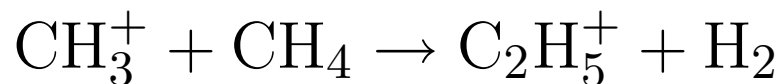
- Metathetical or transfer reactions are those in which an atom or group of atoms breaks a bond and forms a new one, resulting in the transfer of the atom or group of atoms from one molecule to another.
- Some examples are:
 - Atom transfer:



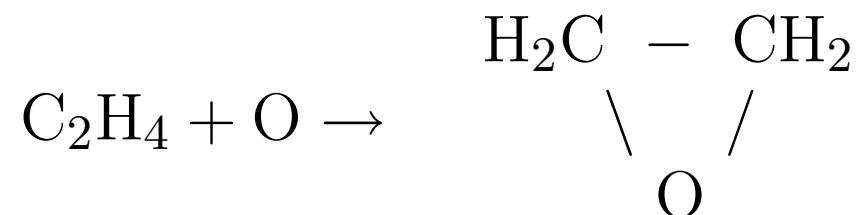
- Proton Transfer:



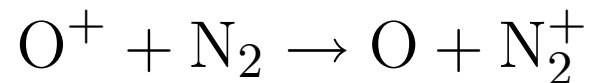
- Condensation:



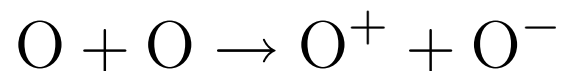
- Atom insertion:



- Charge transfer:



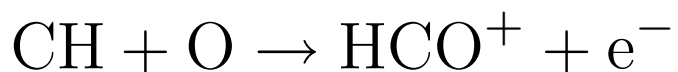
- Ion pair formation:



- Collisional Ionization:



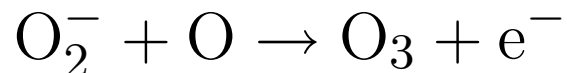
- Associative Ionization:



- This occurs when the ionization energy is furnished by a new bond.
- Penning Ionization:



- This occurs when the ionization energy is provided by an excited reactant.
- Associative detachment:

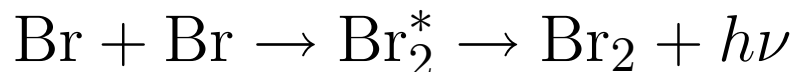


- This may be viewed as the ion-molecule equivalent of associative detachment.

- Dissociation:



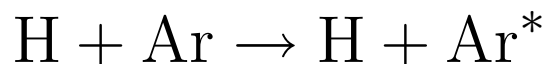
- This requires sufficient kinetic energy in the collision to cause dissociation.
- Recombination requires the removal sufficient energy to stabilize the bond.
 - This may occur by redistribution of energy within the molecule, if the molecule is big enough.
 - However this energy must be removed or the molecule will fall apart again.
 - This may occur by a collision or by the emission of a photon.



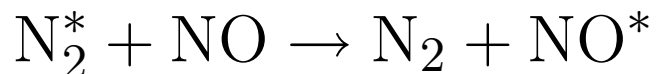
- This is also known as chemiluminescence:



- Excited states may be produced by collisional excitation:



- Excitation may also be transferred by a collision:

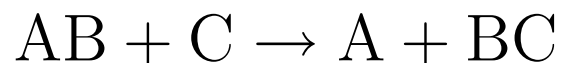


- These are just some of possible bimolecular reactions.

Interactions between Reactive Molecules

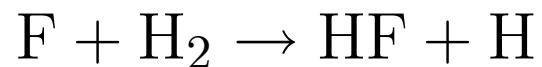
- Interactions between reactive molecules depends on the forces between them.

- However, the forces between reactive molecules are much more difficult to measure than those between nonreactive molecules.
- Many more variables are involved in the potential since bonds are being broken and formed.
- The internal structure must also be taken into account.
- Consider the exchange reaction:



- Three variables are required to describe the relative positions of A, B, and C.
 - Additional variables are required if A, B, or C are polyatomic.
- *Ab initio* potentials are available for only a few systems.

- Scattering experiments allow experimental access to details of the potential.
- One of the best known potentials is that for:



- The interaction depends on R_{HF} , R_{HH} and the angle α where:
 - R_{HF} is the shorter of the two HF separations
 - R_{HH} is the separation of the two H atoms
 - α is the angle between R_{HF} and R_{HH} .
- It also depends on the internal energy states of F and H_2 or HF and F.
- If all are in the ground state, then the potential is as shown in Figure 30.4.

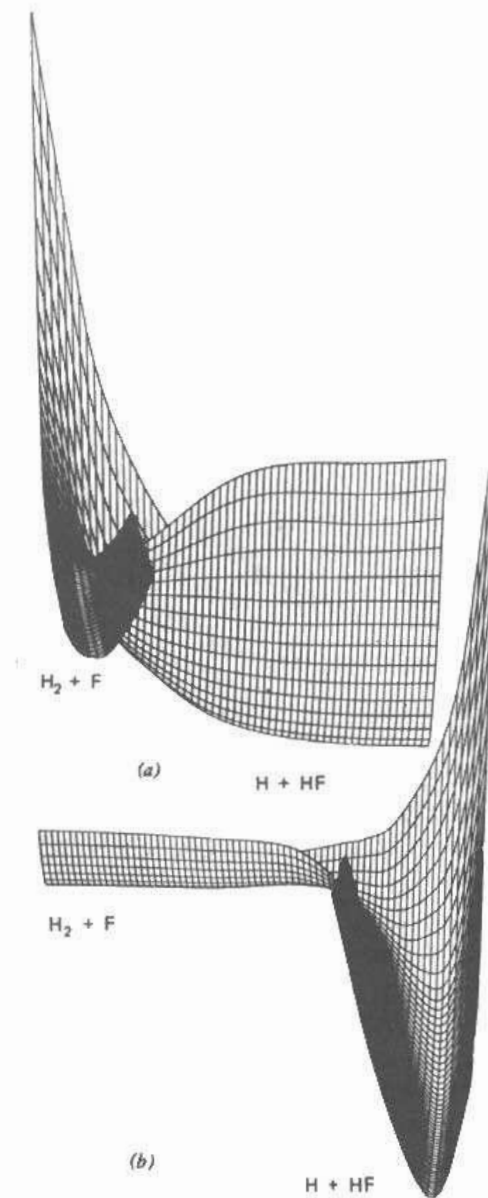


Figure 30.4 Two views of the potential energy surface for the linear F-H-H system: (a) from the $H_2 + F$ channel; (b) from the $HF + H$ channel. The horizontal axes represent R_{H-F} and R_{H-H} and the vertical axis represents energy. Each small "square" on the surface represents a square region in space $0.05a_0$ on a side (where a_0 is the Bohr radius, 0.5292 \AA). From C. F. Bender, S. V. O'Neil, P. K. Pearson, and H. F. Schaefer, III, *Science* **176**, 1412 (1972).

- The construction of a potential energy surface assumes that the Born-Oppenheimer approximation holds and the nuclear and electronic motions may be separated such that the energy of interaction depends only on the positions of the nuclei.
- Consider the potential for $\alpha = \pi$ corresponding to a collinear conformation of the atoms.
 - For a fixed value of α , the interaction potential depends only on R_{HF} and R_{HH} .
 - In this case, it is possible to represent the potential as a contour map (See Figure 30.5.)
- Consider the limiting regions:
 - When R_{HF} and R_{HH} are large, all three atoms are far apart and the energy does not depend strongly on their location. This gives the plateau region.

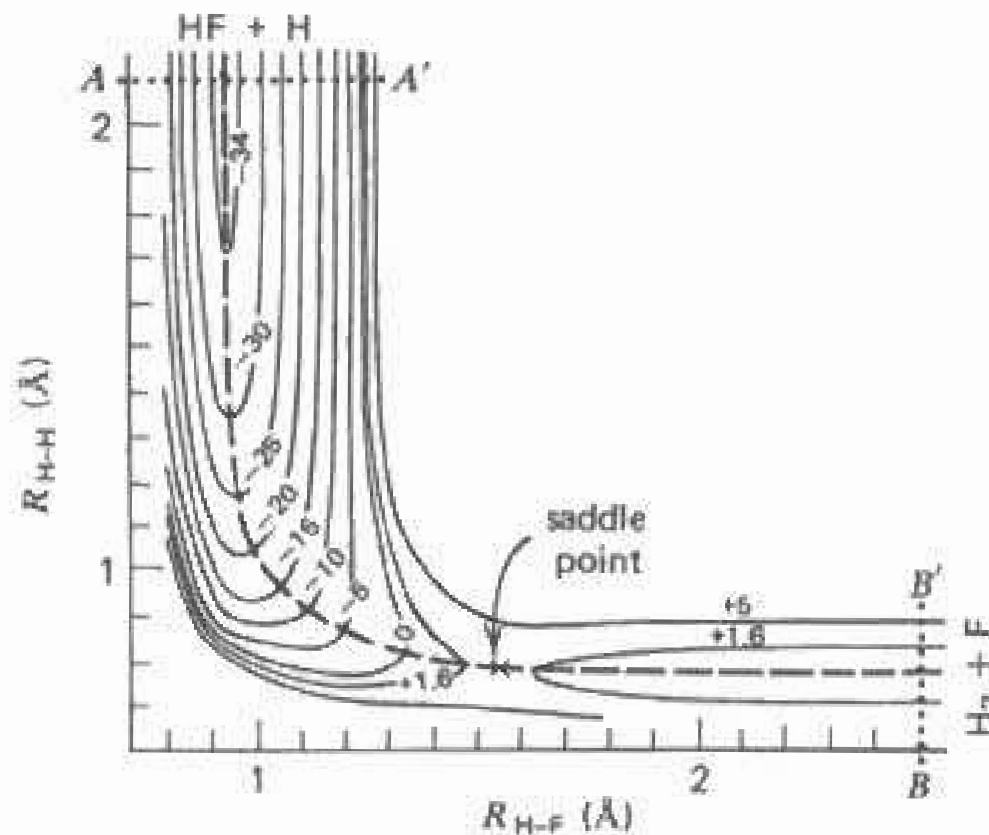


Figure 30.5 “Contour map” of the linear F–H–H potential energy surface, as calculated by Bender et al. The zero of energy is taken to be the limiting energy for $\text{H}_2 + \text{F}$, and the energy contours are labeled in kilocalories per mole ($1 \text{ kcal/mol} = 4.184 \text{ kJ/mol} = 0.043364 \text{ eV}$). The cross sections indicated by dotted lines are discussed in the text; the heavy dashed line represents the reaction coordinate.

- When two atoms are close together and the third is far away, the potential extrapolates to the diatomic potential of the two closest atoms when the distance to the third atom is held constant.
- This gives two valleys in the F-H-H potential energy surface, one corresponding to the limiting case of $\text{HF} + \text{H}$, the other to $\text{H}_2 + \text{F}$.
- The valleys are linked by a “pass” with a saddle point.
- Since the two valleys are not identical, the location of the saddle point is asymmetric and is more towards one valley than the other.
- The minimum energy path is sometimes considered the reaction coordinate and is the curve connecting the deepest portions of each valley through the saddle point.

- The reaction coordinate may be thought of as roughly the path followed by the system when a reaction occurs.
- The barrier height is the difference between the energy of the reactants and the energy at the saddle point.
 - The barrier height can be different for the reaction carried out in the reverse direction.
 - This is represented schematically in Figure 30.6.
 - The difference in barrier heights is related to the endo- or exo-thermicity of the reaction.
- The calculation of a potential *a priori* is challenging, therefore approximations are used.
 - The semi-empirical methods such as LEPS (London, Eyring, Polanyi, Sato) are used.
 - LEPS uses the diatomic potentials plus an empirically determined interaction term for the overall potential.

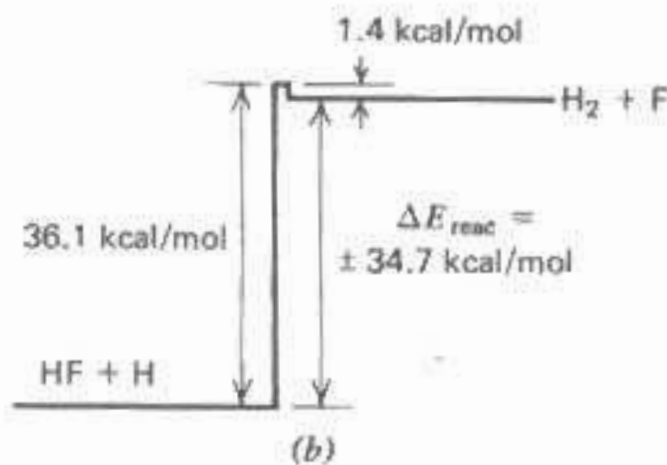
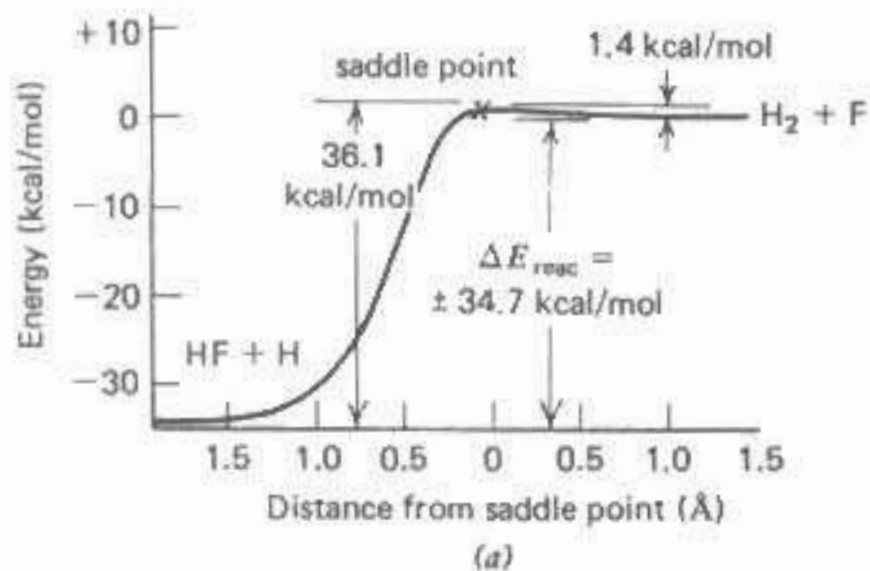


Figure 30.6 (a) Potential energy along the reaction coordinate for the reaction



(b) Schematic representation of the potential barrier.

- The diatomic potential is:

$$E_{AB} = \frac{J_{AB} \pm K_{AB}}{1 + S_{AB}^2}$$

where:

- J_{AB} is the Coulomb integral
 - K_{AB} is the exchange integral
 - S_{AB} is the overlap integral.
- These may be determined from spectroscopic data or from *a priori* calculations.
 - If these are known for all three pairs of atoms, then the LEPS potential may be determined, provided κ may be evaluated.
 - κ is a overlap integral and is usually evaluated empirically.

- The complete LEPS potential is:

$$E_{ABC} = \frac{J_{AB} + J_{BC} + J_{CA}}{1 + \kappa}$$

$$- \frac{\left\{ \frac{1}{2} [(K_{AB} - K_{BC})^2 + (K_{BC} - K_{CA})^2 + (K_{CA} - K_{AB})^2] \right\}^{1/2}}{1 + \kappa}$$

- E_{ABC} is not the sum of E_{AB} , E_{BC} , and E_{CA} .
- Intermolecular potentials are nonadditive.
- The force between A and B depends on the position of C.
- The surface is not symmetric unless the system is symmetric.
- When the surface is not symmetric, one of the channels “bends” to meet the saddle point.

- Chemically accurate potentials can be complicated.
- The LEPS potential form is not robust enough to capture the behaviour of the real potential.
- Some potentials have a “well” on top of the barrier.
 - This means that a long lived complex may form.
 - It is possible for an interacting system to spend a long time near the top of a barrier without a well being present.
 - This means that the view of energy versus reaction coordinate is not an adequate description of a reacting system.
- Some systems involve more than one electronic state.
 - If a system involves only one combination of electronic states, it is adiabatic and involves only one potential energy surface.

- Some systems involve more than one combination of electronic states and thus more than one potential energy surface.
- These potentials may intersect.
- In the case where there is only one independent variable (such as an interatomic separation) then the intersection of potential curves is referred to as curve crossing.
- The term curve crossing is commonly used for multidimensional potentials, but is only rigorously applicable to a 1-D potential.
- Consider Figure 30.7 (a) which shows the crossing of two curves.
- Whether a system can cross from one curve to the other depends on symmetry considerations in the associated quantum mechanics.

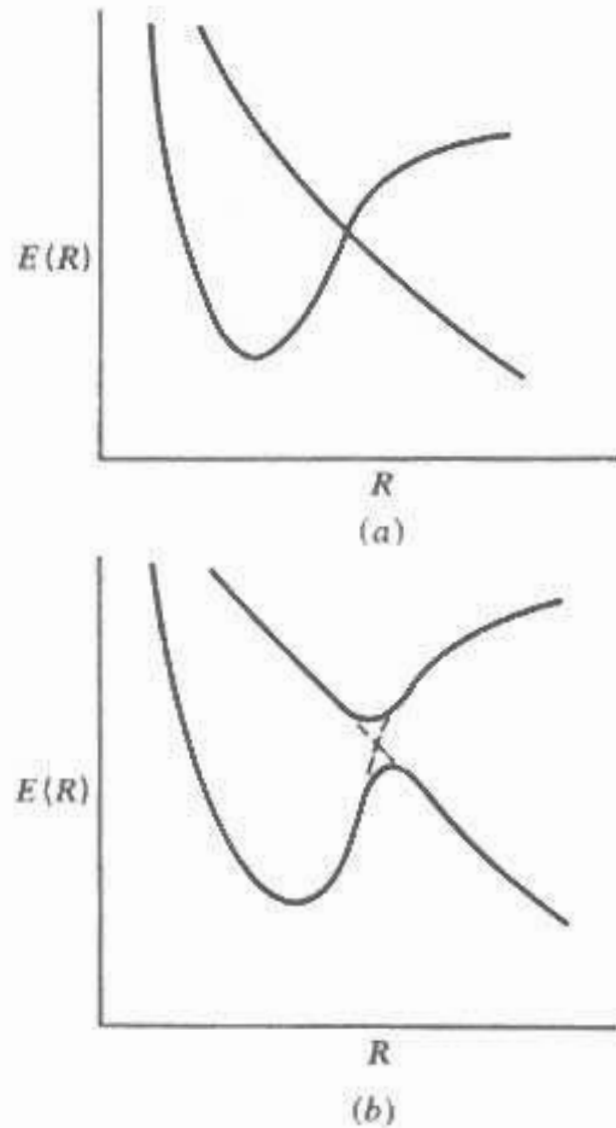


Figure 30.7 Interaction between two potential curves of the same symmetry. (a) Crossing of approximate curves. (b) Avoidance of crossing of exact curves.

- If the curves do not cross, then the actual electronic state associated with the avoided crossing is a linear combination of the two states.
- The noncrossing states can be so close together that the Born-Oppenheimer approximation does not hold, especially if R is changing rapidly.
- In such cases a transition from one curve to another occurs.
- For multidimensional potentials of systems with more than two atoms, the crossings can be much more complicated with multidimensional geometrical features associated with the intersection of the surfaces.
- The symmetry rules governing whether or not crossing occurs become more complicated in higher dimensions.

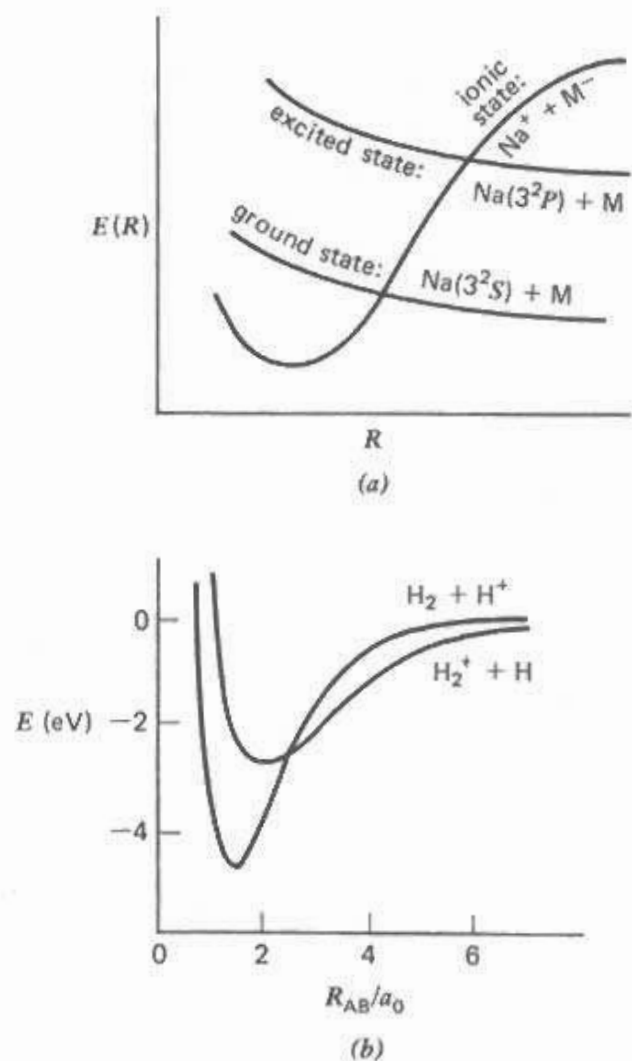
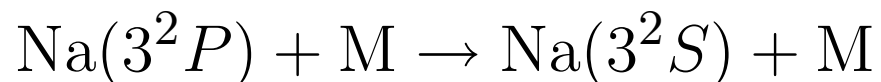


Figure 30.8 Some examples of curve-crossing reactions. (a) Schematic diagram of the sodium quenching process, in which the system proceeds from the excited state to the ground state via the intermediate ionic state. (For clarity the crossing points are shown unmodified.) (b) Limiting curves for $\text{H}_2^+ + \text{H}$ and $\text{H}_2 + \text{H}^+$, each with the third atom far distant; in the complete H_3^+ system, the crossing point at $2.5a_0$ becomes a “seam” between two potential energy surfaces (see text).

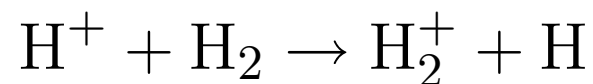
- An example of a nonadiabatic transition is:



which releases 2.09 eV of energy and is shown in Figure 30.8 (a).

- This reaction has an ionic transition state which crosses both the ground state $\text{Na}(3^2S)$ and the excited state $\text{Na}(3^2P)$.
- The exact nature of the potential depends on the nature of M and whether it has internal structure.
 - The presence of internal structure allows for additional curve crossing.
 - Transfer of energy between electronic and vibrational forms is easier than transfer between electronic and translational forms.

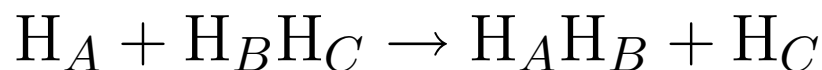
- Another example of a nonadiabatic reaction is:



and is shown in Figure 30.8 (b).

- The limiting curves for H_2 and H_2^+ cross at about $2.5 a_0$.
- The potential surfaces have a seam or an avoided crossing.
 - Surface hopping probabilities may be determined and agree with experiment.
- So far, mostly collinear cuts of the potential have been considered.
- But the potential varies with angle.

- The most widely studied reaction is:



- This potential is symmetric for all values of the angle θ formed by R_{AB} and R_{BC} ,
- The saddle point is found along the line $R_{AB} = R_{BC}$.
 - But its height will vary with the value of θ .
 - At $\theta = \pi$ (collinear) the height of the saddle point is about 0.5 eV.
 - At $\theta = \pi/2$ the height of the saddle point is about 1.2 eV.
 - At $\theta = \pi/3$ the height of the saddle point is about 2.8 eV.
 - This means that reaction is most likely for linear or near linear. conformations.

Collisions between Reactive Molecules

- How does the initial and final state affect the reactivity of molecules?
- How long do reacting molecules spend interacting with each other (relative to vibrational or rotational period)?
- How is energy distributed while the collision is occurring?
- How is energy distributed in the products?
- Which degrees of freedom do or do not participate in the reaction?
- In principle, all of this may be addressed by solving the time-dependent Schrodinger equation for the entire reacting system.
- In practice, this is feasible for only relatively simple systems.
- Therefore, insight into these questions is gained by using classical mechanics to describe binary collisions.

- There are three types of molecular collision:
 - Elastic (involving only translational motion)
 - Inelastic (involving changes in internal vibrational, rotational, or electronic state).
 - Reactive (in which chemical species are not the same before and after collision).
- Any of these may occur in an encounter between a given pair of molecules.
- Consider the linear collision of H with HF($v=0$).
 - The potential energy is described by Figure 30.5.
 - If the total energy of the collision is below the barrier height, then only elastic or inelastic collisions occur, classically.
 - Quantum mechanically, tunnelling may be possible.

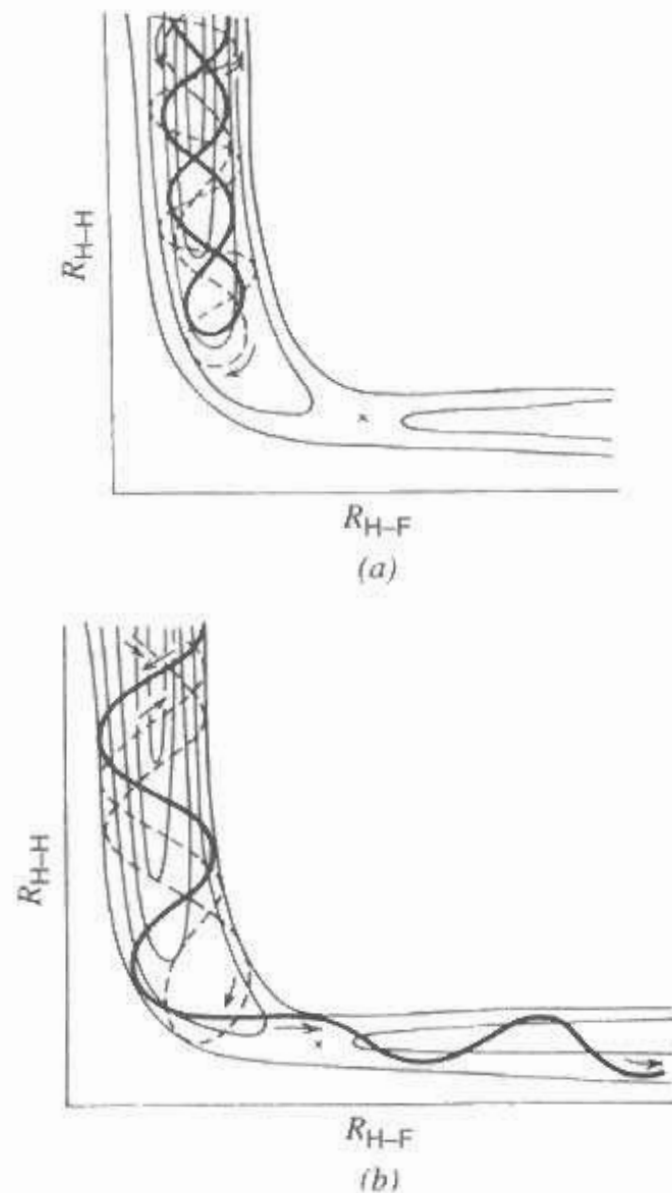


Figure 30.9 Some possible trajectories (schematic) in a collision between HF and H. (a) Insufficient energy for reaction: elastic (—) and inelastic (---) collisions. (b) Sufficient energy for reaction: reactive (—) and elastic nonreactive (---) collisions.

- In Figure 30.9 (a), an elastic trajectory is shown as a dark solid line.
 - Translational energy is less than the barrier height.
 - Vibrational energy is conserved.
- The dashed line shows an inelastic trajectory at the same translational energy, but a different vibrational phase.
 - Translational energy is converted into vibrational energy.
- Figure 30.9 (b) shows two trajectories with energy in excess of the barrier height but with different vibrational phases.
 - The solid line is a reactive trajectory with some of the internal energy of the reactant converted into translational energy of products.
 - The dashed line is an elastic trajectory.

- This makes it clear that more than energy is involved in determining whether a system will react.
- For some systems, there are many possible final states.
- For example, for the collinear collision of H with HF can have the following outcomes
 - H and HF in initial states
 - H and HF with HF in a different vibrational state.
 - F and H₂ with the H₂ in any of several vibrational states.
- In cases where potential energy surfaces intersect, there can be multiple products.



- In this case the ionic channel is dominant.
- The outcomes of chemical reactions are constrained by conservation laws.
- Consider the trajectories in Figure 30.9.
 - Any trajectory can be reversed by changing the sign of the time coordinate.
 - This is an illustration of the law of microscopic reversibility.
 - As a consequence the transition probability from one initial state to one final state is equal to the transition probability in the reverse direction.
- Any collision involves a continuous exchange of kinetic and potential energy.
- There is also exchange between internal and kinetic energy.

- The total energy of an interacting system may be considered as defining a plane at a fixed height on the energy axis of a potential energy surface.
 - Then the kinetic energy at any value of the coordinates is the difference between the total energy and the potential energy surface.
 - All portions of the potential energy surface above the total energy plane are inaccessible to the system since they would correspond to negative kinetic energy.
- The higher the barrier height, the fewer trajectories are able to cross the barrier and the smaller the rate coefficient.
- The barrier height may be defined as the energy difference between the saddle point and the initial energy of the reactants.

- The barrier heights in the forward and reverse directions are related:

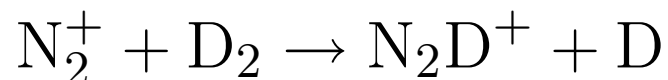
$$\begin{aligned}\Delta E_f^* - \Delta E_r^* &= [E(\text{saddlepoint}) - E^0(\text{reac})] \\ &\quad - [E(\text{saddlepoint}) - E^0(\text{prod})] \\ &= E^0(\text{prod}) - E^0(\text{reac}) = \Delta E_{\text{reac}}^0\end{aligned}$$

where;

- E^0 is the ground state energy.
- ΔE_{reac}^0 is the energy of reaction. (See Figure 30.6.)
- The threshold energy is the minimum initial relative kinetic energy required experimentally for a particular reaction to be observed.
 - It may be greater or less than the barrier height ΔE^* .

- If the threshold energy is less than the barrier height, then tunnelling is involved.
- If the threshold energy is greater than the barrier height, then more than just kinetic energy is involved in determining whether or not the reaction will occur.
- Activation energy E_a is an empirical parameter derived from the temperature dependence of the rate coefficient.
 - In many cases, the temperature dependence is approximately proportional to $e^{-E_a/k_B T}$.
 - When simple theories predict that the barrier height, the threshold energy, and the activation energy are the same, they are not.
- In many reacting systems, the reactants are not in the ground state, but may have internal energy.

- The electronic state of the reactants defines the potential energy surface, provided there are no electronic transitions during the reaction.
- The vibrational, rotational, and translational motion may be described by a trajectory on the potential energy surface. (Figure 30.9 does not include rotational motion.)
 - Interconversion of internal and translational energy complicates the analysis of reaction dynamics.
- Scattering experiments provide insight into reaction dynamics.
- Consider Figure 30.10 which shows the angular distribution measured for:



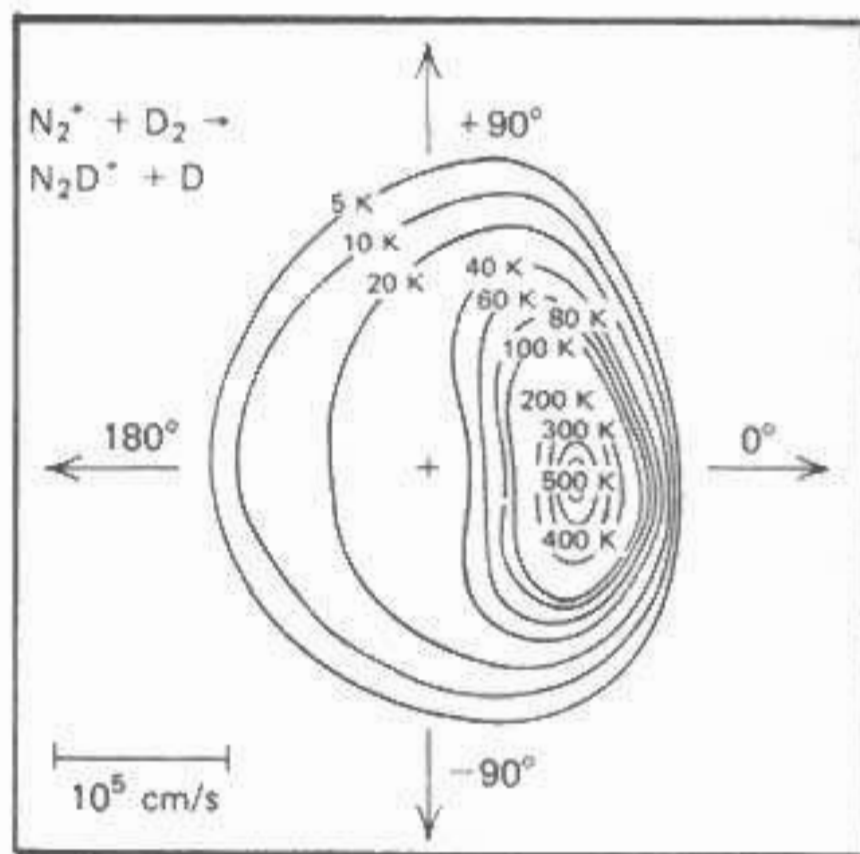


Figure 30.10 Intensity contour map for N_2D^+ formed in $N_2^+ + D_2$ collisions at 3.12 eV initial relative kinetic energy. The magnitude of the product velocity is indicated by distance from the origin (+). The asymmetry of the map (relative to the $\pm 90^\circ$ line) indicates a direct-interaction mechanism. From B. H. Mahan, *Acc. Chem. Res.* **3**, 393 (1970).

- The N_2^+ ions are prepared at a kinetic energy of 3.12 eV, while the D_2 atoms are thermally distributed.
- The beams are crossed and scattering of the N_2D^+ product is observed.
- Figure 30.10 is in center of mass coordinates.
 - The contours give relative probability of the final velocity.
 - The final relative speed is the distance from the origin.
 - The scattering angle is the polar angle.
- The angular distribution is asymmetric with the maximum probability in the forward direction and maximizing at $\phi = 0^\circ$.
 - This means that the collisions contributing to this maximum are grazing ones.

- This also means that the interaction was short lived.
- If the interaction had been long-lived, then the information about how the molecules came together would have been lost as the reactants orbited about each other.
 - Long-lived interactions are characterized by more isotropic product distributions.
- A direct-interaction mechanism is one in which the time of interaction is short relative to a rotational or vibrational period.
- A complex-formation mechanism is one in which the time of interaction is long relative to a rotational or vibrational period.
 - The long-lived aggregate is a complex.

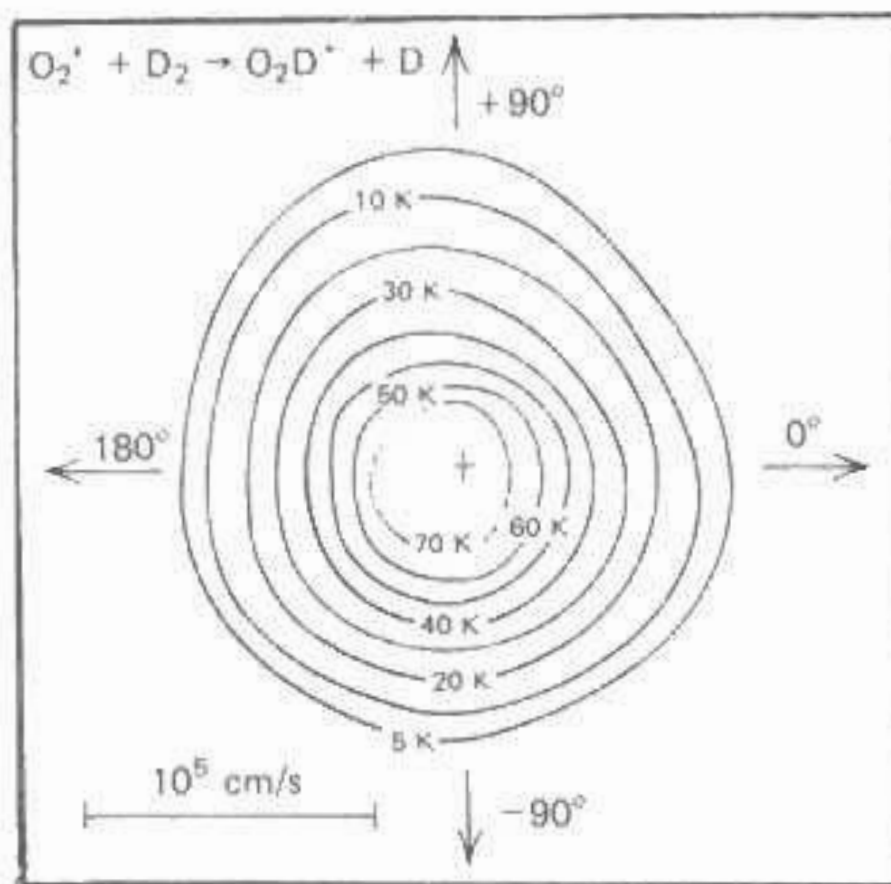
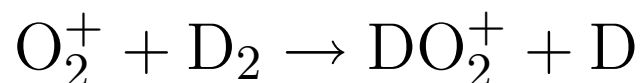


Figure 30.11 Intensity contour map for DO_2^+ formed in $\text{O}_2^+ + \text{D}_2$ collisions at 2.76 eV initial relative kinetic energy. The intensity is nearly isotropic, indicating the formation of a long-lived D_2O_2^+ complex. From B. H. Mahan, *Acc. Chem. Res.* **3**, 393 (1970).

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- An example of a reaction that occurs by a complex-formation mechanism is:



- The results of a cross beamed experiment are shown in Figure 30.11.
 - The distribution is nearly isotropic, as would be expected of a long-lived interaction.
 - This usually occurs as the result of a local minimum in the strong interaction region of the potential hypersurface.
 - The more difficult it is for the complex to leave this region, the longer lived the complex.

- Scattering measurements allow additional information about the collision to be determined, including the energy balance.
- The initial kinetic energy is known.
- The final relative kinetic energy corresponding to any point on the map may be determined.
 - In Figure 30.10, the peak of maximum intensity corresponds to kinetic energy that is less than the initial kinetic energy by about 1.3 eV.
 - But the reaction between N_2^+ and D_2 has an exothermicity by 1.0 eV.
 - Therefore there must be about 2.3 eV of internal energy in the product, but the form of internal energy cannot be determined by this type of experiment.

- Lower final kinetic energies of N_2D^+ are not possible because the internal energy would be in excess of that required for dissociation.
- In contrast, in Figure 30.11, the peak is at the origin which means that the final kinetic energy is zero and all the potential energy and the initial kinetic energy has been converted to internal energy of the products.
- When the initial kinetic energy is so high that it would exceed the dissociation energy of the product were it be converted into internal energy, the the intensity contour map would resemble Figure 30.12.
 - Figure 30.12 is also for N_2^+ and D_2 reacting to form N_2D^+ , but at an initial relative kinetic energy of 8.1 eV.
 - Note that there is a “crater” around the origin.

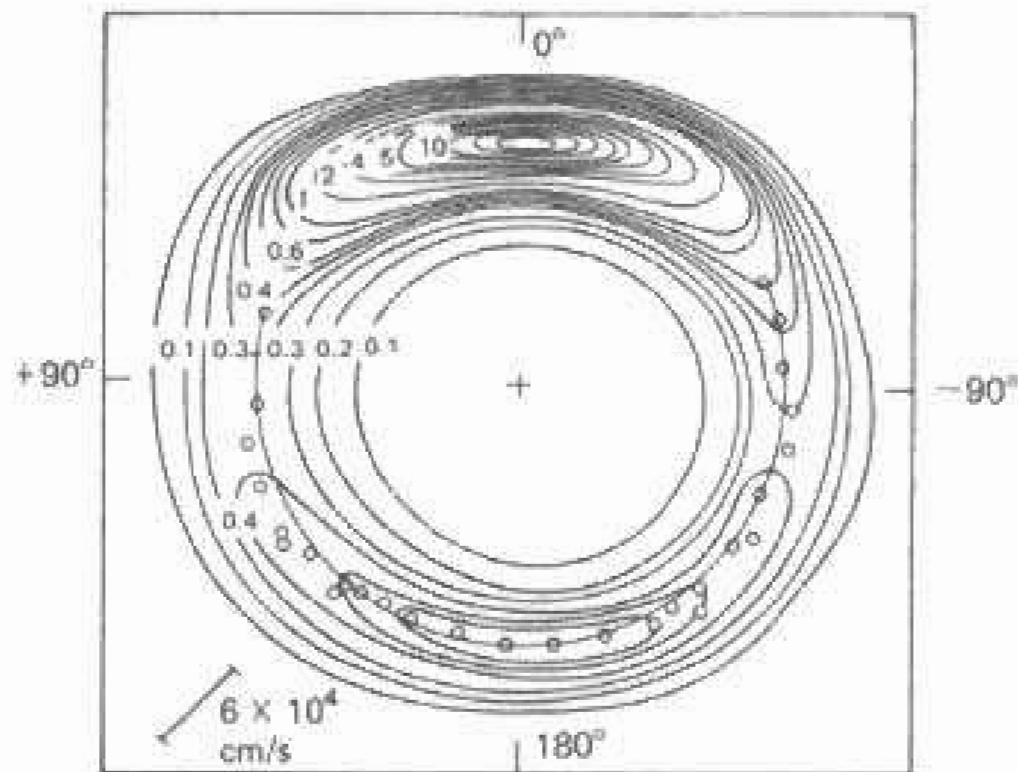


Figure 30.12 Intensity contour map for N_2D^+ formed in $\text{N}_2^+ + \text{D}_2$ collisions at 8.1 eV initial relative kinetic energy. As in Fig. 30.10, the map is asymmetric about the $\pm 90^\circ$ line; however, the high initial energy produces a “crater” about the origin. The small circles are experimental intensity maxima. From B. H. Mahan, *Acc. Chem. Res.* **1**, 271 (1968).

- More refined detection techniques are needed to determine the distribution of internal energy in products.
- Spectra taken at high speed can determine the state of the products, provided there is no collisional quenching of products.
 - This condition is met if a beam of one reactant is directed into a low density gas of the other reactant.
- If there is no electronic excitation, then the energy distribution may be analyzed with a triangle plot.
 - In a triangle plot (Figure 30.13), vibrational energy is plotted against rotational energy.
 - A diagonal line on this plot can be constructed to represent the total energy.
 - The distance of a rotational, vibrational point from this line will give the total translational energy.

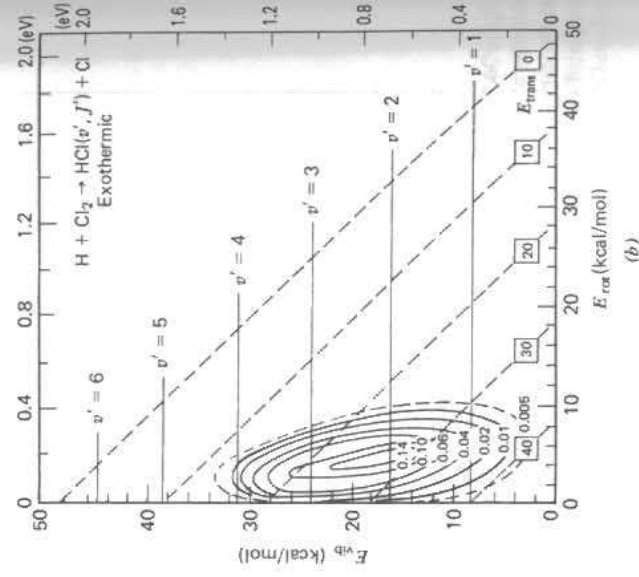
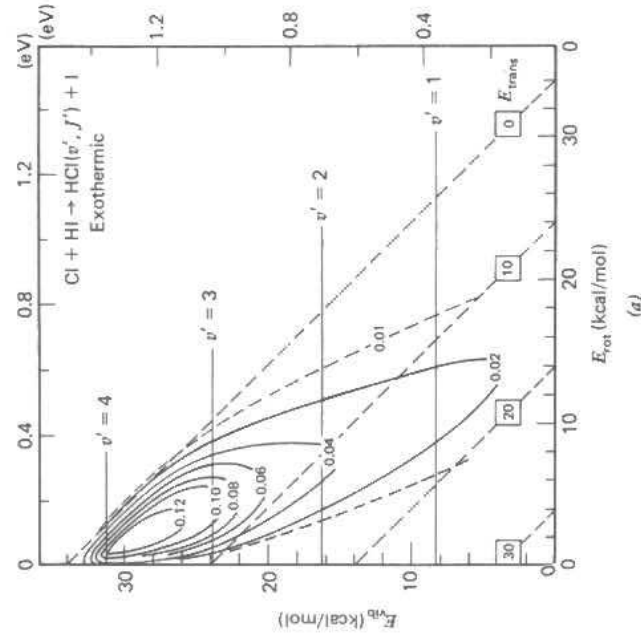
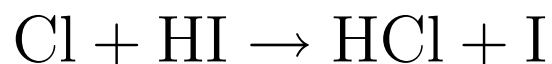


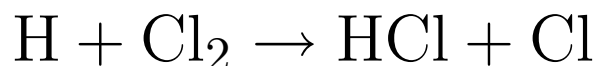
Figure 30.13 Triangular plots for the reactions (a) $\text{Cl} + \text{HI}$, (b) $\text{H} + \text{Cl}_2$. In each case the ordinate and abscissa, respectively, give the vibrational and rotational energy of the products; the broken diagonal lines give the translational energy on the same scale. The contours show the relative intensity of the various states observed. (The horizontal solid lines indicate the amounts of energy corresponding to the various product vibrational levels.) From D. H. Maylotte, J. C. Polanyi, and K. B. Woodall, *J. Chem. Phys.* **57**, 1547 (1972); K. G. Anlauf, D. S. Home, R. G. Macdonald, J. C. Polanyi, and K. B. Woodall, *ibid.*, 1561.

- Figure 30.13 (a) is for the reaction:



with a total energy of 34 kcal mol^{-1} .

- Nearly all the energy winds up as vibration with very little rotation or translation.
- Figure 30.13 (b) is for the reaction:



with a total energy of $48.4 \text{ kcal mol}^{-1}$.

- The product energy is divided nearly evenly between translation and vibration, with very little in rotation.
- Many studies have been carried out which measure product translational, vibrational, and rotational energies and angular distributions.

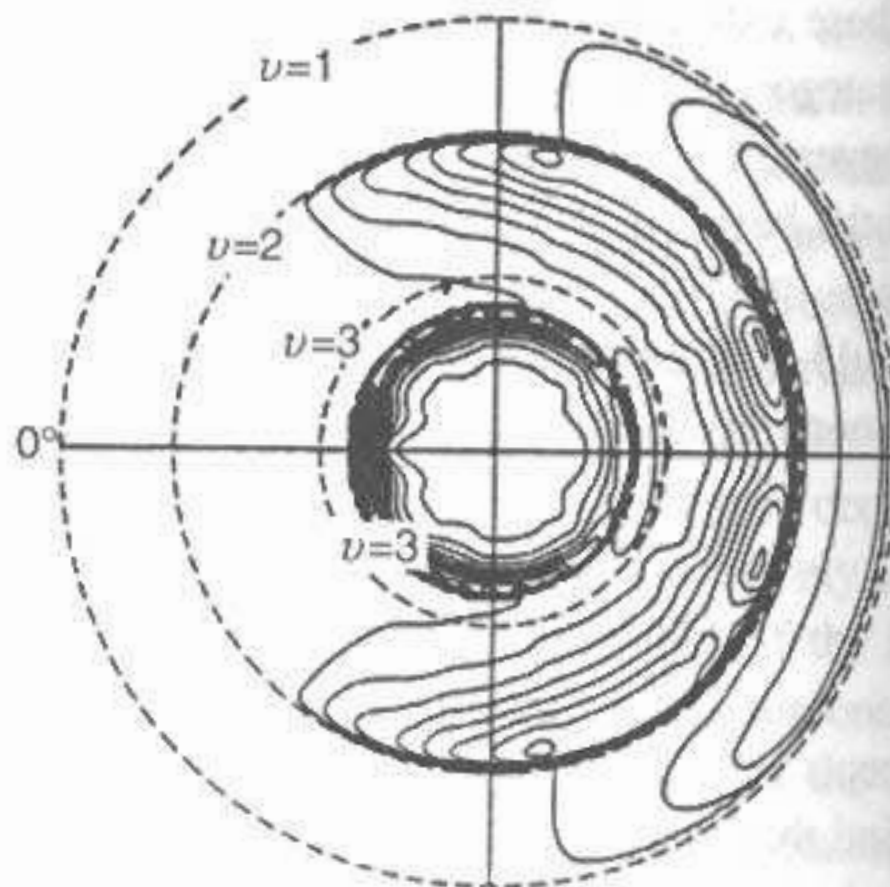
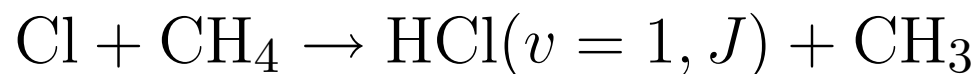


Figure 30.14 Contour map for center-of-mass velocity flux for the reactions $\text{F} + \text{H}_2 \rightarrow \text{HF}(v = 1, 2, 3) + \text{H}$; the initial relative velocity is 11.5 kJ/mole. For description, see text. From D. M. Neumark *et al.*, *J. Chem. Phys.* **82**, 3045 (1985).

- In Figure 30.14 is a contour map for center-of-mass velocity for $F + H_2 \rightarrow H + HF$ at a total energy of 11.5 kJ mol^{-1} .
 - Different distances from the scattering center indicate the velocity range associated with certain final vibrational states for HF.
 - $v = 1$ and $v = 2$ are mostly scattered backwards, while $v = 3$ is scattered forwards.
 - There is also evidence of resonance effects in the case of $v = 3$ and also evidence of increased interaction time.
- Reactivity can be influenced by the internal energy of reactants.
- Consider the reaction



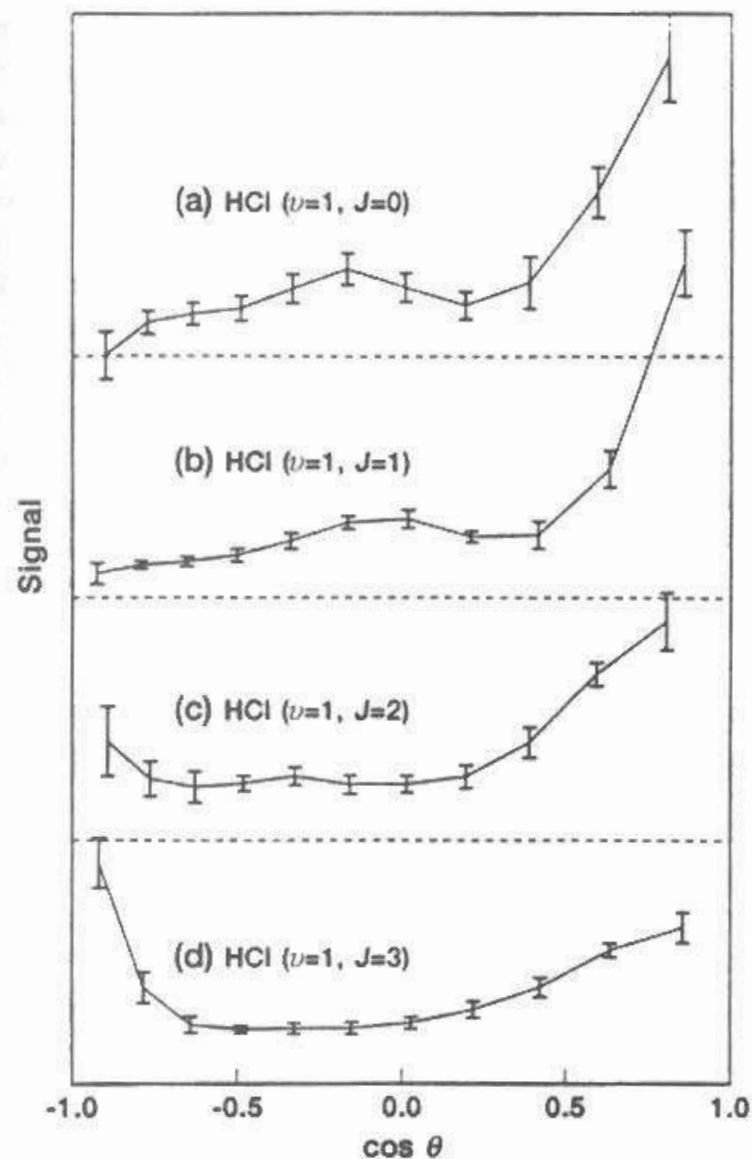


Figure 30.15 Differential scattering cross-section for the reaction $\text{Cl}(^2\text{P}_{3/2}) + \text{CH}_4(\nu_3 = 1) \rightarrow \text{HCl}(\nu = 1, J) + \text{CH}_3$ vs. the scattering angle θ , for $J = 0, 1, 2, 3$. The initial relative kinetic energy is 0.16 eV. From W. R. Simpson, *et al.*, *J. Phys Chem.* **100**, 7938 (1996).

F
a
H
u
J

a
fi
fi
n
ii
n
c

c
e
t

- The CH_4 molecule was excited in the C-H stretching mode.
- Figure 30.15 shows angular distribution for HCl products in various states.
- The angular distribution becomes more backward as the final rotational state increases.
- Figure 30.16 shows the distribution integrated over all angles for HCl in the $v = 1$ and the $v = 0$ final state plotted against rotation state.
 - When $v = 0$ only a few J transitions are important, while for $v = 1$, a wider range of J transitions are observed,
- The effect of excitation in the reactants depends on which mode is being excited and whether it is available to assist in the reaction.

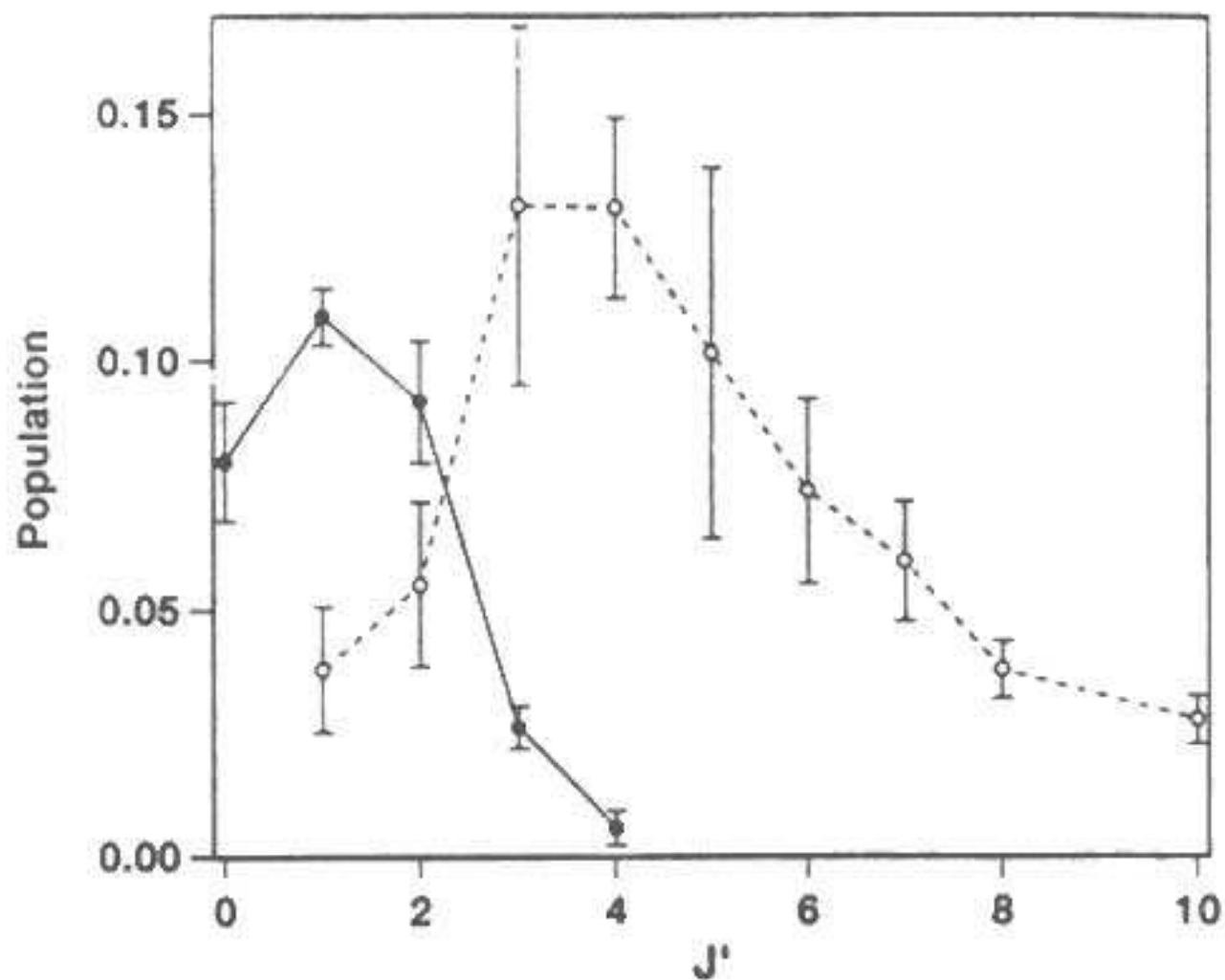
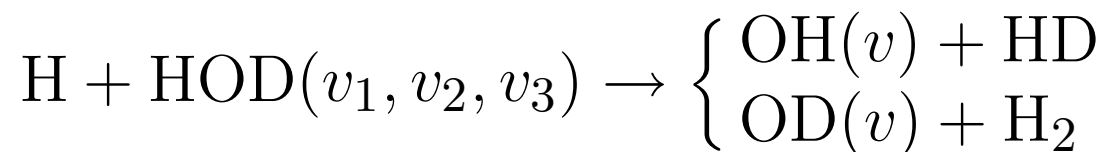


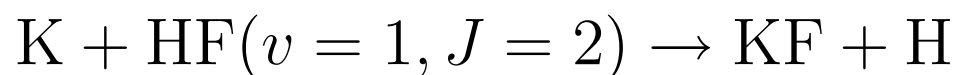
Figure 30.16 Integral product state distributions (integrated over all scattering angles) for the same reactants as in Fig. 30.15, for HCl ($v=0$, open circles; $v=1$, filled circles) and for various values of J' , the rotational state of HCl. From W. R. Simpson, *et al.*, *J. Phys Chem.* **100**, 7938 (1996).

- Consider the reaction:



- Vibrational excitation of either the OH or the OD bond leads to cleavage of that bond.
- Vibrational energy was about 100 times more effective than the same amount of energy as translation.
- Bond specific chemistry is not always possible.
- It is only feasible when the excitation energies for different bonds is sufficiently different.
- If the excitation energies for bonds are similar, then energy flows readily from one bond to the other.

- Steric effects are important in many chemical reactions.
- It is possible to study this if the reactants can be aligned.
- HF may be aligned with polarized light.
 - The state specific integral cross section for:



(note typo in book) has been studied for two approach geometries, perpendicular or parallel, at a total energy of 0.46 eV.

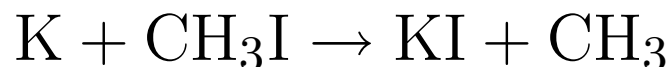
- Alignment with polarized light does not perfect align the molecules, but rather increases the probability of HF molecule being either near perpendicular or parallel.

- The reactive cross sections are different with the relative difference:

$$\frac{\sigma_{||} - \sigma_{\perp}}{\frac{1}{2}(\sigma_{||} + \sigma_{\perp})}$$

of 0.17.

- This indicates that a collinear conformation favours the formation of products.
- Molecules in an S electronic state or with a permanent dipole may be aligned with an electric field.
 - In this situation, rotations of symmetric tops become librations.
- This has been applied to

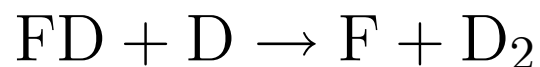


- The direction in which the KI product is scattered depends on whether it attacks the I end of the molecule (backward scattering) or the CH₃ side (forward scattering).
- In many cases, the products of chemical reactions are formed in excited states.
 - For $F + D_2 \rightarrow FD + D$, the FD product is most likely to be found in the $v = 3$ and its distribution over v states is highly non-equilibrated.
 - If the pressure is low enough, the product molecules will equilibrate by the emission of radiation (chemiluminescence).
- Lasers are important in studies of molecular dynamics.
 - **Laser Amplification by Stimulated Emission of Radiation.**

- Lasers produce an intense beam of coherent and monochromatic photons.
- This radiation is produced by transitions to a state of lower energy.
- Consider two states separated by $h\nu$.
- If there is sufficient population in the upper state, then an a photon of energy $h\nu$ can stimulate the emission of another photon on energy $h\nu$.
- If suitable mirrors are used, those photons may be reflected back, leading to stimulated emission of more photons.
- But in order for a laser to function, the population inversion must exist.
 - This population inversion may be created by physical methods such as irradiation or electrical discharge.

- The population inversion may also be created by a chemical reaction that produces a non-equilibrium distribution of products, such as the $F + D_2$.
- It has been possible to produce chemical lasers with most diatomic and triatomic gases.
- Lasers can be used to study chemical reactions with laser induced fluorescence (LIF).
 - A tunable laser can be used on the reaction products to excite them to an electronically excited state.
 - The resulting fluorescence can be measured.
 - If the spectrum is known then the fluorescence may be correlated with the internal energy state of the product and relative populations of final states may be determined.

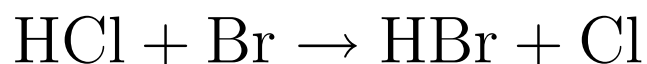
- Consider the reverse of the $F + D_2$:



with the same total energy as the forward reaction.

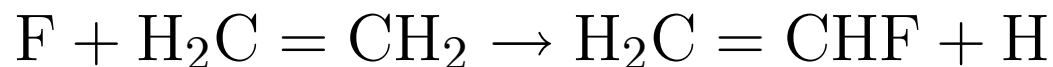
- How should this energy be distributed to maximize the probability of the reverse reaction occurring?
 - It was observed that the forward reaction produced products preferentially in the $v = 3$ state.
 - Therefore placing vibrational energy at $v = 3$ in FD should maximize the probability of the reverse reaction.
 - This effect is vibrational enhancement.
 - This is in accordance with microscopic reversibility.
- Vibrational enhancement can be very pronounced.

- Consider the reaction:



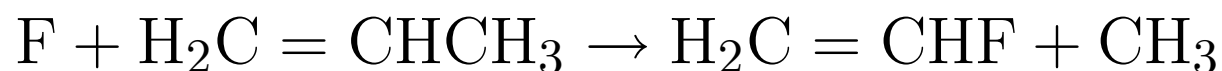
- The rate coefficient in units of $\text{L mol}^{-1}, \text{s}^{-1}$ for $v = 0$, $v = 1$, and $v = 2$ are respectively 1×10^{-2} , 2×10^4 , and 1×10^9 .
- This vibrational enhancement effect may be considered in terms of the potential energy surface.
 - A large vibrational amplitude can make it easier for the trajectory to “turn the corner” into the product channel if the molecule has the right vibrational phase.
 - In contrast, translational energy makes the system rebound in the reactant channel.

- For the reverse trajectory ($\text{H}_2 + \text{F}$), translational energy leads to the formation of vibrationally excited HF.
 - Products are formed in a non-equilibrium distribution from a direct interaction.
- What may be inferred about the distribution of products for a complex interaction?
- Many theories about complex interaction assume an equilibrium distribution of energies in the complex, but many experimental studies demonstrate that this may not always be so.
- Consider:



- The angular distribution of products is consistent with a long-lived complex.

- The energy distribution of the results is consistent with only 5 of the 12 vibrational modes of the product being activated.
- The reason for this is that there are only certain geometries, i.e. angles, which are consistent with the reaction occurring because both reactants and products are planar.
- For the reaction:



there is a higher density of states and a greater probability of a statistical distribution of energy in the products.

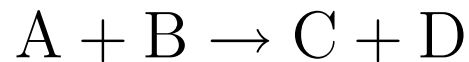
- Nonequilibrium distribution of products may also result from photo-fragmentation reactions.

- Since only photons of a certain frequency are absorbed, the activated state of the molecule that results has a nonstatistical energy distribution.
- Whether or not this shows up in the energy distribution of products depends on how readily energy may be distributed in activated reactant molecule.
- Recombination and dissociation may be considered as reverse reactions for each other.
- In order to cause dissociation, the energy required to break the bond must come from somewhere, either from a collision or from absorption of a photon.
 - All dissociation reactions involve a three body collision (if a photon can be counted as a particle) at some point.
 - Therefore recombination must also involve a third body to remove enough energy to stabilize the bond.

- But the probability of three molecules colliding simultaneously are low.
- It is more probable that two molecules form a complex and the third molecule collides before this complex falls apart.
- It would be sufficient for the third molecule to have a glancing collision with the complex, leaving the nascent recombined product in a highly excited state.
- The excited product could then lose energy as a result of subsequent collisions.
- It would also be possible for the subsequent collisions to excite the molecule until it decomposes.
- Both dissociation and recombination may be regarded as taking place by ladder-climbing models.

Hard-Sphere Collision Theory

- Consider the reaction:



where A and B are hard-sphere reactants.

- The reaction between A and B is instantaneous with new hard-spheres C and D being produced immediately.
- The diameters of A and B are d_A and d_B .
 - A collision occurs if the impact parameter is less than

$$d = \frac{1}{2}(d_A + d_B)$$

- The scattering angle will be:

$$b = d \cos \frac{\chi}{2}$$

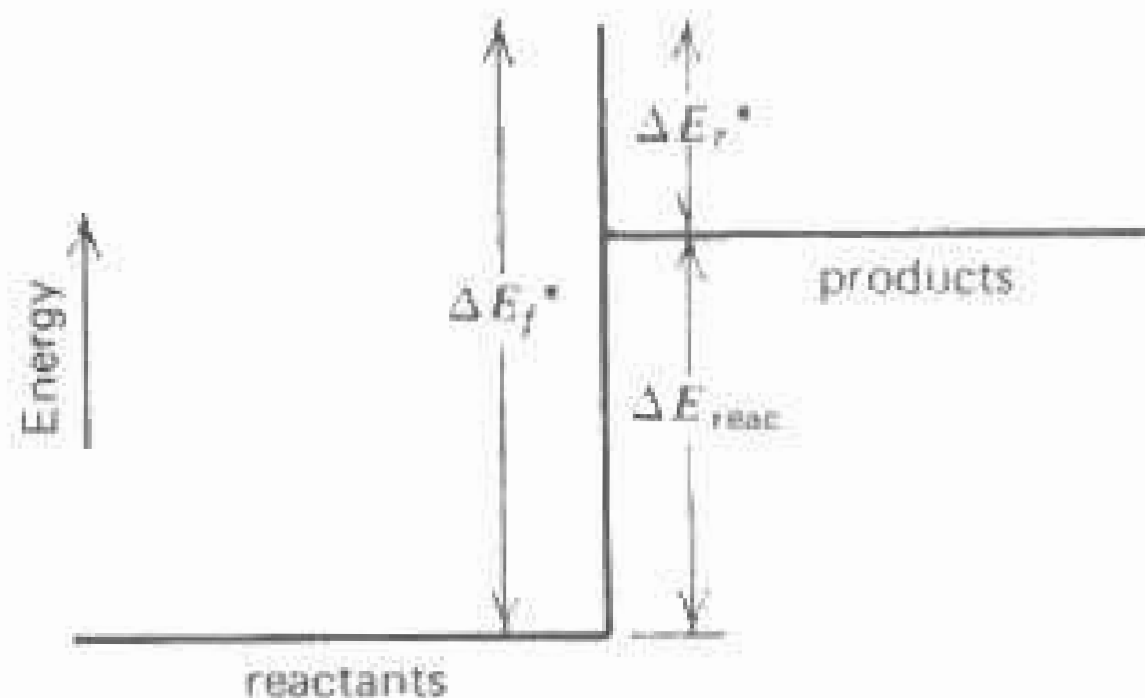


Figure 30.17 Reaction coordinate for the hard-sphere model; the barrier is of zero thickness. Here ΔE_{reac} is the energy change in the (forward) reaction, whereas ΔE_f^* and ΔE_r^* are the barrier heights for the forward and reverse reactions, respectively.

- The potential energy in the collision is:

$$V(d_{AB}) = E \left(1 - \frac{b^2}{d^2} \right)$$

- Figure 30.17 shows the reaction coordinate on the simplified potential.
 - The potential is constant before and after impact at the ground state value for reactants and products respectively.
 - At the point of impact is an impenetrable barrier of finite height and zero width.
 - It is assumed that reaction is possible only if the potential energy at the point of impact exceeds ΔE_f^* , i.e. $V(d) \geq \Delta E_f^*$.

- It is further assumed that all collisions with $V(d) \geq \Delta E_f^*$ have a constant probability of reaction.
 - But collisions with sufficient energy do not always lead to reaction.
 - A simple assumption would be that the reaction probability for $V(d) \geq \Delta E_f^*$ is a constant.
 - This may not be true, since reaction probability may increase with energy above threshold, but is sufficient to make a rough estimate of the cross section.
- Let b^* be the maximum impact parameter that can lead to dissociation.
 - b^* is the value of b at which $V(d) = \Delta E_f^*$.

$$b^* = d \left(1 - \frac{\Delta E_f^*}{E} \right)$$

- All impact parameters b such that $b^* < b \leq d$ lead only to elastic scattering.
- All impact parameters $b \leq b^*$ lead to reaction with probability $P(b, E)$.
 - It is assumed that $P(b, E) = p$.
- The cross section for elastic scattering is the hard sphere cross section $\sigma(v, \chi) = d^2/4$.
- The reactive cross section is:

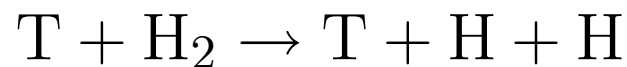
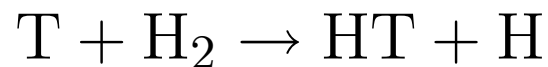
$$\begin{aligned}\sigma_R(v, \chi) &= \frac{pd^2}{4} \quad (b \leq b^*) \\ &= 0 \quad (b > b^*)\end{aligned}$$

- From this the total reactive cross section may be determined.

$$\begin{aligned}
 \sigma_R(E) &= 2\pi \int_0^\pi \sigma_R(v, \chi) \sin \chi \, d\chi \\
 &= 2\pi \int_0^{b^*} \frac{\sigma_R(v, \chi)}{\sigma(v, \chi)} b \, db \\
 &= 2\pi \int_0^{b^*} p \, b \, db \\
 &= 2\pi \left(\frac{b^{*2}}{2} \right) \\
 &= 2\pi \, p \, d^2 \left(1 - \frac{\Delta E_f^*}{E} \right)
 \end{aligned}$$

- $\sigma_R(E)$ needs to be known in order to determine the rate coefficient.

- The dependence of cross section on energy is illustrated in Figure 30.18 for the reaction of T with H₂.
- This reaction can lead to two outcomes:



- The energy dependence of the cross section for the two reactions is different.
 - For exchange, the cross section peaks then declines with increasing energy.
 - For dissociation the cross section increases slowly, but continues to increase with energy.
 - The dependence of the cross section for dissociation on energy would be well-described by the hard-sphere model.

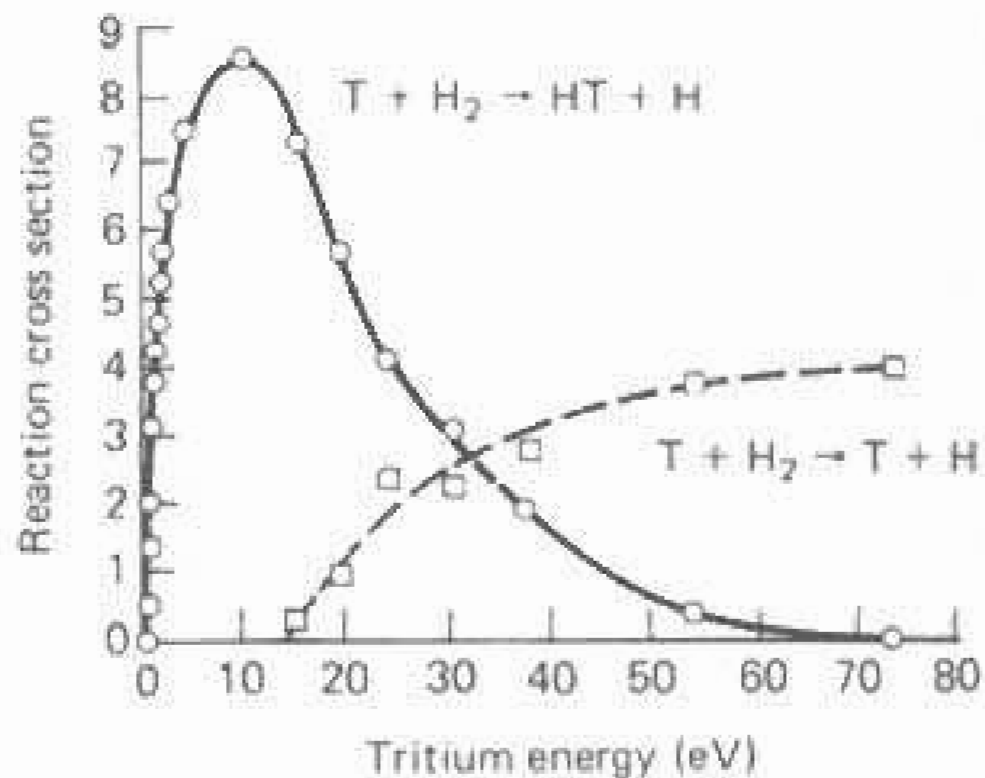
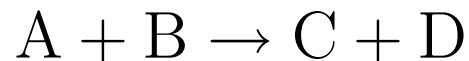


Figure 30.18 Total reaction cross sections for the T-H₂ reaction. (The cross sections are given in “atomic units,” that is, in terms of a_0^2 , where a_0 is the Bohr radius, 0.529 Å.) From J. Dubrin, *Ann. Rev. Phys. Chem.* **24**, 97 (1973).

Hard-Sphere Collision Theory

- The hard-sphere model has limitations, but is useful in the development of an expression for a rate coefficient k in terms of microscopic quantities in the case of a dilute gas where there are only bimolecular collisions.
- The fact that not all collisions lead to reaction must be taken into account.
- This model will allow for exploration of temperature dependence of reaction rate.
- Consider the reaction:



- Assume that each of these species has only one internal quantum state.
- Therefore only translational energy is present.

- The frequency of elastic collisions has already been considered.
- This will be extended to reactive collisions.
- n_A is the number density of species A.
- The probability density of A velocities is $\mathcal{F}(v_A)$.
- $\mathcal{F}(v_A)$ may be approximated by the Maxwell-Boltzmann distribution since the loss of A during the course of the reactions may be assumed to not perturb the velocity distribution.
- This assumption is equivalent of assuming that the chemical reaction is slow relative to the relaxation rate at constant temperature.
- In order to maintain constant temperature, heat must be added or removed depending on whether the reaction is endothermic or exothermic.

- Consider the collision rate in terms of a cross beam experiment.
 - Beams of A and B collide within volume τ .
 - The flux of product C can be measured as a function of scattering angles α and β (which can be converted to χ and ϕ) and \mathbf{v}_A and \mathbf{v}_B .
 - From this σ_R , the reactive cross section, may be determined as a function of relative speed and of the scattering angles:

$$dN_C(\alpha, \beta, \mathbf{v}_A, \mathbf{v}_B)$$

$$= \sigma_R(v, \alpha, \beta) v n_A n_B \mathcal{F}_A(\mathbf{v}_A) \mathcal{F}_B(\mathbf{v}_B) d\mathbf{v}_A d\mathbf{v}_B \tau d\Omega'$$

where $dN_C(\alpha, \beta, \mathbf{v}_A, \mathbf{v}_B)$ is the number of C molecules arriving per unit time at detector of solid angle $d\Omega$.

- A macroscopic rate experiment measures the total rate of appearance of reactants or disappearance of products.
 - Therefore it is necessary to integrate over all angles and velocities:

$$dN_C = \int_{\alpha, \beta} \int_{\mathbf{v}_A} \int_{\mathbf{v}_B} dN_C(\alpha, \beta, \mathbf{v}_A, \mathbf{v}_B)$$

to get dN_C with dimensions of molecules per unit time.

- But rates are usually measured in terms of change in concentration per unit time:

$$\left(\frac{dn_C}{dt} \right)_f = n_A n_B \int_{\alpha, \beta} \int_{\mathbf{v}_A} \int_{\mathbf{v}_B} \sigma_R(v, \alpha, \beta) v$$

$$\mathcal{F}_A(\mathbf{v}_A) \mathcal{F}_B(\mathbf{v}_B) d\mathbf{v}_A d\mathbf{v}_B d\Omega'$$

- The total reactive cross section may be defined as:

$$\sigma_R(v) = \int_{\alpha, \beta} \sigma_R(v, \alpha, \beta) d\Omega'$$

- This simplifies the theoretical rate equation to:

$$\left(\frac{dn_C}{dt} \right)_f = n_A n_B \int_{\mathbf{v}_A} \int_{\mathbf{v}_B} \sigma_R(v) v \mathcal{F}_A(\mathbf{v}_A) \mathcal{F}_B(\mathbf{v}_B) d\mathbf{v}_A d\mathbf{v}_B$$

- This is of the form:

$$\left(\frac{dn_C}{dt} \right)_f = \kappa_f n_A n_B$$

where : $\kappa_f = \int_{\mathbf{v}_A} \int_{\mathbf{v}_B} \sigma_R(v) v \mathcal{F}_A(\mathbf{v}_A) \mathcal{F}_B(\mathbf{v}_B) d\mathbf{v}_A d\mathbf{v}_B$

- Note that this is of the form of a rate coefficient for a bimolecular reaction and permits the calculation of a rate coefficient that should be able to be compared with an experimental rate coefficient for the same elementary reaction.
 - This has been derived for the case of dilute gases.
 - Rate expressions for higher density and in condensed phases experimentally follow this form.
 - The macroscopically measure rate coefficient may be connected with the microscopic cross section, which is a statistical average of a molecular quantity.
 - As in the case of transport coefficients, a model (such as hard spheres) must be adopted for the molecular quantity.
 - The model of reactive hard spheres has been used.

- The reactive hard spheres model assumes that there is a reaction probability p at values of E above ΔE_f^* and a reaction probability of zero below this.
 - Thus $\sigma_R(v)$ may be expressed in terms of $\sigma_R(E)$ where $E = \frac{1}{2}mv^2$.
- $\mathcal{F}_A(\mathbf{v}_A) \mathcal{F}_B(\mathbf{v}_B)$ may be replaced by the Maxwell-Boltzmann equilibrium velocity distribution if both beams can be assumed to have the same temperature.
 - This does not imply that the system is at chemical equilibrium.
 - The Maxwell-Boltzmann distribution describes relative numbers of molecules of a given chemical species with different velocities.
 - Chemical equilibrium deals with relative total concentrations of different chemical species.

- It is assumed the chemical reaction does not perturb the velocity distribution, that is the the rate of reaction is small compared to the rate of relaxation of the velocity distribution.
 - There are exceptions to this limiting assumption.
- If this is generalized to the vibrational and rotational distributions, then vibrational and rotational relaxation must be considered.
- If the equilibrium velocity distribution can be assumed then:

$$\kappa_f = \pi p d^2 \left(\frac{m_A}{2\pi k_B T} \right)^{3/2} \left(\frac{m_B}{2\pi k_B T} \right)^{3/2} \times$$

$$\int_{\mathbf{v}_A} \int_{\mathbf{v}_B} v \left(1 - \frac{\Delta E_f^*}{E} \right) e^{-(m_A v_A^2 + m_B v_B^2)/2k_B T} d\mathbf{v}_A d\mathbf{v}_B$$

- In order to consider the evaluation of this for $E > \Delta E_f^*$, the integral must be transformed into center of mass velocity:

$$\begin{aligned} \kappa_f &= \pi p d^2 \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \\ &\times \int_{\mathbf{V}} \left(\frac{m_A + m_B}{2\pi k_B T} \right)^{3/2} e^{-(m_A + m_B)V^2/2k_B T} d\mathbf{V} \\ &\times \int_{\mathbf{v}} v \left(1 - \frac{\Delta E_f^*}{E} \right) e^{-(\mu v^2)/2k_B T} d\mathbf{v} \end{aligned}$$

- Note that the integral over \mathbf{V} is unity since the velocity distribution is normalized.
- The integration over \mathbf{v} will involve transformation to spherical coordinates.

$$\begin{aligned}
& \int_{\mathbf{v}} v \left(1 - \frac{\Delta E_f^*}{E} \right) e^{-(\mu v^2)/2k_B T} d\mathbf{v} \\
&= \int_{\theta=0}^{\pi} \int_{\phi=0}^{2\pi} \int_{v=(2\Delta E_f^*/\mu_{AB})^{1/2}}^{\infty} v^3 \left(1 - \frac{\Delta E_f^*}{E} \right) e^{-(\mu v^2)/2k_B T} \\
&\quad \times \sin \theta \, d\theta \, d\phi \, dv \\
&= 4\pi \int_{v=(2\Delta E_f^*/\mu_{AB})^{1/2}}^{\infty} v^3 \left(1 - \frac{\Delta E_f^*}{E} \right) e^{-(\mu v^2)/2k_B T} dv
\end{aligned}$$

- Note that the lower limit corresponds to $E = \Delta E_f^*$ since there can be no reaction below the threshold value.
- This can be transformed to an integral over energy with:

$$E = \frac{1}{2}\mu_{AB}v^2, \quad dE = \mu_{AB}v dv$$

- Thus:

$$\kappa_f = \pi p d^2 \left(\frac{\mu_{AB}}{2\pi k_B T} \right)^{3/2} 4\pi \left(\frac{2}{\mu_{AB}^2} \right) \\ \times \int_{\Delta E_f^*}^{\infty} (E - \Delta E_f^*) e^{-E/k_B T} dE$$

- Upon integration, this yields:

$$\kappa_f = \pi p d^2 \left(\frac{8k_B T}{\pi \mu_{AB}} \right)^{1/2} e^{-\Delta E_f^*/k_B T}$$

- Recall that $\pi d^2 (8k_B T / \pi \mu_{AB})^{1/2}$ is the number of collisions per unit time per unit volume for unit concentrations of each of A and B.
- The fraction of all collisions with energy greater than E_f^* is $\exp(-\Delta E_f^*/k_B T)$

- p is the probability that a collision with sufficient energy will lead to reaction.
 - p is sometimes known as the steric factor.
 - p has assumed to be constant, but this restriction can be lifted if $p(E)$ is included in the integral.
- Thus the rate of reaction will be $\kappa_f n_A n_B$
- This derivation indicates a temperature dependence of κ due to the $T^{1/2}$ and $\exp(-\Delta E_f^*/k_B T)$
 - The latter term dominates when $\Delta E_f^* \gg k_B T$
 - The $T^{1/2}$ term in the pre-exponential factor plays a minor role.
 - As illustrated in Figure 30.19, most reactive collisions have energy only slightly above ΔE_f^*

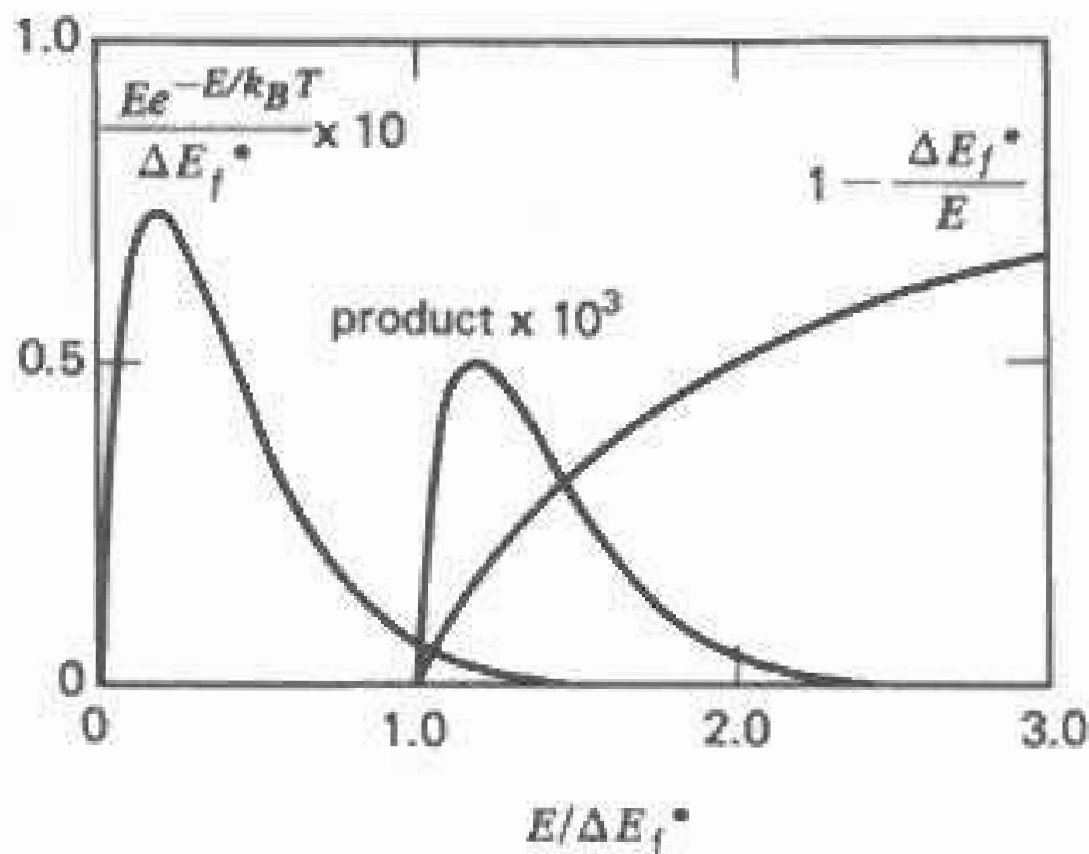


Figure 30.19 Factors contributing to the hard-sphere rate constant, Eq. 30.40, as functions of energy. We plot the reactive-cross-section factor $1 - (\Delta E_f^*/E)$, the relative-speed frequency factor $E \exp(-\Delta E_f^*/k_B T)$, and their product, all for $\Delta E_f^*/k_B T = 5$. In general, $\exp(-\Delta E_f^*/k_B T)$ has its peak at $E = k_B T$, and the product has its peak at $E/\Delta E_f^* = 1 + (k_B T/\Delta E_f^*)$.

- This model works well for reactions with no threshold energy.
- Consider the recombination reaction:



- The threshold energy to this reaction is 0.
- The steric factor is estimated to be $1/4$ since only one of the four collisions will lead to a bonded product due to electronic symmetry properties.
- This model predicts the rate coefficient to within a factor of 2.
- In the case of ion-molecule reactions the hard-sphere cross section may be replaced with that determined by a model that takes into account induced dipoles, the agreement is improved.

- The exponential temperature dependence is the strongest part of the temperature dependence and is consistent with the empirical observations that gave rise to the Arrhenius equation:

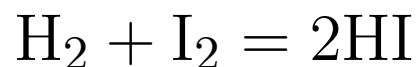
$$k = Ae^{-E_a/RT}$$

where:

- A is the frequency factor
- E_a is the activation energy.
 - Note that E_a is purely an empirical quantity and is not rigorously identified with the barrier height or the threshold energy.
- A modified form of this equation is:

$$k = AT^n e^{-E_a/RT}$$

- Both n (typically small) and E_A are experimentally determined.
- When $E_A \gg RT$, the exponential factor dominates.
- n is difficult to determine unless measurements can be made over a wide temperature range.
- Most reactions are studied over a temperature range sufficient only to determine E_a .
- Consider the reaction:



- The rate expression for the forward reaction is:

$$\frac{d[\text{I}_2]}{dt} = k_f [\text{H}_2][\text{I}_2]$$

- If the Arrhenius expression holds then a plot of $\ln k_f$ versus T^{-1} will be linear with slope E_A/R (Figure 30.20(a)).
- If the modified form of the equation holds, then a plot of $\ln(k_f/T^n)$ versus T^{-1} will be linear with slope E_A/R (Figure 30.20(b) for $n = 1/2$).
- Neither fit is significantly better than the other.
- Both fits give similar values of E_A/R .
- This is illustrative of the difficulties in determining n within the limitations of the experimental data.
- The pre-exponential factor is critical in determining the absolute value of a rate coefficient.
- The value calculated from theoretical approaches is often much in excess of the experimental values.

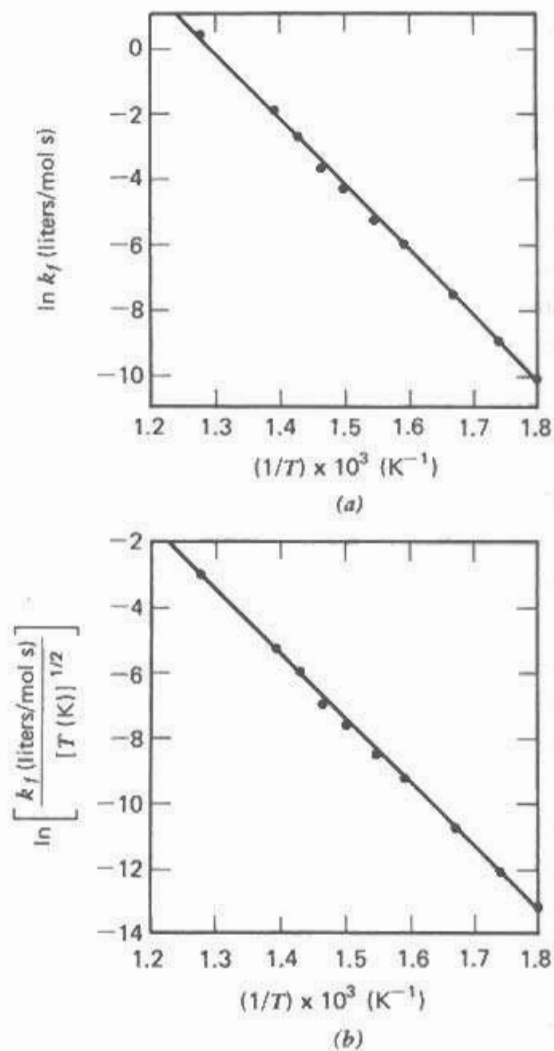


Figure 30.20 Temperature dependence of the rate constant for the reaction $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$. (a) Plot of $\ln k_f$ versus T^{-1} , linear if Eq. 30.42 is correct. (b) Plot of $\ln(k_f/T^{1/2})$ versus T^{-1} , linear if Eq. 30.43 is correct with $n = \frac{1}{2}$. In each case the slope as plotted should be equal to $-E_a/R$; the lines drawn in (a) and (b) give E_a values of 165 kJ/mol and 163 kJ/mol, respectively.

- The probability factor p must be considered carefully.
- If it is adjusted to match this model to experimental values, p can be of the order of 10^{-2} to 10^{-3} .
- This indicates the need for a more accurate theory and model.

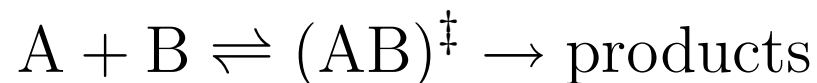
Activated-Complex Theory

- A satisfactory theory should be able to predict a rate coefficient from the properties of the molecules involved.
- Kinetic theory does reasonably well, but there are issues around determination of the reactive cross section $\sigma_R(v)$.
 - This is non-trivial for any potential other than the hard-sphere potential.
 - A chemically accurate potential must be known.

- The calculation of the cross section may be carried out using either classical or quantum mechanics.
- The classical approach involves running large numbers of classical trajectories sampled appropriately from the possible starting conditions.
 - This can be computationally intensive.
- The quantum mechanical approach allows direct determination of the reactive cross section.
 - All possible transitions must be considered.
 - Since the number of transitions possible increases rapidly with total energy, a quantum calculation can become intractable for all but a few low energies.
- In order to be useful, a model needs to be tractable, but also more realistic than hard-sphere.

- Activated complex theory is also known as transition state theory and as absolute reaction rate theory.
- It was developed in the 1930's by Henry Eyring and collaborators.
- It provides a conceptual framework.
- It may also be used to calculate rate coefficients.
- In a simplified form, the theory considers a chemical reaction occurring by means of an intermediate state or activated complex (also known as a transition state).
 - It assumes that an equilibrium is established between the reactants and the activated complex.
 - Methods of statistical mechanics may be used to describe this equilibrium.
 - The activated complex then either returns to reactants or goes on to products.

- The simplest form of the theory assumes a one-dimensional motion along a reaction coordinate.
- The activated complex is in the region around the top of the energy barrier.
- ‡ as a superscript is used to denote the activated complex.
 - The energy difference between reactants and the activated complex is ΔE^\ddagger .
 - A bimolecular reaction may be written as:



- The fundamental assumption is that an equilibrium is established between the reactants and the activated complex.

- All degrees of freedom, except the reaction coordinate, within the complex are equilibrated.
- An equilibrium coefficient may be defined:

$$K_V^\ddagger = \frac{[(AB)^\ddagger]}{[A][B]}$$

- Since the activated complex is not a stable species, K_V^\ddagger is a quasiequilibrium coefficient.
- The concentration of the activated complex is:

$$[(AB)^\ddagger] = K_V^\ddagger [A][B]$$

- This concentration is negligible relative to reactants or products.

- If the rate of the forward and reverse reactions can be estimated, then the quasiequilibrium coefficient may be estimated.
- The forward rate must be related to the rate at which complexes break up to form products.
- This may be written as:

$$\frac{[(AB)^{\ddagger}]}{\tau_f}$$

where τ_f is the average time required for a complex to go to products.

- The reverse rate is the rate at which the complex returns to reactants.
- Both are occurring simultaneously.

- It is assumed that whether the activated complex goes to products or back to reactants is an uncorrelated random event.
 - This means that they can be considered separately.
- The transmission coefficient κ may be defined as the fraction of activated complexes that go on to form products.
- The value of κ depends on the details of the potential energy surface.
 - Trajectory calculations have been used to estimate κ .
 - Some reactions have κ slightly less than unity.
 - Some treatments of activated complex theory use κ as an adjustable parameter that is used to match theory and experiment.

- Assume that κ is 1.
- To determine the rate of the reaction from activated complex to product, the time for the breakup of the activated complex to products must be considered.
- The formation of products involves the breaking of a bond.
 - This implies vibrational excitation of a bond near the dissociation limit.
 - It may be argued that the bond will break the first time it stretches.
 - This means that the vibrational period will give an idea of the timescale for the formation of products.
 - The breakup rate is approximately $\nu[(AB)^\ddagger]$ where ν is the vibrational frequency.

- Thus:

$$-\left(\frac{d[A]}{dt}\right)_f = \nu[(AB)^\ddagger] = \frac{k_B T}{h} K_V^\ddagger [A][B]$$

- The unbound vibrational degree of freedom that leads to dissociation of the transition state is separated from the remaining degrees of freedom.
- This gives:

$$K_V^\ddagger = \frac{k_B T}{h\nu} (K_V^\ddagger)'$$

- Therefore the rate of break up of the transition state is:

$$-\left(\frac{d[A]}{dt}\right)_f = \frac{k_B T}{h} (K_V^\ddagger)' [A][B]$$

- The forward rate coefficient is:

$$k_f = \frac{k_B T}{h} (K_V^\ddagger)'$$

- This is further modified by allowing for the fact that not all complexes break up in this way and using the transmission coefficient κ .

$$k_f = \kappa \frac{k_B T}{h} (K_V^\ddagger)'$$

- $(K_V^\ddagger)'$ is determined from the partition function.
 - For a perfect gas at standard pressure p :

$$K_V = \left(\frac{RT}{p} \right)^{-\Delta\nu} K(T)$$

- In this case, $\Delta\nu$ is the difference in stoichiometric coefficients.
- $K(T)$ is the equilibrium coefficient in terms of fugacity:

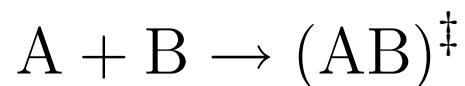
$$K(T) = \prod_i \left(\frac{f_i}{p} \right) = \lim_{p_0 \rightarrow 0} \prod_i \left(\frac{p_i}{\rho} \right)$$

- From statistical mechanics it may be shown that:

$$K(T) = \prod_i \left(q_{1i} \frac{k_B T}{p} \right)^{\nu_i} e^{-\Delta E_0^0 / RT}$$

where q_{1i} is the single molecule partition function per unit volume per unit time and ΔE_0^0 is the difference between zero point energies between reactants and products.

- This may be applied to:



where $\Delta v = 1$ to yield:

$$(K_V^{\ddagger})' = N_A \frac{q_1[(AB)^{\ddagger}]}{q_1(A)q_1(B)} e^{-(\Delta E_0^0)^{\ddagger}/RT}$$

where N_A is Avogadro's number.

- The next step is to evaluate the partition functions.
 - Standard methods may be used to evaluate the partition functions for the reactants.
 - For the activated complex, this is more difficult.
 - q_1 may be factored into translational, rotational, and vibrational components.

- Evaluation of the translational partition function is straightforward.
- Evaluation of the rotational partition function is feasible if the structure of the molecule is known.
- Evaluation of the vibrational partition function is challenging.
 - The vibrational degree of freedom involving the reaction coordinate must be treated separately.
 - Because the activated complex is not stable, the spectrum is usually not known, but some knowledge of the vibrational energy levels is essential to evaluating the partition function.
 - Sometimes the spectrum can be determined for the activated complex by femtosecond or picosecond spectroscopy.

- If a bond in the activated complex is weak, then it will be difficult to determine its vibrational frequency because it could break before it vibrated enough for the frequency to be determined.
- All the partition function terms contribute to the pre-exponential part of the rate coefficient expression, so they do not strongly affect the temperature dependence of the rate coefficient.
- Most of the temperature dependence is contained in $e^{-(\Delta E_0^\ddagger/RT)}$.
- E_0^\ddagger may be identified with the difference between the zero-point (ground state) energy of $(AB)^\ddagger$ and the zero point (ground state) energy of the reactants A and B.
 - This may be identified as the barrier height.

- To determine E_0^{\ddagger} , some knowledge of the potential energy surface and its dependence on the reaction coordinate is needed.
 - This does not mean that the full potential has to be calculated.
 - Information about the initial reactants and the activated complex (saddle point region) is sufficient.
 - A number of approximation methods exist.
 - The understanding of transition state theory has evolved with time.
 - See vignette by D. G. Truhlar.
- One semi-empirical approach is the “bond energy bond order” (BEBO) method developed by H. S. Johnston *et al.*

- The BEBO method is based on:
 - the relationship between bond length and bond order proposed by Pauling:

$$R = R_s - 0.26 \ln n$$

where R_s is the single bond length.

- the relationship between bond energy and order:

$$E = E_s n^p$$

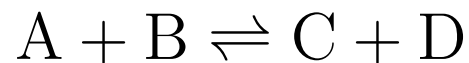
where E_s is the energy of a single bond and p is an empirical factor (≈ 1).

- As the reaction proceeds, the total bond order remains constant while one bond is broken and another is formed.
- The BEBO method allows the calculation of energy along the reaction coordinate.

- For the $\text{H} + \text{H}_2$ system, BEBO predicts a barrier height of 41 kJ mol^{-1} which compares well with 40 kJ mol^{-1} predicted by quantum mechanics and with 36 kJ mol^{-1} found as the experimental activation energy.
- Generally activation energies may be predicted fairly well.
- Prediction of A , the pre-exponential factor, is much more difficult and is often only correct to within an order of magnitude.
- Predictions about temperature dependence of reaction rate rely on some of the relationships between kinetics and thermodynamics.
- The relationship between rate coefficients and equilibrium coefficients will be considered.

Activated Complex Theory: Thermodynamic Interpretation

- Consider the general reaction:



- The forward direction is associated with collisions of A and B molecules.
- The reverse direction is associated with collisions of C and D molecules.
 - The rate of formation of A is:

$$\left(\frac{dn_A}{dt} \right)_r = \kappa_r n_C n_D$$

where κ_r is the reverse rate coefficient.

- Therefore the net reaction rate is:

$$-\frac{dn_A}{dt} = -\left(\frac{dn_A}{dt}\right)_f - \left(\frac{dn_A}{dt}\right)_r = \kappa_f n_A n_B - \kappa_r n_C n_D$$

in terms of number densities.

- In terms of concentrations, this is:

$$-\frac{d[A]}{dt} = k_f [A][B] - k_r [C][D]$$

where k_f and k_r are the macroscopic rate coefficients.

- If $[A]$, $[B]$, $[C]$, and $[D]$ are molar concentrations then:

$$\frac{k_f}{\kappa_f} = \frac{k_r}{\kappa_r} = N_A \quad \text{should hold.}$$

- But k_f and k_r are determined experimentally.
- K_f and K_r are usually evaluated theoretically.
- If the reaction is elementary, then the two treatments should agree.
- If they do not agree, it is usually because the reaction is not elementary.
- Mix gases A and B in a vessel.
 - After some time, the concentrations of A and B will decrease and the concentrations of C and D increase.
 - Eventually the concentrations no longer change with time, which means the system is at equilibrium.
 - The net rate of change of all species is zero.
 - Therefore:

$$k_f[A]_{eq}[B]_{eq} - k_r[C]_{eq}[D]_{eq} = 0$$

- This may be rearranged to:

$$\frac{k_f}{k_r} = \frac{[C]_{eq}[D]_{eq}}{[A]_{eq}[B]_{eq}} = K_V$$

- Microscopically this is equivalent to:

$$\frac{\kappa_f}{\kappa_r} = \frac{n_{C,eq}n_{D,eq}}{n_{A,eq}n_{B,eq}} = K_V$$

- This means that the microscopic rate coefficients differ from the macroscopic rate coefficients by a constant factor.
- If a system that involves more than one elementary reactions attains equilibrium, then all the elementary steps will have the same rates in both directions.
 - This is the principle of detailed balance.

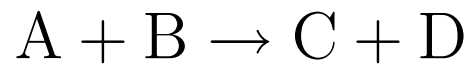
- Assumptions made so far include:
 - k_f , k_r , κ_f , and κ_r are constants with values independent of the distance from equilibrium.
 - If k_f and k_r are observed to vary with concentration, then the mechanism is different from what has been assumed.
 - The assumption that κ_f and κ_r are constant is equivalent to assuming that equipartition of energy over the degrees of freedom has occurred and the distributions are close to the equilibrium distributions.
 - that this applies only to dilute gases.
- The basic principles are generally applicable.
 - If a system is at equilibrium, then the forward and reverse reactions must be the same.

- If the reactions involved are elementary, then the forward rate and the reverse rate may each be written as the product of concentrations multiplied by a rate coefficient.
- If the reactions are not elementary, then the relationship may be quite complex and the ratio of concentrations has no simple relationship to the forward and reverse rate coefficients.
- In the case of elementary reactions, the relationship to thermodynamics may be considered.
 - The equilibrium coefficient is related to the Gibb's free energy:

$$K = e^{-\Delta G^{\circ}/RT}$$

where K is the thermodynamic equilibrium coefficient and is in terms of activities.

- In the limiting case of dilute gases, $K = K_p$, the equilibrium coefficient in terms of pressure.
- Consider the reaction:



where $\Delta\nu = 0$.

- In this case $K_V = K$.
- $\Delta G_f^{\circ\dagger}$ and $\Delta G_r^{\circ\dagger}$ may be defined in terms of the differences between the standard Gibbs free energy of the complex and the standard Gibbs free energy of reactants and products respectively since $\Delta G_f^{\circ\dagger} = -RT \ln(K_v^{\dagger})'$ and similarly for the reverse. Therefore:

$$k_f = \frac{k_B T}{h} e^{-\Delta G_f^{\circ\dagger}/RT}$$

- It may be shown:

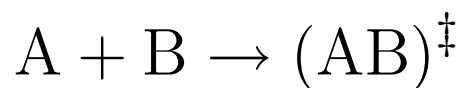
$$\Delta G^\circ = \Delta G_f^{\circ\dagger} - \Delta G_r^{\circ\dagger}$$

from $K = k_f/k_r$.

- This assumes that the transmission coefficient in both forward and reverse reactions is unity.
- Activated complex theory also makes predictions about the temperature dependence of reactions.
 - Consider that the reactants and the activated complex in equilibrium with each other. Therefore:

$$\Delta G^{\circ\dagger} = \Delta H^{\circ\dagger} - T\Delta S^{\circ\dagger} == RT \ln K^\ddagger$$

for the reaction:



- Usually K^\ddagger is taken as $K_V^\ddagger = [(AB)^\ddagger]/[A][B]$ with reference to a standard state of unit concentration.
- $\Delta G^{\circ\ddagger}$, $\Delta H^{\circ\ddagger}$, and $\Delta S^{\circ\ddagger}$ are the free energy, enthalpy, and entropy of activation.
- Differentiation of the rate coefficient yields:

$$\frac{d \ln k_f}{dT} = \frac{1}{RT^2} [\Delta H^{\circ\ddagger} + RT]$$

- Thus

$$E_a = \Delta H^{\circ\ddagger} + RT$$

for perfect gases.

- $\Delta H^{\circ\ddagger}$ is usually obtained from experimental thermochemical data.
- $\Delta H^{\circ\ddagger}$ and $\Delta E^{\circ\ddagger}$ are closely related to the barrier height.

- The entropy of activation is related to the number of available configurations of the complex.
- A “tight” activated complex has a lower entropy than a “loose” activated complex.
- $\Delta S^{\circ\dagger}$ is usually negative since formation of the activated complex usually removes translational and rotational degrees of freedom.
 - These would be replaced with vibrational degrees of freedom of the complex, but these new vibrational degrees of freedom are not necessarily active.
- The factor $e^{\Delta S^{\circ\dagger}/R}$ may be considered analogous to the steric factor.
- Some typical values of $\Delta H^{\circ\dagger}$ and $\Delta S^{\circ\dagger}$ are given in Table 30.1

Table 30.1 Enthalpies and Entropies of Activation for Some Gaseous Reactions (Calculated for 300°C, Standard State of 1 Mol/L)

Reaction	ΔH^{\ddagger} (kJ/mol)	ΔS^{\ddagger} (J/mol K)
$\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$	17.53	-62.55
$\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$	21.37	-83.56
$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6$	-5.82	-61.87
$\text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2$	85.12	+29.26
<i>cis</i> -CHCl=CHCl \rightarrow <i>trans</i> -CHCl=CHCl	227.45	-16.65
$\text{CH}_3\text{CH}_2\text{Cl} \rightarrow \text{C}_2\text{H}_4 + \text{HCl}$	230.83	-1.93
<i>cis</i> -Hexatriene-1,3,5 \rightarrow cyclohexadiene-1,3	121.53	-30.38

- Activated complex theory predicts a non-Arrhenius temperature dependence since:

$$k_f = \kappa \frac{k_B T}{h} N_A \frac{q_1[(AB)^\ddagger]}{q_1[(A)]q_1[(B)]} e^{-(\Delta E_0^\ddagger)/RT}$$

- In addition to the temperature dependence of $k_B T/h$, the partition functions q_1 have temperature dependence.
 - The partition function may be considered to be the product of translational, vibrational, and rotational partition functions for the species in question.
 - Translational and rotational partition function contribute at factor of $T^{1/2}$ for each degree of freedom.
 - Each vibrational degree of freedom contributes $(1 - e^{-h\nu/kT})^{-1}$

- This predicts a T^m dependence where m is a small integer or half-integer when the vibrational partition function may be approximated.
 - When $h\nu \gg k_B T$, the vibrational partition function is approximated as unity.
 - When $h\nu \ll k_B T$, the vibrational partition function is approximated by $k_B T / h\nu$
 - Activated complex theory does not always predict m .
- Thus the predicted rate coefficient has the form:

$$k = AT^m e^{-(\Delta E_0^\ddagger)/RT}$$

which upon differentiation gives:

$$\frac{d \ln k}{dT} = \frac{\Delta E_0^\ddagger}{RT^2} + \frac{m}{T} = \frac{E_a}{RT^2}$$

- Thus:

$$\Delta E_0^{0\ddagger}(m) = E_a - mRT$$

- Note the relationship between E_a and $\Delta H^{0\ddagger}$ from which the relationship between $\Delta E_0^{0\ddagger}$ and $\Delta H^{0\ddagger}$ may be derived.
- It is to be noted that the literature in this area has used these interchangeably.
 - The difference is of the order of a few kJ mol^{-1} at room temperature and may be ignored if E_a is of the order of 100 kJ mol^{-1} or more, but can be quite significant if E_a is less than 10 kJ mol^{-1} .
- None of these energies is to be confused with the barrier height.
- Experimental measurements give thermal averages of threshold energies.

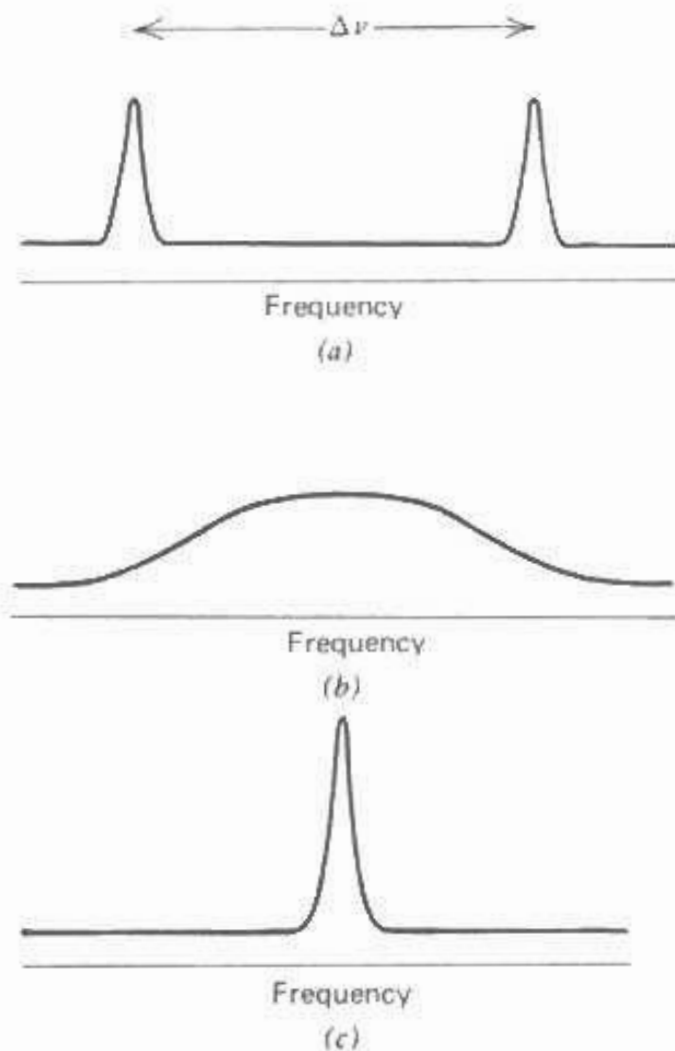


Figure 30.21 Nuclear magnetic resonance spectra of exchange reactions: (a) no reaction, two peaks separated by chemical shift $\Delta\nu$; (b) exchange rate comparable to $\Delta\nu$, two peaks coalesce into one broad line; (c) exchange rate much greater than $\Delta\nu$, single sharp line.

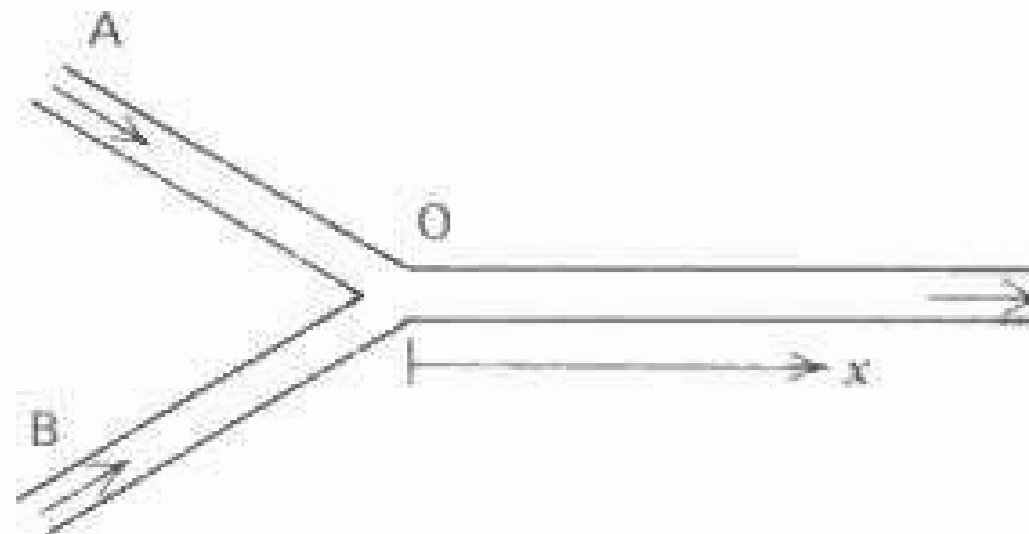


Figure 30.22 Schematic diagram of a flow system.

this is the application of a stimulus to an already homoeo-

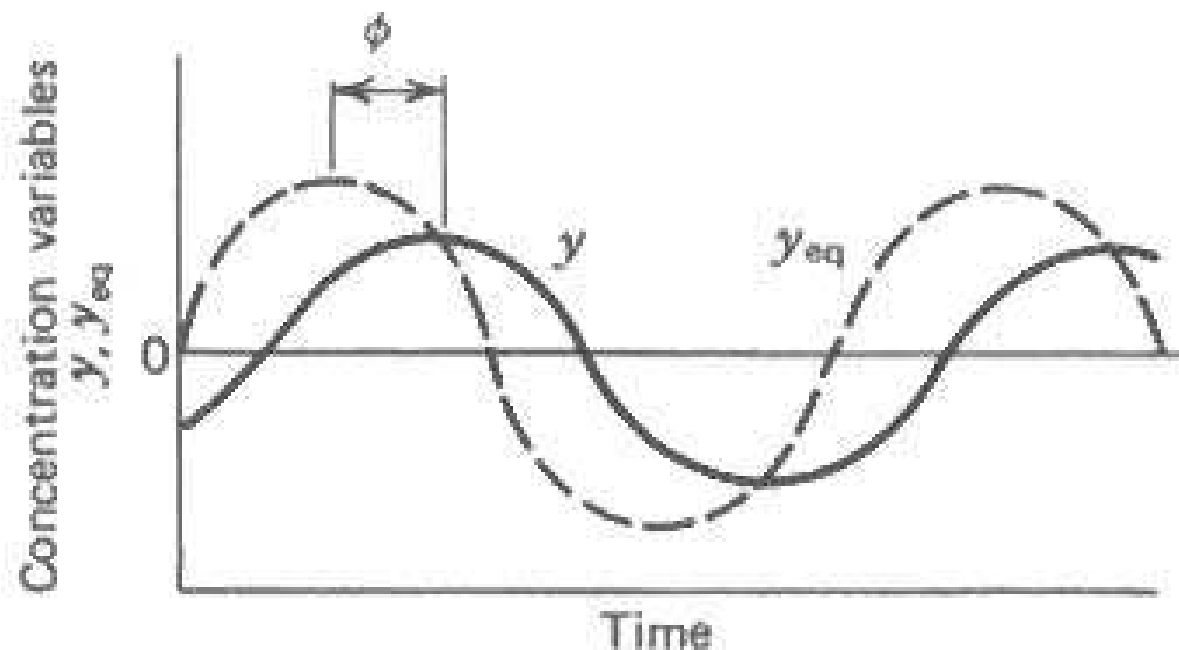


Figure 30.23 Variation of concentration with time in a reaction system perturbed by a periodic sound wave: - - -, equilibrium concentration y_{eq} (in phase with pressure variation); —, actual concentration y . The two sinusoidal curves differ in amplitude by the factor $1 + \omega^2 \tau^2$, and in phase by the lag ϕ defined in Eq. 30.132.

Analysis of Data for Complex Reactions

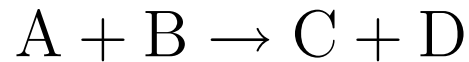
- A third order reaction obeys the rate law:

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

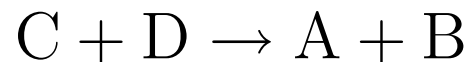
where A, B, C are the same or different.

- If the stoichiometry is known, the rate coefficient may be obtained from experimental data.
- But it is of interest how third order reactions occur.
 - Three species colliding simultaneously is much less likely than a bimolecular collision.
 - Third order rate expressions can result from a sequence of bimolecular reactions.

- Consider a general forward reaction with rate coefficient k_f :



and its reverse with rate coefficient k_r :



- An equilibrium will be established regardless of whether the reaction was initiated by mixing A and B or by mixing C and D.
 - If a reaction goes to completion, the position of equilibrium is so far toward products that the effect of the reverse reaction is negligible.
 - But if the equilibrium coefficient is between 10 and 10^{-1} then the effect of the reverse reaction is non-negligible.

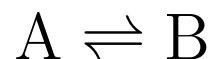
- Consider the reaction $\text{H}_2 + \text{I}_2 \rightleftharpoons 2\text{HI}$ which has significant rates in both directions at moderate temperatures.
 - Forward and reverse reactions are observed to be both second order.
 - The actual mechanism is quite complicated.
- The reaction rate is given by:

$$-\frac{d[\text{I}_2]}{dt} = k_f[\text{H}_2][\text{I}_2] - k_r[\text{HI}]^2$$

with k_f and k_r are related by K_V :

$$\frac{k_f}{k_r} = \left(\frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]} \right)_{eq} = K_V$$

- Therefore k_f and k_r may be determined experimentally by measuring the concentration as a function of time and fitting the data to the two simultaneous equations.
- Consider a simple case:



- The initial conditions have only A present.
Therefore:

$$[B] = [A]_0 - [A]$$

- This gives as the rate equation:

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

$$-\frac{d[A]}{dt} = k_f[A] - k_r([A]_0 - [A])$$

- When this is integrated from 0 to t, the result is:

$$\ln \left(\frac{k_f[A]_0}{(k_f + k_r)[A] - k_r[A]_0} \right) = (k_f + k_r)t$$

- At equilibrium, $d[A]/dt = 0$ and:

$$k_f[A]_{eq} - k_r([A]_0 - [A]_{eq}) = 0$$

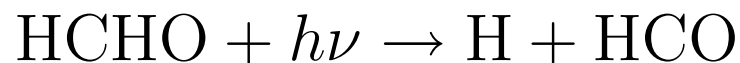
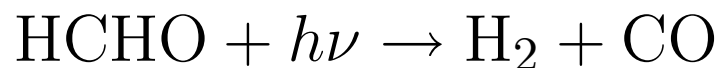
$$[A]_{eq} = \frac{k_r[A]_0}{k_f + k_r}$$

- For this it may be shown:

$$\ln \left(\frac{[A]_0 - [A]_{eq}}{[A] - [A]_{eq}} \right) = (k_f + k_r)t$$

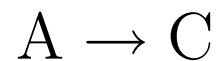
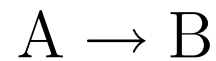
Simultaneous Reactions

- Some reactions have more than one set of products.
- Such reactions are described as parallel, simultaneous, or competitive.
- One example is the photolysis of formaldehyde:



- The ratio of products is determined by the wavelength of light.
- The simultaneous reactions can have separate mechanisms, orders, and rate coefficients.

- Consider the reaction system:



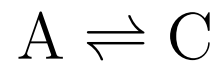
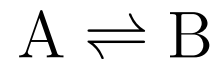
with rate coefficients k_1 and k_2 respectively.

- There are no other reactions involving A, B, or C in the system.
- If only A is initially present, then

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

- Such a reaction is kinetically controlled since the relative rates of reaction control the ratio of products.

- Consider now the system:



with rate coefficients k_{1f} , k_{1r} , k_{2f} and k_{2r} and equilibrium coefficients K_1 and K_2 .

- Such a system is thermodynamically controlled and:

$$\frac{[B]}{[C]} = \frac{K_1}{K_2}$$

- If more reactions are involved, the more complicated the situation will be and although the same principles apply, numerical methods may be required in order to model it.

Consecutive Reactions

- Consider the system:



- This type of system is typical of a radioactive decay sequence.
- If the reactions are first order then:

$$-\frac{d[A]}{dt} = k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$

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

- The solution for the case where $k_1 \neq k_2$ is:

$$[A] = [A]_0 e^{-k_1 t}$$

$$[B] = \frac{k_1 [A]_0}{k_2 - k_1} \left(e^{-k_1 t} - e^{-k_2 t} \right)$$

$$[C] = [A]_0 \left(1 + \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_1 - k_2} \right)$$

- The solution for the case where $k_1 = k_2 = k$ is:

$$[A] = [A]_0 e^{-kt}$$

$$[B] = kt[A]_0 e^{-kt}$$

$$[C] = [A]_0 \left(1 - kte^{-kt} - e^{-kt} \right)$$

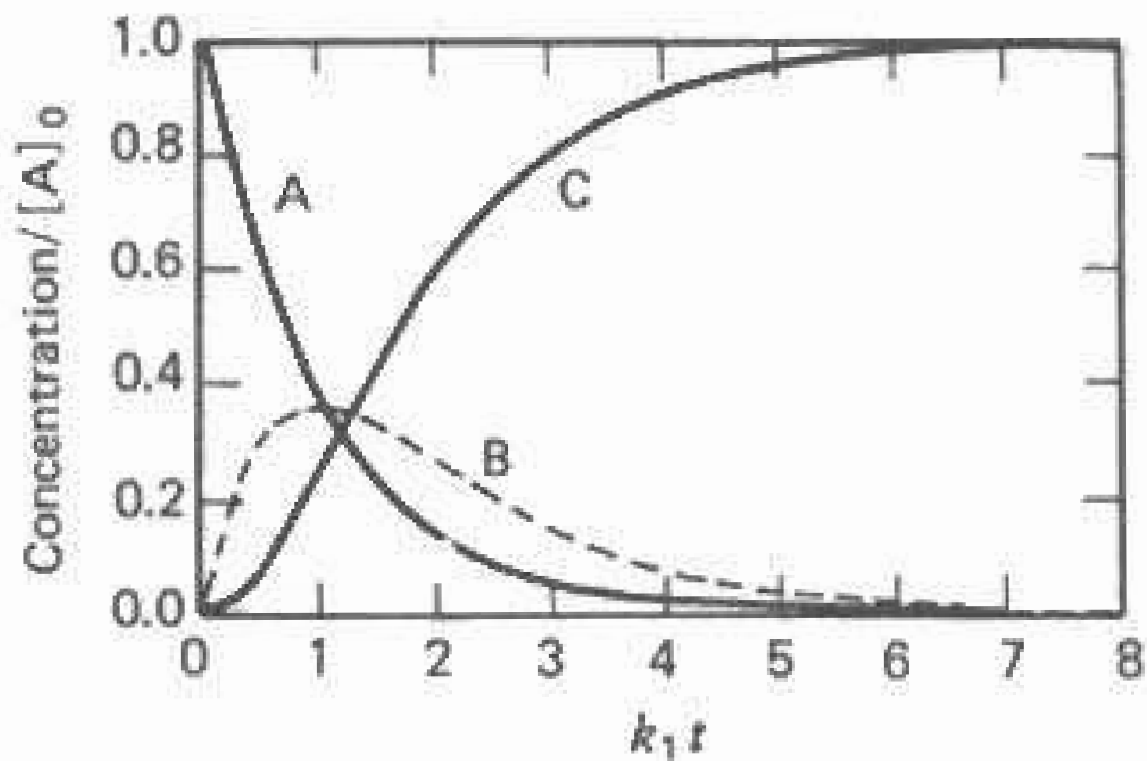
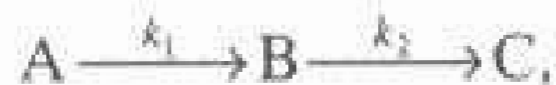


Figure 30.24 Variation of concentration with time for the consecutive reactions



with $k_1 = k_2$.

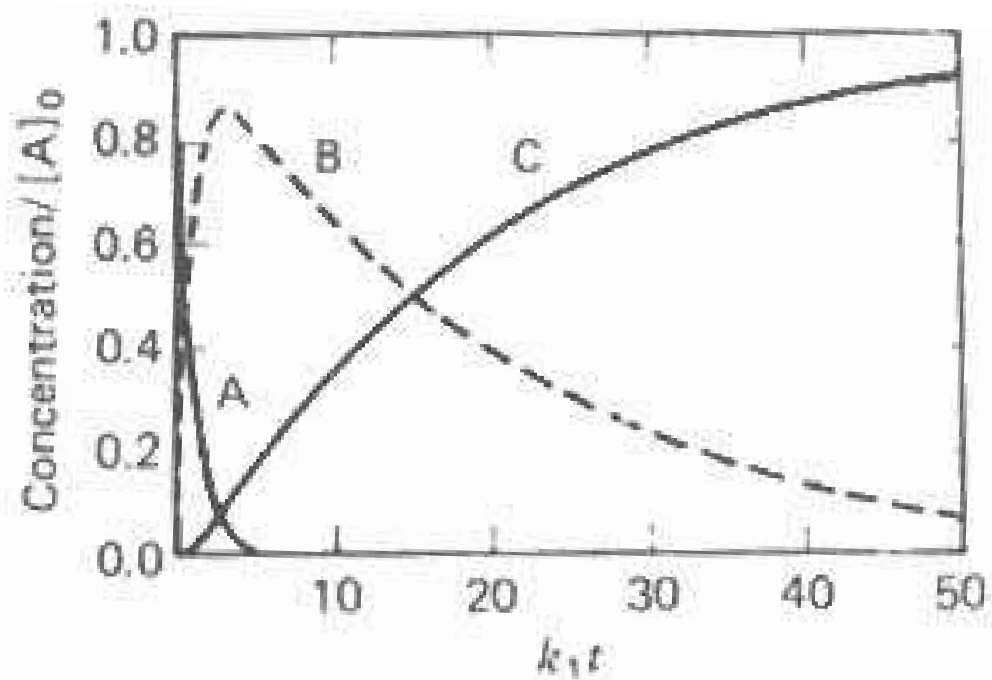


Figure 30.25 Same as Fig. 30.21, but for the case $k_1 = 20k_2$.

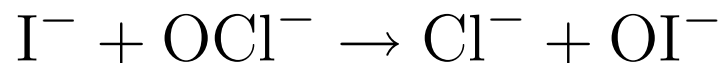
- The variation of $[A]$, $[B]$, and $[C]$ depends on the ratio of the rate coefficients.
- Figures 30.24 and 30.25 illustrate two cases.
- If $k_1 > k_2$ then $[B]$ will increase considerably then decay.
 - The maximum of $[B]$ will be high.
 - The decay of $[B]$ after the maximum will be approximately first order with k_2 as the decay coefficient.
 - The rate of formation of C is dominated by the value of k_2 .
 - The second step is the rate determining step.
- If $k_1 < k_2$ the first step is rate determining and B is consumed almost as fast as it forms.
 - The steady-state approximation applies to this case.

Mechanisms of Chemical Reactions

- Most reactions proceed in a sequence of elementary reactions rather than in a single step.
 - The mechanism of the reaction is this sequence of single steps.
- The exact mechanism cannot be predicted from theory, but in practice is postulated (or guessed) based on chemical principles and then tested.
- The mechanism must be consistent with:
 - the known stoichiometry of the reaction,
 - the experimentally determined rate expression,
 - the experimental temperature dependence,
 - other experimental measurements such as isotope effects, presence of radicals during the reaction, and stereochemistry.

- A mechanism consists of a series of elementary steps.
- Each step describes the collision or dissociation leading to products.
 - The molecularity of each elementary step is determined by the number of molecules involved in each elementary reaction.
- The overall sum of the reaction steps must yield the stoichiometric equation.
- Mechanisms tend to lead to rather unwieldy equations.
 - Simplifying assumptions may be made if appropriate.
- The main assumptions involve either a rate-determining step or the steady-state hypothesis.

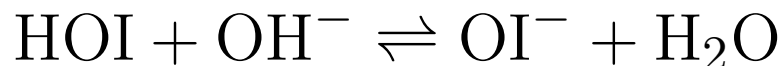
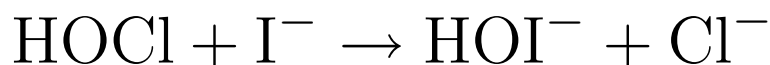
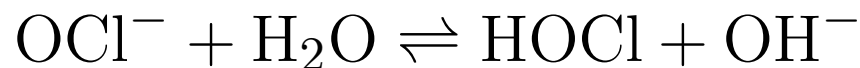
- Consider a mechanism with a rate determining step.
- The overall reaction is:



- The empirically determined rate law is:

$$-\frac{d[\text{I}^-]}{dt} = k \frac{[\text{I}^-][\text{OCl}^-]}{[\text{OH}^-]}$$

- A mechanism consistent with this is:



- Reactions 1 and 3 have equilibrium coefficients K_1 and K_3 and reaction 1 has the rate coefficient k_2 .
- Reaction 2 is rate determining.
- Reactions 1 and 3 are in rapid quasi-equilibrium.
- The concentration of I^- is fairly constant throughout the reaction, decreasing very slowly with the rate:

$$-\frac{d[I^-]}{dt} = k_2[HOCl][I^-]$$

- The concentration of HOCl is determined by the quasi-equilibrium of reaction 1:

$$K_1 = \frac{[HOCl][OH^-]}{[OCl^-]}$$

- Thus:

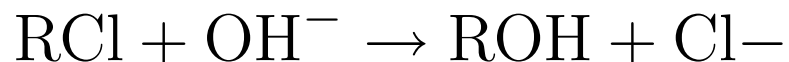
$$[\text{HOCl}] = \frac{K_1[\text{OCl}^-]}{[\text{OH}^-]}$$

- Therefore:

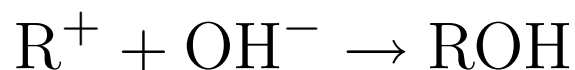
$$-\frac{d[\text{I}^-]}{dt} = k_2 \frac{K_1[\text{OCl}^-]}{[\text{OH}^-]} [\text{I}^-]$$

- This corresponds to $k = k_2 K_1$.
- The third reaction does not affect the rate.
- This gives some guidelines for mechanisms:
 - Rapid quasiequilibrium reaction steps after a rate determining step do not appear in the rate expression.
 - A dependence of the rate on the reciprocal of a concentration is indicative of a rapid quasiequilibrium prior to the rate determining step.

- Continued:
 - The molecularity of a sole rate determining step is the molecularity of the overall reaction.
 - The predicted rate equation is obtained from the rate determining step.
 - There is no correspondence between stoichiometry and the empirical rate law unless it is a single step.
- Consider now a reaction to which the stationary state hypothesis is applied:



- This reaction has the mechanism:



- If the second step is rate-determining, then the rate law will be:

$$\frac{d[\text{ROH}]}{dt} = \frac{k_1 k_2 [\text{RCl}][\text{OH}^-]}{k'_1 [\text{Cl}^-]}$$

- However this is not consistent with the observed rate law.
- The alternative is to assume that the first step is not in equilibrium.
 - Further assume that R^+ is consumed as soon as it is formed.
 - Thus, according to the steady-state hypothesis:

$$\frac{d[\text{R}^+]}{dt} = 0 = k_1 [\text{RCl}] - k'_1 [\text{R}^+] - k_2 [\text{R}^+][\text{OH}^-]$$