

Reactions in the Gas Phase

In the previous chapters, we have considered reactions on an empirical basis in terms of several concentration–time relationships that apply to many types of chemical systems. Our intuition indicates that while the *overall* reaction may be described in this way, on a *molecular* level individual reacting “units” must on some microscopic scale collide or make contact in some way. These units (molecules, ions, atoms, radicals, and electrons) must be involved in some simple step at the instant of reaction. These steps through which individual units pass are called *elementary reactions*. The sequence of these elementary reactions constitutes the *mechanism* of the reaction.

In many cases, there must be energy transfer between the reacting molecules. For reactions that take place in the gas phase, molecular collisions constitute the vehicle for energy transfer, and our description of gas phase reactions begins with a kinetic theory approach to collisions of gaseous molecules. In simplest terms, the two requirements that must be met for a reaction to occur are (1) a collision must occur and (2) the molecules must possess sufficient energy to cause a reaction to occur. It will be shown that this treatment is not sufficient to explain reactions in the gas phase, but it is the starting point for the theory.

4.1 COLLISION THEORY

Normally, the rate of a reaction is expressed in terms of a rate constant multiplied by a function of concentrations of reactants. As a result, it is the rate constant that contains information related to the collision frequency, which determines the rate of a reaction in the gas phase. When the rate constant is given by the Arrhenius equation,

$$k = Ae^{-E_a/RT} \quad (4.1)$$

E_a is related to the energy barrier over which the reactants must pass as products form. For molecules that undergo collision, the exponential is related to the number of molecular collisions that have the required energy to induce reaction. The pre-exponential factor, A , is related to the frequency of collisions. Therefore, we can describe the reaction rate as

$$\text{Rate} = (\text{Collision frequency}) \times (\text{Fraction of collisions with at least the threshold energy})$$

or

$$\text{Rate} = Z_{AB} \times F \quad (4.2)$$

where Z_{AB} is the frequency of collisions between molecules of A and B and F is the fraction of those collisions having sufficient energy to cause reaction.

The collision frequency between two different types of molecules can be calculated by means of the kinetic theory of gases. In this discussion, in which collisions are occurring between molecules of A and B, we will consider the molecules of B as being stationary and A molecules moving through a collection of them. If we imagine a molecule of A moving through space where molecules of B are located, collisions will occur with molecules of B whose centers lie within a cylinder of length ν_{AB} and radius $r_A + r_B$ where ν_{AB} is the average relative velocity of A and B and $r_A + r_B$ is the sum of the radii of molecules A and B. A diagram showing this situation is shown in Figure 4.1.

We can define the cross-sectional area of the cylinder, $\pi(r_A + r_B)^2$, the *collisional cross section*, σ_{AB} . In 1 second, a molecule of A travels a distance of ν_{AB} (where ν_{AB} is the average molecular velocity of A relative to B) and it will collide with all molecules of B that have centers that lie within the cylinder. Therefore, the number of collisions per second will be given by

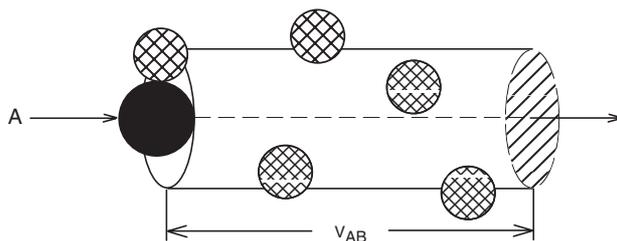


FIGURE 4.1 Model used for calculating collision frequency.

the number of B molecules/cm³ multiplied by the volume of the cylinder. This can be expressed by the equation

$$Z_A = \nu_{AB} \sigma_{AB} C_B \quad (4.3)$$

Although A does not continue in a straight line after colliding with B, the calculated collision frequency will still be correct as long as there is no gradient in concentration of B within the container and the velocity of A remains constant. The preceding result is for a single molecule of A. To obtain the total number of collisions between molecules of A and B, Z_{AB} , the result must be multiplied by C_A , the number of molecules of A per cm³. Therefore, the collision frequency is

$$Z_{AB} = \nu_{AB} \sigma_{AB} C_A C_B \quad (4.4)$$

Because we have considered molecules of B to be stationary (velocity = 0), the relative velocity ν_{AB} is just the root-mean-square velocity of A,

$$\nu_A = \left(\frac{8\mathbf{k}T}{m\pi} \right)^{1/2} \quad (4.5)$$

where T is the temperature (K), \mathbf{k} is Boltzmann's constant, and m is the mass of A. Note that Boltzmann's constant is denoted in bold to distinguish it from a rate constant. If we represent the reduced mass of a pair of molecules A and B as μ , then

$$\frac{1}{\mu} = \frac{1}{m_A} + \frac{1}{m_B} \quad (4.6)$$

or, in the more familiar form,

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (4.7)$$

The relative velocity of A and B can now be written as

$$\nu_{AB} = \left(\frac{8\mathbf{k}T}{\pi\mu} \right)^{1/2} \quad (4.8)$$

Having derived an expression for the relative velocity of the molecules, the collision frequency is expressed as

$$Z_{AB} = \left(\frac{8\mathbf{k}T}{\pi\mu} \right)^{1/2} \sigma_{AB} C_A C_B \quad (4.9)$$

Frequently, the collision diameter, $d = (d_A + d_B)/2$, is used and the concentrations are written in terms of numbers of molecules/cm³, n_A and n_B , per unit volume. Then,

$$Z_{AB} = d^2 \pi \left(\frac{8kT}{\pi\mu} \right)^{1/2} \frac{n_A n_B}{V^2} \quad (4.10)$$

If we consider 1 cm³ of gaseous H₂ at 1 atm and 300 K, using a collision diameter of 0.21 nm (2.1×10^{-8} cm) we obtain a collision frequency of about 1.8×10^{29} collisions per second per cm³. Therefore, at this collision frequency, if every collision led to a reaction, 1 mole of a gas could react in a time that is determined as

$$\frac{6.02 \times 10^{23} \text{ molecules}}{1.8 \times 10^{29} \text{ molecules sec}^{-1}} = 3.3 \times 10^{-6} \text{ sec}$$

Since most gaseous reactions occurring between colliding molecules do not take place on this timescale, other factors than just the collision frequency must be considered. We must now consider these other factors as will now be described.

One factor that has been ignored to this point is that although a collision frequency can be calculated, the collision between the molecules must occur with sufficient energy for the reaction to occur. As we have previously seen, that minimum energy is the activation energy. Figure 4.2 shows a Maxwell-Boltzmann distribution of energies of gaseous molecules.

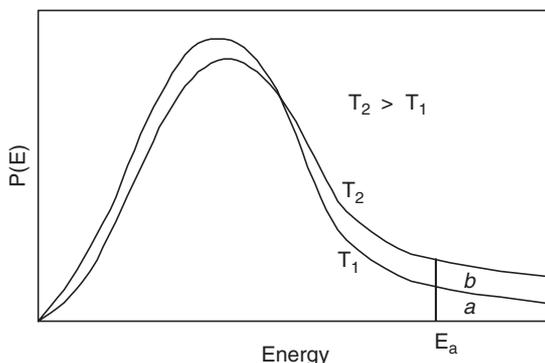


FIGURE 4.2 Distributions of molecular energies. The fraction of molecules having an energy greater than E_a is given by a at T_1 but it is given by $a + b$ at T_2 .

If the minimum energy to cause a reaction is the activation energy, E_a , the fraction (F) of the molecules possessing that energy or greater (represented by the areas a and b under the curve) is given by

$$F(E) = \frac{\int_E^{\infty} e^{-E/RT} dE}{RT} \quad (4.11)$$

When expressed in terms of the activation energy, F can be shown to be

$$F = e^{-E_a/RT} \quad (4.12)$$

Even if the activation energy is small, the fraction of the molecules having a collision energy leading to reaction will be a very small fraction of the total number of collisions. The reaction rate should be given by

$$\text{Rate} = \text{Collision frequency} \times \text{fraction with } E > E_a$$

$$\text{Rate} = d^2 \pi \left(\frac{8kT}{\pi\mu} \right)^{1/2} C_A C_B e^{-E/RT} \quad (4.13)$$

It should be noted from this equation that the collision theory of reaction rates predicts that the pre-exponential factor is not independent of temperature, but rather depends on $T^{1/2}$. This occurs because the average *kinetic energy* of an ideal gas is directly proportional to T but the *average velocity* of the molecules, which determines collision frequency, is proportional to $T^{1/2}$. Over a narrow range of temperature, this dependence on temperature is not usually observed. The fact is that a rather slight increase in temperature changes the average molecular velocity only very slightly because it depends on the factor $(T_2/T_1)^{1/2}$. However, the area under the curve corresponding to molecules having energies greater than E_a is increased slightly (see Figure 4.2). Therefore, the dominant temperature effect occurs in the $e^{-E_a/RT}$ factor where the fraction of molecules having $E > E_a$ is calculated. As was illustrated in Chapter 2, an increase in temperature of 10° can double or triple the rate of a reaction.

When reaction rates calculated using collision theory are compared to the experimental rates, the agreement is usually poor. In some cases, the agreement is within a factor of 2 or 3, but in other cases the calculated and experimental rates differ by 10^5 to 10^7 . The discrepancy is usually explained in terms of the number of *effective* collisions, which is only a fraction of the total collisions owing to steric requirements. The idea here is that in order for molecules to react, (1) collision must occur, (2) the

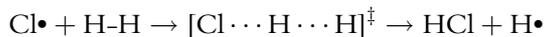
collision energy must be sufficient, and (3) the molecules must have a proper orientation. To compensate for the difference between calculated and observed rates, a steric factor, P , is introduced. It is defined as

$$P = \frac{\sigma_{\text{obs}}}{\sigma_{\text{calc}}} \quad (4.14)$$

This steric factor can be regarded as an orientation factor but it can also be interpreted in terms of the entropy change involved in forming the transition state.

4.2 THE POTENTIAL ENERGY SURFACE

In Chapter 1, it was shown that in one step in the reaction between H_2 and Cl_2 a chlorine radical reacts with a molecule of H_2 . If we speculate about the structure of this three-body species, we realize that repulsions will be minimized if the structure is linear. Therefore, it is reasonable to assume that the elementary reaction step can be represented as shown in the sequence



and that it passes through a linear $\text{Cl}\cdots\text{H}\cdots\text{H}$ transition state or activated complex. That the transition state is linear in this case follows from the fact that to form a bent transition state would bring the terminal atoms closer together, which would increase repulsion. To relate the energy of this system to the bond distances is now the problem. While we might approach this problem in a number of ways, one simple approach is to extend a relationship used for a diatomic molecule to include a second bond.

The bond energy of a diatomic molecule varies with the bond length as shown in Figure 4.3. The energy is most favorable at the bottom of the potential well which corresponds to the equilibrium bond length. One equation that models the kind of relationship shown in Figure 4.3 is the Morse equation,

$$E = D_e [e^{-2\beta(r-r_0)} - 2e^{-\beta(r-r_0)}] \quad (4.15)$$

where r is the internuclear distance, r_0 is the equilibrium internuclear distance, D_e is the bond dissociation energy, and β is a constant. Attraction between the atoms increases as they get closer together (the energy becomes more negative), but at distances smaller than r_0 , repulsion increases and becomes dominant at very short internuclear distances.

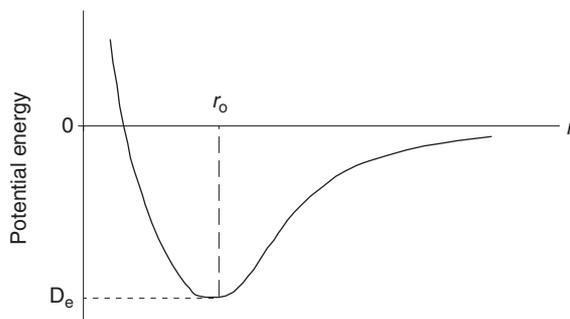


FIGURE 4.3 Potential energy curve for a diatomic molecule.

For a linear triatomic transition state, it is assumed that a second potential energy curve results so that the total energy is a function of two bond distances. Therefore, a diagram can be constructed that shows energy on one axis (usually chosen to be the vertical axis), one of the bond distances on another, and the second bond distance on the third axis, which generates a three-dimensional energy surface. If we suppose the reaction



takes place with the formation of a linear transition state $\text{A} \cdots \text{B} \cdots \text{C}$, the result is a three-dimensional surface which is analogous to a contour map. In order to go from $\text{AB} + \text{C}$ to the products $\text{BC} + \text{A}$ it is not necessary to go over the area of highest energy (which corresponds to highly stretched bonds in the structure $\text{A} \cdots \text{B} \cdots \text{C}$). Instead, the reaction proceeds along a path where the energy rises less steeply along a “valley.” Along that path, the energy barrier is lower, being similar to a pass over a mountain range between two peaks. Such a path passes over a highest point, sometimes referred to as a “saddle” point, which is lower in energy than on either side. The path representing the changes in configuration as the reaction takes place is called the *reaction coordinate*.

Since electronic energy levels for molecules differ by perhaps 200–400 kJ/mol and the motion of electrons is rapid compared to the motion of nuclei within the molecules, it is possible to determine the energy as if the nuclei were at rest (this is known as the Born-Oppenheimer approximation). The assumption is made that the coulombic and exchange energies are related by an approximately constant ratio (normally it is assumed that the exchange energy is approximately 15% of the coulombic energy). For a diatomic molecule, the energy can be written as

$$E = \frac{Q \pm J}{1 \pm S} \quad (4.17)$$

where Q , J , and S are the coulombic, exchange, and overlap integrals, respectively. For a triatomic molecule, the energy can be written as

$$E = Q_A + Q_B + Q_C \pm (1/2) [(J_A - J_B)^2 + (J_B - J_C)^2 + (J_A - J_C)^2]^{1/2} \quad (4.18)$$

where Q_A is the coulombic term for B–C, J_A is the exchange term for B–C; Q_B and J_B are the coulombic and exchange terms for A–C, and Q_C and J_C are the coulombic and exchange terms for A–B. This method, developed by London, does not reproduce known energies very accurately and it results in a shallow “basin” at the top of the saddle point. While more exact calculations based on the variation method and semi-empirical procedures provide results that are in qualitative agreement with experimental results, especially for simple molecules, the details of these methods will not be presented here. It is sufficient to point out that *ab initio* calculations have largely replaced the older type of calculations.

Another facet of the potential energy barrier to reaction is that of quantum mechanical tunneling. Classically, an object must have an energy at least equivalent to the height of a barrier in order to pass over it. Quantum mechanically, it is possible for a particle to pass *through* a barrier even though the particle has an energy that is less than the height of the barrier. In the particle in the one-dimensional box quantum mechanical model, the walls of the box are made infinitely high to prevent the particle from “leaking” from the box. The *tunneling coefficient* (also referred to as the *transmission probability* or *transparency*) of a barrier is determined by the height and thickness of the barrier and the mass and energy of the particle. For a given barrier, the transparency decreases as the mass of the particle increases so that tunneling is greater for light atoms, i.e., H, H⁺, etc. However, the transparency increases as the energy approaches the barrier height (see Section 3.9).

The potential energy surface may be almost symmetrical if the diatomic molecule AB is very similar to BC. On such surfaces, the mapping of energies gives “hills” of similar energy because the bond energies are approximately equal. In a more general case, the reactant and product molecules will have considerably different bond energies so the potential energy surface will not be as nearly symmetrical. In such a case the product molecule lies at a lower energy than the reactant showing that the reaction is exothermic.

An alternative method of showing a potential energy surface is based on the same principle as that used to prepare a topographical map. In a topographical map, lines connect points of equal altitude creating contours that have specific altitudes. Where the contour lines are closely spaced, the altitude is changing abruptly, and where the contour lines are widely separated the surface is essentially flat. Slices through the surface at specific constant energies of the transition state provide the contour lines. This case corresponds to the reaction in which the molecules BC and AB have similar bond energies. For the case where BC and AB have greatly different bond energies, the surface will have one of the “valleys” as being deeper and having steeper walls, as indicated by more closely spaced contour lines.

4.3 TRANSITION STATE THEORY

A collision theory of even gas phase reactions is not totally satisfactory, and the problems with the steric factor that we described earlier make this approach more empirical and qualitative than we would like. *Transition state theory*, developed largely by Henry Eyring, takes a somewhat different approach. We have already considered the potential energy surfaces that provide a graphical energy model for chemical reactions. Transition state theory (or activated complex theory) refers to the details of how reactions become products. For a reaction like



it is assumed that there is a variation in potential energy which is related to atomic coordinates by an appropriate potential energy function. The term *phase space* is applied to the coordinate and momentum space for the system. In order for a reaction to occur, the transition state must pass through some critical configuration in this space. Because of the nature of the potential function used to express the energy of the system as a function of atomic positions, the system energy possesses a saddle point. This saddle point lies lower in energy than the fully dissociated arrangement, $A + B + C$, or the highly “compressed” arrangement, $A-B-C$.

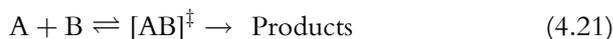
The essential feature of transition state theory is that there is a “concentration” of the species at the saddle point, the *transition state* or *activated complex*, that is in equilibrium with reactants and products. The Boltzmann Distribution Law governs the concentration of that transition state, and the rate of reaction is proportional to its concentration. Since the concentration

of the transition state is small because of its energy being higher than that of the reactants, this critical configuration represents the “regulator” of the rate of flow of reactants to products.

The concentration of the transition state is not the only factor involved, since the frequency of its dissociation into products comes into play because the rate at which it decomposes must also be considered. Therefore, the rate can be expressed as

$$\text{Rate} = (\text{Transition state concentration}) \times (\text{Decomposition frequency}) \quad (4.20)$$

In order for the transition state to separate into products, one bond (the one being broken) must acquire sufficient vibrational energy to separate. When it does separate, one of the $3N - 6$ vibrational degrees of freedom (for a linear molecule it is $3N - 5$) is lost and is transformed into translational degrees of freedom of the products. Central to the idea of transition state theory is the assumption that the transition state species is in equilibrium with the reactants. Thus,



For the formation of the transition state, $[AB]^\ddagger$, the equilibrium constant is

$$K^\ddagger = \frac{[AB]^\ddagger}{[A][B]} \quad (4.22)$$

from which we find that the concentration of the transition state is

$$[AB]^\ddagger = K^\ddagger[A][B] \quad (4.23)$$

Since the reaction rate is expressed as the product of the concentration of the transition state and the frequency of its decomposition, we can now write

$$\text{Rate} = [AB]^\ddagger \times (\text{frequency}) = (\text{frequency})K^\ddagger[A][B] \quad (4.24)$$

As we have seen previously (for example, see Eq. 2.191)

$$K^\ddagger = e^{-\Delta G^\ddagger/RT} \quad (4.25)$$

and we know that

$$\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (4.26)$$

Therefore, the equilibrium constant for formation of the transition state can be written as

$$K^\ddagger = e^{-\frac{\Delta H^\ddagger - T\Delta S^\ddagger}{RT}} = e^{-\frac{\Delta H^\ddagger}{RT}} \times e^{\frac{\Delta S^\ddagger}{R}} \quad (4.27)$$

Substituting for K^\ddagger in Eq. (4.24) yields

$$\text{Rate} = (\text{frequency})[A][B]e^{-\frac{\Delta H^\ddagger}{RT}} \times e^{\frac{\Delta S^\ddagger}{R}} \quad (4.28)$$

Having obtained an expression for the rate in terms of concentrations and thermodynamic quantities, the frequency of decomposition of transition state must now be addressed.

If we consider the vibration of the transition state when it is at the top of the potential energy barrier, we should now recall that the classical high-temperature limit in energy for a vibrational mode can be expressed as

$$E_{\text{vib}} = \mathbf{k}T(\text{erg per molecule})$$

where \mathbf{k} is Boltzmann's constant and T is the temperature (K). Since $\mathbf{k} = R/N_o$ (where N_o is Avogadro's number),

$$E_{\text{vib}} = RT(\text{Joule per mole})$$

It should also be remembered that for each degree of translational freedom the energy is $\mathbf{k}T/2$, which is $RT/2$ per mole. If we now assume that the frequency of the decomposition of the transition state is equal to the frequency of the vibration being lost due to breaking a bond as products are formed, the energy can be expressed as

$$E = h\nu = \mathbf{k}T$$

Solving for the frequency gives

$$\nu = \frac{\mathbf{k}T}{h}$$

which can also be written as

$$\nu = \frac{RT}{hN_o} \quad (4.29)$$

Because the reaction rate can be expressed in terms of the concentration of the transition state, the rate can now be given by

$$\text{Rate} = k[AB]^\ddagger \quad (4.30)$$

Substituting νK^\ddagger for the rate constant gives

$$\text{Rate} = \nu K^\ddagger [A][B] \quad (4.31)$$

When we substitute the result shown in Eq. (4.29) for the frequency in this equation we obtain

$$\text{Rate} = \frac{RT}{hN_o} K^\ddagger [A][B] \quad (4.32)$$

The rate constant can now be written as

$$k = \frac{kT}{h} K^\ddagger = \frac{kT}{h} e^{-\frac{\Delta G^\ddagger}{RT}} \quad (4.33)$$

A somewhat more elegant approach to deriving an expression for the rate of passage over the potential energy barrier is based on statistical mechanics. According to this procedure, it is assumed that there is a certain distance, d , at the top of the barrier, which must be the distance where the transition state exists. It is within this distance that a vibrational mode of the complex is transformed into translational motion of the products. The rate of passage of the transition state through distance d is related to the molecular velocity in one direction. If the mass of the transition state is m^\ddagger , the average velocity is

$$\nu = \left(\frac{2kT}{\pi m^\ddagger} \right)^{1/2} \quad (4.34)$$

Therefore, the time required for the transition state to pass through distance d is given by

$$\frac{d}{\nu} = d \left(\frac{m^\ddagger \pi}{2kT} \right)^{1/2} \quad (4.35)$$

The number of complexes crossing the potential barrier through distance d per unit time is

$$\frac{d[\ddagger]}{dt} = \frac{\frac{[\ddagger]}{2}}{d \left(\frac{\pi m^\ddagger}{2kT} \right)^{1/2}} = \frac{[\ddagger]}{d} \left(\frac{kT}{2\pi m^\ddagger} \right)^{1/2} \quad (4.36)$$

Note that we are using $[\ddagger]$ to represent the transition state and $[\ddagger]$ to represent the *concentration* of the transition state. Now, the concentration

of the transition state, $[‡]$, is to be evaluated. If the difference between the zero-point energies of the reactants and the transition state is represented as $E_o^{‡}$, the equilibrium constant for formation of the transition state is given by

$$K^{‡} = \frac{Q^{‡}}{Q_A Q_B} e^{-\frac{E_o^{‡}}{RT}} \quad (4.37)$$

where Q_A, Q_B , and $Q^{‡}$ are the partition functions of reactants A and B and the transition state, respectively. If the vibrational mode of the transition state is factored out of Q we can write

$$Q^{‡} = Q^{‡'} \times q_v^{‡} \quad (4.38)$$

where $q_v^{‡}$ is the vibrational mode of the bond being broken. Now we can approximate the vibrational mode as

$$q_v^{‡} = \frac{1}{1 - e^{-\frac{h\nu}{kT}}} = \frac{kT}{h\nu^{‡}} \quad (4.39)$$

and the equilibrium constant $K^{‡}$ is given by

$$K^{‡} = \frac{kT}{h\nu^{‡}} \frac{Q^{‡'}}{Q_A Q_B} e^{-\frac{E_o^{‡}}{RT}} \quad (4.40)$$

which is of the same form found earlier with the rate constant, k , being given by

$$k = \frac{kT}{h} \frac{Q^{‡'}}{Q_A Q_B} e^{-\frac{E_o^{‡}}{RT}} \quad (4.41)$$

The resemblance of this equation to the Arrhenius equation is apparent when the pre-exponential factor includes the frequency factor and the equilibrium constant in terms of partition functions. This expression for k is similar to that obtained from collision theory.

An approximate rate constant, k_a , can be calculated from probability that the reactants in the distribution of quantum state will collide and react in accord with the collision frequency. The approximate constant is greater than the measured rate constant, k . One approach to improving transition state theory with respect to calculating the rate constant is to alter the configuration of the transition state used in the energy calculations in order to effect a change in k_a . In fact, the calculations are performed in such a way that the calculated rate constant is a minimum and thereby approaches the observed k . Just as energy minimization is accomplished by means of the

variation method in quantum mechanical calculations, this procedure is referred to in this connection as *variational transition state theory*.

Because the free energy of activation is given by

$$\Delta G^\ddagger = -RT \ln K^\ddagger \quad (4.42)$$

this procedure amounts to configuration optimization to minimize K^\ddagger or maximize ΔG^\ddagger . In practice, a series of transition states is considered and the calculations are performed to obtain the desired minimization. It is of some consequence to choose the reaction path with respect to the energy surface. Generally, the path chosen is the path of steepest descent on either side of the saddle point. This path represents the path of minimum energy. While the details will not be presented here, the rate constant can now be treated as a function of a coordinate related parameter, z , so that

$$k(z)^{\text{VT}} = \frac{\mathbf{kT}}{h} \frac{Q^{\text{VT}}}{Q_A Q_B} e^{-\frac{E(z)}{RT}} \quad (4.43)$$

The parameter z is related to the path (chosen as a function of coordinates) of the transition state. This expression can also be written as

$$k(z)^{\text{VT}} = \frac{\mathbf{kT}}{h} K^\ddagger e^{-\frac{\Delta G^\ddagger(z)}{RT}} \quad (4.44)$$

The value of $k(z)^{\text{VT}}$ can now be minimized with respect to z . Accordingly, the rate constant is minimized with respect to a parameter related to configuration of the transition state in the same way that energy is minimized with respect of variables in a trial wave function. Although this topic will not be described further here, details have been published in several places (for example, see Truhlar, 1980).

4.4 UNIMOLECULAR DECOMPOSITION OF GASES

The collision theory of gaseous reactions requires two molecules to collide, suggesting that such reactions should be second-order. Many decompositions, e.g., N_2O_5 , appear to be first-order at sufficiently high pressures of the gas. However, some such reactions do appear to be second-order at low gas pressure. In 1922, Lindemann proposed an explanation of these observations.

Molecules transfer energy as a result of molecular collisions. Therefore, translational energy can be transferred to one molecule by another thereby

raising the translational and vibrational energy of the second molecule. The activation of molecules by collision can thus be accomplished. However, the activated molecule need not react immediately, and, in fact, it may become deactivated by undergoing subsequent collisions before it reacts. For reaction to occur, the activated molecule that has increased vibrational energy must have some bond activated to the point where bond rupture occurs.

The elementary reactions by which A is converted into products can be shown as



In this scheme, A^* is the activated molecule of A. Although the process producing A^* is bimolecular, the decomposition of A^* is unimolecular. The change in $[A]$ with time can be expressed by the equation

$$-\frac{d[A]}{dt} = k_1[A]^2 - k_{-1}[A][A^*] \quad (4.47)$$

Since A^* is an activated molecule, a reactive intermediate, the steady state approximation is assumed to apply (see Section 2.4). The rate of formation of A^* is assumed to be equal to its rate of decomposition. Therefore,

$$\frac{d[A^*]}{dt} = 0 = k_1[A]^2 - k_{-1}[A][A^*] - k_2[A^*] \quad (4.48)$$

The first term on the right-hand side of the equation represents the rate of activation of A while the second and third terms represent deactivation and decomposition of A^* , respectively. Solving Eq. (4.48) for $[A^*]$, we obtain

$$[A^*] = \frac{k_1[A]^2}{k_{-1}[A] + k_2} \quad (4.49)$$

Substituting this result in Eq. (4.47), we obtain

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \quad (4.50)$$

At high pressures, the number of A molecules per unit volume is large, and deactivation of A^* can occur by frequent collisions with other molecules of A. Under these conditions, we will consider the rate of deactivation

of A^* to be large compared to the rate of decomposition. Therefore, $k_{-1}[A] \gg k_2$ and

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_{-1}[A] + k_2} \approx \frac{k_1 k_2 [A]^2}{k_{-1}[A]} = k[A] \quad (4.51)$$

where $k = k_1 k_2 / k_{-1}$. Therefore, at relatively high pressure where $[A]$ is high, the reaction appears to be unimolecular (first-order) in $[A]$.

At low pressures of A , the rate of decomposition of A^* is greater than the rate of its deactivation by collision with A because there are fewer molecules of A available. Under these conditions, the increase in vibrational energy can cause bond rupture and decomposition. Therefore, in this case, $k_2 \gg k_{-1}[A]$ and

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A]^2}{k_2} = k_1 [A]^2 \quad (4.52)$$

This equation shows that at low pressures of the reacting gas, the reaction should be bimolecular (second-order). Thus, the observed bimolecular dependence at low pressure and the unimolecular dependence at high pressure are predicted by a mechanism involving activation of molecules by collision.

The activation of reactant molecules by collision was described earlier. However, this is not the only vehicle for molecular activation. It is possible for a non-reactant gas (a so-called third body) to cause activation of molecules of the reactant. If we represent such a species by M , the processes of activation, deactivation, and product production are given by



Therefore, the rate of disappearance of A can be written as

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] \quad (4.55)$$

The net change in concentration of A^* with time is given by the difference between the rate at which it is formed as represented in Eq. (4.53) and the rate at which it is removed by undergoing reaction as shown in Eq. (4.54).

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0 \quad (4.56)$$

Therefore, rearrangement gives

$$0 = k_1[A][M] - (k_{-1}[M] + k_2)[A^*] \quad (4.57)$$

and solving for $[A^*]$ yields

$$[A^*] = \frac{k_1[A][M]}{k_{-1}[M] + k_2} \quad (4.58)$$

Substituting for $[A^*]$ in Eq. (4.55) gives

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[M] \frac{k_1[A][M]}{k_{-1}[M] + k_2} \quad (4.59)$$

Factoring out the quantity $k_1[A][M]$ on the right-hand side enables us to write this equation in the form

$$-\frac{d[A]}{dt} = k_1[A][M] \left(1 - \frac{k_{-1}[M]}{k_{-1}[M] + k_2} \right) \quad (4.60)$$

The quantity inside the parentheses can be made into a single fraction to give

$$-\frac{d[A]}{dt} = k_1[A][M] \left(\frac{k_{-1}[M] + k_2}{k_{-1}[M] + k_2} - \frac{k_{-1}[M]}{k_{-1}[M] + k_2} \right) \quad (4.61)$$

This equation can now be written as

$$-\frac{d[A]}{dt} = k_1[A][M] \left(\frac{k_{-1}[M] + k_2 - k_{-1}[M]}{k_{-1}[M] + k_2} \right) \quad (4.62)$$

and simplified to obtain

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [M][A]}{k_{-1}[M] + k_2} \quad (4.63)$$

The results obtained by considering activation by a third body must now be compared to those described earlier for activation by collision of reactant molecules.

At high pressure, the rate of deactivation by collisions with M is likely to be greater than the rate of reaction, so $k_{-1}[M] \gg k_2$ and neglecting k_2 in the denominator of Eq. (4.63) gives

$$-\frac{d[A]}{dt} \approx \frac{k_1 k_2 [M][A]}{k_{-1}[M]} \approx k'[A] \quad (4.64)$$

This approximation shows that the reaction follows a first-order rate law. At low pressure, the concentration of M is low, so $k_{-1}[M] \ll k_2$ and

$$-\frac{d[A]}{dt} \approx \frac{k_1 k_2 [M][A]}{k_2} \approx k_1 [A][M] \quad (4.65)$$

Therefore, the reaction appears to be first-order in A and first-order in M. If the species M is simply another molecule of reactant A, this equation becomes

$$-\frac{d[A]}{dt} = k_1 [A]^2 \quad (4.66)$$

which is the second-order rate expression found earlier. These results are in accord with experience for the unimolecular decomposition of a large number of gaseous compounds.

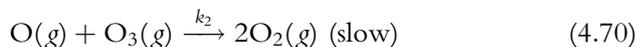
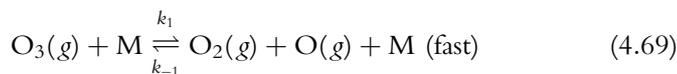
Ozone decomposes by a mechanism that appears to be somewhat different from that described earlier, but it provides a rather simple application of the steady state approximation. The overall reaction is



for which the observed rate law is

$$-\frac{d[\text{O}_3]}{dt} = \frac{k[\text{O}_3]^2}{[\text{O}_2]} \quad (4.68)$$

Therefore, the reaction is second-order in ozone but the reaction is inhibited by O_2 . This reaction is believed to involve a third body (an inert molecule or particle) in the steps



The rate constant for the second reaction is much smaller than that for the first, so the second reaction is rate determining. Therefore, the rate equation is written as

$$-\frac{d[\text{O}_3]}{dt} = k_2 [\text{O}][\text{O}_3] \quad (4.71)$$

The rate of O formation is given by

$$\frac{d[\text{O}]}{dt} = k_1 [\text{M}][\text{O}_3] \quad (4.72)$$

and the rate of consumption of O is

$$-\frac{d[\text{O}]}{dt} = k_{-1}[\text{M}][\text{O}][\text{O}_2] \quad (4.73)$$

Therefore, applying the steady state approximation,

$$k_1[\text{M}][\text{O}_3] = k_{-1}[\text{M}][\text{O}][\text{O}_2] \quad (4.74)$$

Solving this equation for [O] we obtain

$$[\text{O}] = \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} \quad (4.75)$$

which when substituted in Eq. (4.71) gives

$$-\frac{d[\text{O}_3]}{dt} = k_2[\text{O}_3] \cdot \frac{k_1[\text{O}_3]}{k_{-1}[\text{O}_2]} = k \frac{[\text{O}_3]^2}{[\text{O}_2]} \quad (4.76)$$

This is the form of the observed rate law where $k = k_1k_2/k_{-1}$.

The approach of Lindemann is based on collisional activation of molecules as a result of energy transfer. C. N. Hinshelwood (Nobel Prize in 1956) extended this approach to include changes in vibrational energies that can be distributed internally to supply sufficient energy to the bond being broken. This approach provided a better fit to observed kinetics in the region of low pressure.

In the late 1920s, O. K. Rice and H. C. Ramsperger as well as L. S. Kassel developed an approach (now known as the RRK theory) to unimolecular decomposition reactions which is based on statistically treating the molecules as coupled oscillators. In this way, energy is presumed to be distributed about the energized molecule until it vibrates in a way that results in bond rupture. In this treatment, it is assumed that the amount of energy, E^* , must be localized in the bond being broken and that the probability of this happening is given by

$$P = \left(\frac{E - E^*}{E} \right)^{N-1} \quad (4.77)$$

where N is the number of vibrational modes ($3N - 5$ for linear molecules and $3N - 6$ for nonlinear molecules). The rate constant is presumed proportional to the probability, so it is given by

$$k = \left(\frac{E - E^*}{E} \right)^{N-1} \quad (4.78)$$

It can then be shown that at high pressure

$$k = e^{-E^*/kT} \quad (4.79)$$

A later modification of the RRK theory presented by R. A. Marcus (*J. Chem. Phys.*, 1952, 20, 359) (Nobel Prize in 1992) resulted in the so-called RRKM theory. In this case, the mechanism of the reaction consists of the following steps



The essential idea is that the activated *molecule*, A^* , becomes the *transition state* or *activated complex*, A^\ddagger , which then leads to product formation. This is presumed to occur when the energy at the reactive site becomes as large as E_a , the activation energy. The rate at which A^* is transformed into A depends on the number of degrees of vibrational freedom. Therefore, the theory is concerned with the treatment of the vibrational frequencies of A^* and A in the calculations.

From the preceding processes, we can write the rate law

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] \quad (4.83)$$

Applying the steady state approximation with regard to A^* gives

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_{-1}[A^*][M] - k_2[A^*] = 0 \quad (4.84)$$

Therefore, the concentration of A^* can be expressed as

$$[A^*] = \frac{k_1[A][M]}{k_2 + k_{-1}[M]} \quad (4.85)$$

From Eq. (4.84), we find that

$$k_{-1}[A^*][M] = k_1[A][M] - k_2[A^*] \quad (4.86)$$

Therefore, substituting for $k_{-1}[A^*][M]$ in Eq. (4.83) yields

$$-\frac{d[A]}{dt} = k_1[A][M] - k_{-1}[A^*][M] = k_1[A][M] - (k_1[A][M] - k_2[A^*]) \quad (4.87)$$

which can be simplified to obtain

$$-\frac{d[A]}{dt} = k_2[A^*] \quad (4.88)$$

Now, substituting the expression shown in Eq. (4.85) for $[A^*]$ gives

$$-\frac{d[A]}{dt} = \frac{k_1 k_2 [A][M]}{k_2 + k_{-1}[M]} = \left(\frac{k_1 k_2 [M]}{k_2 + k_{-1}[M]} \right) [A] \quad (4.89)$$

We can now consider the quantity in brackets as the rate constant for the formation of product or disappearance of A. If $k_{-1}[M] \gg k_2$, the equation reduces to

$$-\frac{d[A]}{dt} = k'[A] \quad (4.90)$$

where $k' = k_1 k_2 / k_{-1}$ and the reaction appears to be first-order in A. If $k_2 \gg k_{-1}[M]$, the rate shown in Eq. (4.89) becomes

$$-\frac{d[A]}{dt} = k_1 [A][M] \quad (4.91)$$

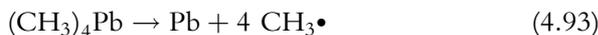
and, when the third body, M, is a second molecule of A, the equation becomes

$$-\frac{d[A]}{dt} = k_1 [A]^2 \quad (4.92)$$

Therefore, the reaction shows a second-order dependence on A. Many of the details of the Marcus theory can be found in the book by Nicholas (1976).

4.5 FREE RADICAL OR CHAIN MECHANISMS

Some of the elementary concepts of free radical mechanisms were presented in Chapter 1. Reactions following free radical mechanisms have reactive intermediates containing unpaired electrons which are produced by homolytic cleavage of covalent bonds. A method of detecting free radicals was published in 1929, and it is based on the fact that metals such as lead react with free radicals. When heated, tetramethyl lead decomposes,



A lead mirror is produced in a heated glass tube when tetramethyl lead is passed through it. Also, the lead mirror in a cool portion of the tube can be

removed by passing tetramethyl lead through a hot portion of the tube first to produce $\text{CH}_3\bullet$ radicals. In the cool portion of the tube, the reaction is



However, if the flow system is arranged so that a long tube is used and considerable distance separates the point where the $\text{CH}_3\bullet$ radicals are generated and they react with the cool lead mirror, the reaction is hindered because of radical recombination.



Perhaps the best known example of a chain process, certainly it is the classic case, is the reaction



This reaction was studied by Bodenstein and Lind nearly 90 years ago, and the rate law found was written as

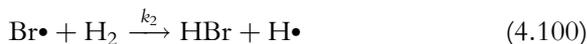
$$\frac{d[\text{HBr}]}{dt} = \frac{k[\text{H}_2][\text{Br}_2]^{1/2}}{1 + k' \left(\frac{[\text{HBr}]}{[\text{Br}_2]} \right)} \quad (4.97)$$

where k and k' are constants with $k' = 10$. The $[\text{HBr}]$ in the denominator indicates that the rate is decreased as $[\text{HBr}]$ increases so that HBr functions as an inhibitor. The reaction has now been studied both thermally and photochemically and the initiation step is now agreed to be



The overall reaction scheme was postulated in 1919 by Christiansen, Herzfeld, and Polyani in three separate publications.

The overall process is now described in terms of the elementary steps



Simplification of the mathematical problem is achieved by application of the steady state hypothesis to those species that occur only in the propagation steps. In this case, it is assumed that $[\text{Br}\bullet]$ and $[\text{H}\bullet]$ are at some low, essentially constant level. Therefore,

$$\frac{d[\text{Br}\bullet]}{dt} = 0 \text{ and } \frac{d[\text{H}\bullet]}{dt} = 0 \quad (4.104)$$

Following the same type of treatment as was used in cases described in Chapter 2, we express $[\text{Br}\bullet]$ and $[\text{H}\bullet]$ in terms of their rates of formation and disappearance. Therefore, for simplicity using $[\text{H}]$ and $[\text{Br}]$ instead of $[\text{H}\bullet]$ and $[\text{Br}\bullet]$, we can write the equation giving the change in concentration of H with time from the preceding elementary steps as

$$\frac{d[\text{H}]}{dt} = k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] = 0 \quad (4.105)$$

The equation giving the change in concentration of Br with time can be written as

$$\frac{d[\text{Br}]}{dt} = 2k_1[\text{Br}_2] - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 = 0 \quad (4.106)$$

Now we can also write the equation that gives the production of HBr as

$$\frac{d[\text{HBr}]}{dt} = k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \quad (4.107)$$

If we subtract Eq. (4.105) from Eq. (4.107), while letting $d[\text{H}]/dt = 0$, we obtain

$$\begin{aligned} \frac{d[\text{HBr}]}{dt} - 0 &= k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] \\ &\quad - \{k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}]\} \end{aligned} \quad (4.108)$$

Simplification of this equation leads to

$$\frac{d[\text{HBr}]}{dt} = 2k_3[\text{H}][\text{Br}_2] \quad (4.109)$$

Adding Equations (4.105) and (4.106) gives

$$\begin{aligned} 0 &= k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] + 2k_1[\text{Br}_2] \\ &\quad - k_2[\text{Br}][\text{H}_2] + k_3[\text{H}][\text{Br}_2] + k_4[\text{H}][\text{HBr}] - 2k_5[\text{Br}]^2 \end{aligned} \quad (4.110)$$

which can be simplified to give

$$2k_1[\text{Br}_2] - 2k_5[\text{Br}]^2 = 0 \quad (4.111)$$

Solving this equation for $[\text{Br}]$ yields

$$[\text{Br}] = \{(k_1/k_5)[\text{Br}_2]\}^{1/2} \quad (4.112)$$

Substitution of this value for $[\text{Br}]$ in Eq. (4.105) gives

$$\begin{aligned} k_2[\text{Br}][\text{H}_2] - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] &= k_2\{(k_1/k_5)[\text{Br}_2]\}^{1/2}[\text{H}_2] \\ - k_3[\text{H}][\text{Br}_2] - k_4[\text{H}][\text{HBr}] &= 0 \end{aligned} \quad (4.113)$$

$$k_2\{(k_1/k_5)[\text{Br}_2]\}^{1/2}[\text{H}_2] - [\text{H}](k_3[\text{Br}_2] - k_4[\text{HBr}]) = 0 \quad (4.114)$$

Solving this equation for $[\text{H}]$ yields

$$[\text{H}] = \frac{k_2\left(\frac{k_1}{k_5}[\text{Br}_2]\right)^{1/2}[\text{H}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (4.115)$$

Substituting this result for $[\text{H}]$ in Eq. (4.109) we obtain

$$\frac{d[\text{HBr}]}{dt} = 2k_3[\text{H}][\text{Br}_2] = \frac{2k_2k_3\left(\frac{k_1}{k_5}[\text{Br}_2]\right)^{1/2}[\text{H}_2][\text{Br}_2]}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (4.116)$$

This equation can be simplified to obtain

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2k_3\left(\frac{k_1}{k_5}\right)^{1/2}[\text{H}_2][\text{Br}_2]^{3/2}}{k_3[\text{Br}_2] + k_4[\text{HBr}]} \quad (4.117)$$

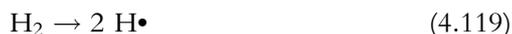
Dividing numerator and denominator of the right-hand side of this equation by $k_3[\text{Br}_2]$ gives

$$\frac{d[\text{HBr}]}{dt} = \frac{2k_2\left(\frac{k_1}{k_5}\right)^{1/2}[\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k_4[\text{HBr}]}{k_3[\text{Br}_2]}} \quad (4.118)$$

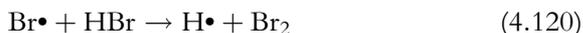
If we let $k = 2k_2(k_1/k_5)^{1/2}$ and $k' = k_4/k_3$, Eq. (4.118) has the same form as the empirical rate law shown in Eq. (4.97). We need now to examine the relationships between the rate constants. The bond energies for the molecular species in Steps 3 and 4 (Eqs. (4.101) and (4.102)) are as follows:

H—H, 436; Br—Br, 193; and H—Br, 366 kJ/mol. Therefore, both Steps 3 and 4 are exothermic having enthalpies of about -173 and -70 kJ/mol, respectively. Activation energies for forming the transition states $[\text{H}\cdot\cdot\cdot\text{Br}\cdot\cdot\cdot\text{Br}]$ and $[\text{H}\cdot\cdot\cdot\text{H}\cdot\cdot\cdot\text{Br}]$ are very low so there will be almost no temperature dependence on the rates of their formation and the temperature effects will approximately cancel. Therefore, the ratio k_4/k_3 is constant, having a value of 10.

Other reactions in the chain process could conceivably include



but the bond energy for H_2 is about 436 kJ/mol while that for Br_2 is 193 kJ/mol. Consequently, any dissociation involving H_2 would be insignificant compared to the dissociation of Br_2 . Likewise, the dissociation of HBr to give $\text{H}\cdot$ and $\text{Br}\cdot$ would be energetically unfavorable as would the reaction



Finally, the reactions



can be considered as unlikely at best owing to the very low stationary state concentrations of these $\text{H}\cdot$ radicals. There are other arguments against these processes as well.

Radicals are generated, consumed, or propagated by a relatively few types of elementary reactions. Radical generation usually involves the homolytic dissociation of some covalent bond.



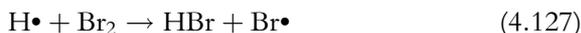
In this case, the process is a high-energy one so it is usually brought about by thermal, photochemical, or electrical means. The consumption of radicals occurs in termination steps, which include processes like



The propagation of radicals can involve a transfer of atoms, which can be shown as



The reaction



is a previously seen example. In other cases, a radical may add to another molecule to produce a different radical.



An example of this type of process is



All of these processes as well as numerous examples of each type are discussed more fully by Nicholas (1976).

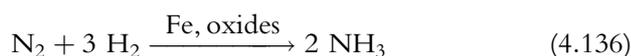
A further complication of chain mechanisms is the process known as *branching*. In this case, one radical results in more than a single radical being produced so the number of radicals present is increasing as the reaction proceeds. This results in an autocatalytic reaction that may, as in the reaction of H_2 and O_2 , lead to an explosion under certain conditions. The reaction of H_2 and O_2 is a very complicated process that depends on the pressure of the gases, the temperature, and the type of reaction vessel. Some of the reactions involved under certain conditions are believed to be the following, although other steps may also be involved.

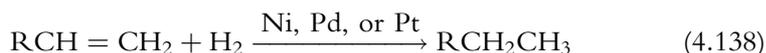


The overall mechanism is quite complex, and the reader is referred to other sources dealing with gas phase reactions for details (Nicholas, 1976).

4.6 ADSORPTION OF GASES ON SOLIDS

A large number of reactions, many of them of great technological importance, involve the reaction of gases on solid surfaces. The reactions





are but a few examples of such cases. Although it is appropriate to consider such interfacial processes in terms of the nature of the solids, the fact that the reactants are gases makes it logical to include this topic as part of the treatment of reactions in the gas phase. When a solid catalyzes a reaction, the gaseous reactants are attached in some way before the reaction takes place. *Heterogeneous catalysis* is a process in which a solid has gaseous reactants attached that subsequently react. Consequently, it is necessary to begin a discussion of heterogeneous catalysis by describing the process of adsorption in some detail.

In the interior of a solid lattice, each unit (atom, molecule, or ion) is surrounded by others on all sides. On the surface, the units are not surrounded on one side and, therefore, they can form bonds to other species. While this process may take place by adsorption of molecules or ions from solutions, we are more concerned here with adsorption of gaseous molecules. It is also possible for gaseous reactants to penetrate below the surface of the solid in some cases. The sites on the solid where the gases are adsorbed are called *active sites*. The solid material doing the adsorbing is called the *adsorbent* and the substance adsorbed is called the *adsorbate*.

Interactions between adsorbates and adsorbents cover a wide range of energies. On the one hand, the interactions may be the result of weak van der Waals forces, while on the other, the bonds may represent strong chemical bonding of the adsorbate to the adsorbent. The distinction is not always a clear one, but physical adsorption (*physisorption*) is generally associated with heats of adsorption of 10–25 kJ/mol, while chemical adsorption (*chemisorption*) is associated with heats of adsorption of 50–100 kJ/mol. In either case, there is presumed to be a relationship between energy and the relative adsorbent/adsorbate position on the surface similar to that shown in Figure 4.4.

In general, it is believed that in cases of physical adsorption the bonding to the surface is so weak that the adsorbent molecules are changed only very slightly by the adsorption process. Therefore, physical adsorption does not weaken the bonds in the adsorbate molecules significantly, and the adsorbent does not function as a catalyst.

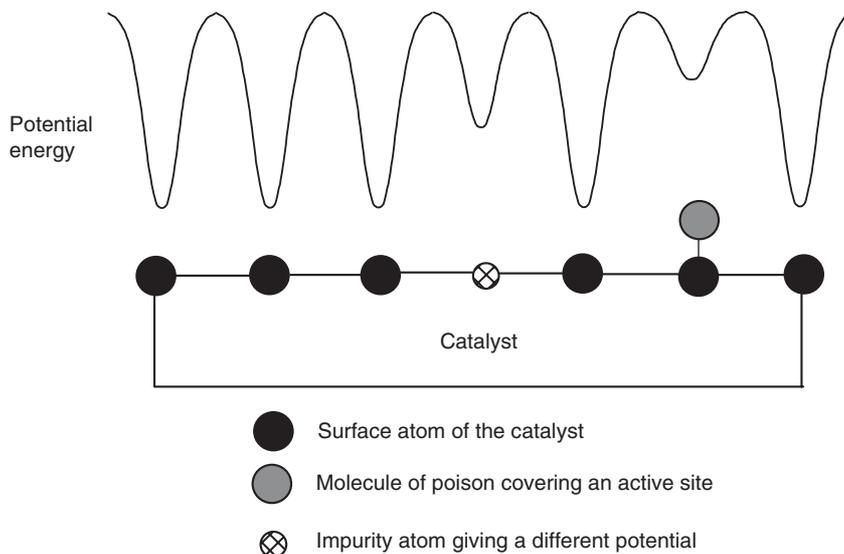


FIGURE 4.4 Variation in potential energy near the surface of a solid catalyst.

On an atomic scale, adsorption can be considered by quantum mechanical techniques. In this treatment, it is assumed that the forces between the adsorbate and the adsorbent are essentially chemical in nature. In that case, the interaction energy is calculated using techniques that are the standard ones in molecular quantum mechanics. However, the energy of a molecule being adsorbed on the surface of a solid is related to distance from the adsorbing site in such a way that the relationship results in a potential energy curve similar to the Morse potential for a diatomic molecule (see Figure 4.3). Calculations should produce curves of similar shape, and the calculated energies should match the measured energies. This is a rather formidable task and the results are not always good. Significant progress has been made in this area using extended Hückel molecular orbital (EHMO), self-consistent field (SCF), and complete neglect of differential overlap (CNDO) approaches. A brief review of these results has been given by White (1990). We will now turn our attention to describing the process of adsorption from a bulk macroscopic point of view.

4.6.1 Langmuir Adsorption Isotherm

For chemisorption, one of the most successful approaches for describing the quantitative relationships is that developed by Irving Langmuir. In this

approach, it is assumed that the adsorption process is taking place isothermally and that the uniform adsorbent surface can be covered with a monolayer of adsorbate. Further, it is assumed that there is no interaction between adsorbed molecules and that the available sites all have the same affinity for the gaseous adsorbent.

If the area of the adsorbent is represented as A and the fraction of the surface that is covered by adsorbate is f , we can derive the relationship for adsorption as follows. For an equilibrium involving adsorption, we can let the rate of condensation be equal to the rate of evaporation. The rate of evaporation will be proportional to f , the fraction of the surface covered, while the rate of condensation will be proportional to $(1-f)$, the fraction of the surface which is uncovered, and the pressure of the gas. Therefore, when these rates are equal, we can write

$$k_c(1-f)P = k_e f \quad (4.140)$$

If this equation is solved for f , we obtain

$$f = \frac{k_c P}{k_e + k_c P} \quad (4.141)$$

where P is the pressure of the gas. Dividing both the numerator and denominator of the right-hand side of Eq. (4.141) by k_e and letting $K = k_c/k_e$ gives

$$f = \frac{KP}{1 + KP} \quad (4.142)$$

This relationship, known as the *Langmuir isotherm*, is shown graphically in Figure 4.5.

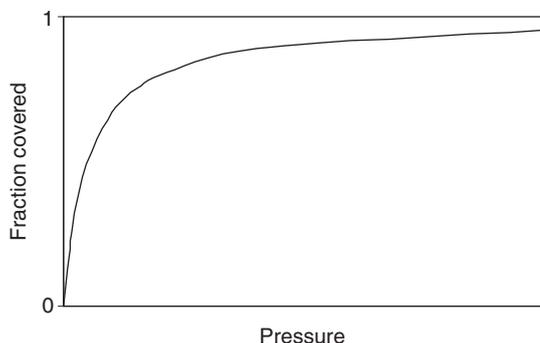


FIGURE 4.5 The Langmuir isotherm for adsorption.

Taking the reciprocal of both sides of Eq. (4.142) gives

$$\frac{1}{f} = \frac{1 + KP}{KP} = 1 + \frac{1}{KP} \quad (4.143)$$

Therefore, when $1/f$ is plotted vs. $1/P$, a straight line having a slope of $1/K$ and an intercept of 1 results, as is shown in Figure 4.6.

The volume of gas adsorbed is proportional to the fraction of the surface covered,

$$V = V_o f \quad (4.144)$$

If the maximum volume adsorbed, V_m , represents complete coverage of the surface,

$$V_m = V_o A \quad (4.145)$$

If we let the area be equal to unity (a unit area), then $A = 1$ and $V/V_m = f$. Therefore,

$$\frac{V}{V_m} = f = \frac{KP}{1 + KP} \quad (4.146)$$

which is another form of the Langmuir isotherm. This relationship provides the basis for the volumetric measurement of the number of moles of gas adsorbed as a function of gas pressure.

If two gases, A and B, are being adsorbed, the fraction of the surface area that remains uncovered is $1 - f_A - f_B$. If we describe the rate of condensation of A in terms of a rate constant for condensation, k_c , as

$$\text{Condensation rate} = k_c P_A (1 - f_A - f_B) \quad (4.147)$$

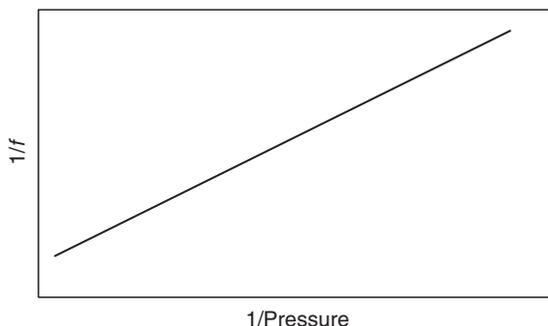


FIGURE 4.6 A reciprocal plot for the Langmuir isotherm.

and the rate of evaporation of A can be expressed in terms of the rate constant for evaporation, k_e , as

$$\text{Evaporation rate} = k_e f_A \quad (4.148)$$

at equilibrium the rates will be equal so we can write

$$k_e f_A = k_c P_A (1 - f_A - f_B) \quad (4.149)$$

or, since k_c/k_e is the equilibrium constant for adsorption, K_A , we obtain the relationship

$$K_A P_A = \frac{f_A}{1 - f_A - f_B} \quad (4.150)$$

For gas B, the corresponding equation is

$$K_B P_B = \frac{f_B}{1 - f_A - f_B} \quad (4.151)$$

Therefore, the fraction covered by A and B can be found by solving these equations for f_A and f_B . We will illustrate this procedure by solving for f_A .

Equation (4.150) can be written as

$$f_A = K_A P_A (1 - f_A - f_B) = K_A P_A - f_A K_A P_A - f_B K_A P_A \quad (4.152)$$

Solving this equation for f_B gives

$$f_B = \frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} \quad (4.153)$$

Equation (4.151) can be written as

$$f_B = K_B P_B (1 - f_A - f_B) \quad (4.154)$$

Therefore, substituting the value for f_B shown in Eq. (4.153), Eq. (4.154) becomes

$$\frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} = K_B P_B \left[1 - f_A - \frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} \right] \quad (4.155)$$

Collecting terms in the brackets over a common denominator gives

$$\frac{K_A P_A - f_A K_A P_A - f_A}{K_A P_A} = K_B P_B \left[\frac{K_A P_A - f_A K_A P_A - K_A P_A + f_A K_A P_A + f_A}{K_A P_A} \right] \quad (4.156)$$

Multiplying both sides of this equation by $K_A P_A$ and simplifying yields

$$K_A P_A - f_A K_A P_A - f_A = f_A K_B P_B \quad (4.157)$$

Modifying this equation by collecting terms containing f_A and factoring out f_A leads to

$$f_A(1 + K_A P_A + K_B P_B) = K_A P_A \quad (4.158)$$

This equation can be solved for f_A to give

$$f_A = \frac{K_A P_A}{1 + K_A P_A + K_B P_B} \quad (4.159)$$

By analogous procedures, it is possible to show that

$$f_B = \frac{K_B P_B}{1 + K_A P_A + K_B P_B} \quad (4.160)$$

If the pressure of gas B is 0 or if B interacts weakly with the adsorbent so that $K_B \approx 0$, Eq. (4.159) reduces to

$$f_A = \frac{K_A P_A}{1 + K_A P_A} \quad (4.161)$$

which is equivalent to Eq. (4.142) shown earlier for the adsorption of a single gas.

4.6.2 B-E-T Isotherm

The relationship between extent of adsorption and gas pressure shown in Figure 4.5 is by no means the only relationship known. Strictly, it applies only when maximum adsorption results in a monolayer of adsorbate on the surface. Two of the other observed types of adsorption behavior are shown in Figure 4.7.

These processes are associated with the formation of multilayers of adsorbate. The equation that can be derived to describe the formation of multilayers is

$$\frac{P}{V(P^\circ - P)} = \frac{1}{V_m c} + \left(\frac{c - 1}{V_m c} \right) \frac{P}{P^\circ} \quad (4.162)$$

where V is the volume of adsorbed gas at standard conditions, P and T are the pressure and temperature of the gas, P° is the saturated vapor pressure of the adsorbate, V_m is the volume of adsorbate at standard conditions required

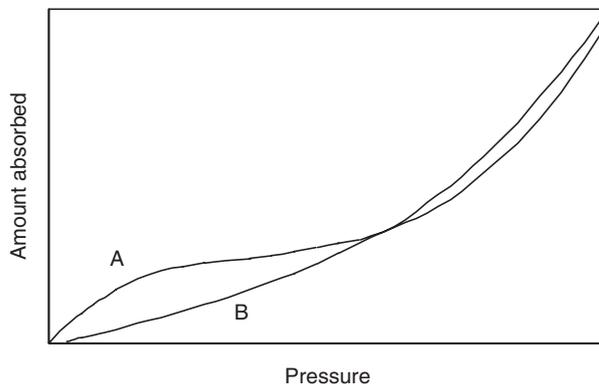


FIGURE 4.7 Adsorption isotherms for a case where there is formation of multilayers.

to give a monolayer, and c is a constant. This equation, known as the *B–E–T isotherm*, is named after Brunauer, Emmett, and Teller, who developed it. The constant c is related to the heat of adsorption of a monolayer, E_{ad} , and the heat of liquefaction of the gas, E_{liq} , by the relationship

$$c = e^{-(E_{ad}-E_{liq})/RT} \quad (4.163)$$

An adsorption isotherm of the type shown as Curve A in Figure 4.7 results when $E_{ad} > E_{liq}$, and an isotherm of the type shown as Curve B in Figure 4.7 corresponds to the case where $E_{liq} > E_{ad}$. While the B–E–T approach is more successful in dealing with more complex adsorption cases, we need not discuss its application further. Details on the derivation and use of the equation can be found in the book by White (1990).

4.6.3 Poisons and Inhibitors

For many catalysts, the presence of very small amounts of certain substances greatly reduces the effectiveness of the catalysts. These substances are usually designated as *poisons* or *inhibitors*. In some cases, the action of the poison persists only as long as the poison is present in contact with the catalyst. The poison may be one of the products of the reaction, in which case the concentration or pressure of the substance appears in the denominator of the rate law. The poison is adsorbed more strongly than the reactants, but once it is removed the catalyst recovers its activity.

Permanent catalyst poisoning occurs when some material reacts with the catalyst to form a chemically altered surface that no longer retains catalytic

properties. A wide range of cases of this type exist. Compounds containing silicon, lead (do not use lead-containing gasoline in an automobile with a catalytic converter!), sulfur, arsenic, phosphorus, etc., along with H_2S and CO , are particularly effective poisons toward metallic catalysts. Some of these poisons also inhibit enzyme action and are toxic to animals as well (Chapter 6).

Figure 4.4 shows a poison atom or molecule occupying a site on a solid catalyst. Because of that interaction, there is a very small residual potential for binding an adsorbate. Figure 4.4 is in some ways misleading in that not every surface atom is an active site. The fact that very small amounts of poisons can destroy catalytic activity suggests that the catalytic activity is confined to a rather small fraction of the total surface. In some cases, it has been found that the active sites are associated with metal atoms in an environment where there are highly unsaturated forces such as for the atoms along a ridge, crack, or pore.

We saw earlier that when a second gas is competing with the reactant for the active sites on the catalyst the fraction of the catalyst covered by the reactant (A) was decreased. If the inhibitor or poison is designated as X, we find

$$f_A = \frac{K_A P_A}{1 + K_A P_A + K_X P_X} \quad (4.164)$$

If the inhibitor has a large equilibrium constant for adsorption, $1 + K_X P_X \gg K_A P_A$ and

$$f_A \approx \frac{K_A P_A}{1 + K_X P_X} \quad (4.165)$$

the rate of the reaction of A (represented as R) will be $k f_A$, or

$$R \approx \frac{k K_A P_A}{1 + K_X P_X} \quad (4.166)$$

and at sufficiently high pressures of X, $K_X P_X \gg 1$, so the rate expression reduces to

$$R \approx \frac{k K_A P_A}{K_X P_X} \quad (4.167)$$

While the reaction is first-order in reactant A, the rate law contains the inhibitor function in the denominator, showing that the rate is decreased as the amount of inhibitor increases, in accord with the assessment presented earlier.

4.7 CATALYSIS

In reactions that are catalyzed by solid surfaces, it is the amount of *adsorbed* gas that determines the rate of the reaction. Therefore, the rate is proportional to the fraction of active sites covered, f .

$$\text{Rate} = kf \quad (4.168)$$

From the Langmuir isotherm (Eq. (4.142)), we determine that

$$\text{Rate} = k \frac{KP}{1 + KP} \quad (4.169)$$

If the reactant gas is one that is strongly adsorbed or if the pressure of the gas is high, the fraction of the surface covered approaches unity and $KP \gg 1$, so

$$\text{Rate} = kf \approx k \quad (4.170)$$

Therefore, the rate is independent of the pressure of the reacting gas and the reaction appears to be zero-order.

When the gas is only weakly adsorbed or the pressure is low, $1 \gg KP$ and

$$\text{Rate} = \frac{kKP}{1 + KP} \approx kKP \quad (4.171)$$

which shows the reaction to be first-order in the gaseous reactant. Figure 4.8 shows the behavior of reaction kinetics in these two limiting cases.

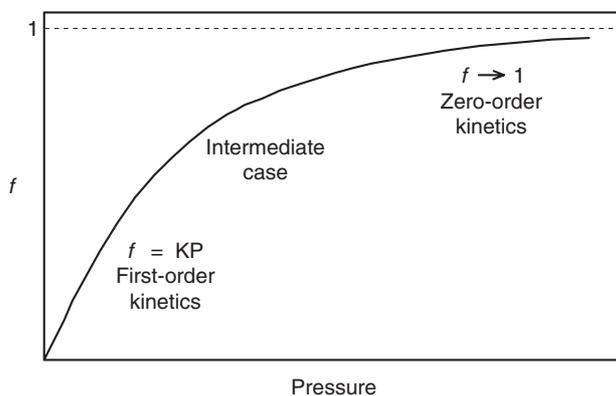


FIGURE 4.8 Kinetics of surface reactions based on the Langmuir adsorption isotherm.

In many instances, the progress of a gaseous reaction can be followed by the change in pressure of the reacting gas. If the reactant is A and its pressure is P_A , the rate equation for a first-order process is

$$-\frac{dP_A}{dt} = k'P_A \quad (4.172)$$

where $k' = kK$. By integration of this equation, we obtain

$$\ln \frac{P_{A,o}}{P_A} = k't \quad (4.173)$$

Such a rate law has been found to correctly model many reactions taking place on solid surfaces.

In the case where the gas is strongly adsorbed or the pressure is high, the process may follow a zero-order rate law. From Eq. (4.172), we see that the rate law can be written as

$$-\frac{dP_A}{dt} = k \quad (4.174)$$

which can be integrated to give

$$P_{A,o} - P_A = kt \quad (4.175)$$

This zero-order rate law has been found to correctly model the reaction of certain gases on the surfaces of solids.

Unfortunately, there are cases where neither of the limiting rate laws adequately represents the reaction as is illustrated in Fig. 4.8. For such intermediate cases,

$$\text{Rate} = kf = k \frac{KP}{1 + KP} \quad (4.176)$$

For a reactant A, the change in pressure of the gas can be used to measure the rate so that

$$-\frac{dP_A}{dt} = \frac{kKP_A}{1 + KP_A} \quad (4.177)$$

Rearranging this equation gives

$$-\frac{(1 + KP_A)}{KP_A} dP_A = k dt \quad (4.178)$$

which can also be written as

$$-\frac{dP_A}{KP_A} - dP_A = k dt \quad (4.179)$$

This equation can be simplified further before integration to give

$$-\frac{1}{K} \cdot \frac{dP_A}{P_A} - dP_A = k dt \quad (4.180)$$

This equation must be integrated between the limits of $P_{A,o}$ at time equals zero and P_A at time t . Therefore, integration of Eq. (4.180) leads to

$$-\frac{1}{K} (\ln P_A - \ln P_{A,o}) - (P_A - P_{A,o}) = kt \quad (4.181)$$

which also can be written as

$$\frac{1}{K} \ln \frac{P_{A,o}}{P_A} + (P_{A,o} - P_A) = kt \quad (4.182)$$

The similarity of this equation to Eq. (6.26) should be noted, since these equations illustrate the similarity between reactions of adsorbed gases on solids and substrates bound to enzyme active sites in enzyme catalysis.

It is also possible to perform kinetic analysis of reactions involving adsorption of gases on solids by representing the fraction of the surface-covered means of the *Freundlich isotherm*,

$$f = kP^n \quad (4.183)$$

where f is the fraction of the surface covered, P is the pressure of the gas, and k and n are constants. Rate laws for the intermediate cases (such as those that appear to be zero-order or first-order depending on the conditions) can be developed using this approximation.

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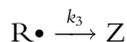
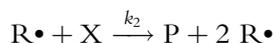
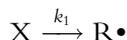
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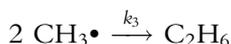
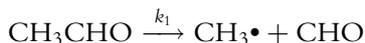
PROBLEMS

1. Unimolecular decompositions can appear to be first- or second-order under certain conditions. What assumptions were applied to the solution of this problem? Write out the mechanism for the unimolecular decomposition of $X(g)$ and derive the rate law. Explain how this rate law accounts for the observations on reaction order.
2. Suppose that a reaction follows the scheme



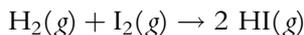
What is a reaction scheme like this called? Derive the rate expression giving $[R\bullet]$ as a function of time. Using your derived rate expression, explain what can happen when the concentration of X is varied between rather wide limits. What type of chemical event does this correspond to?

3. Consider the decomposition of CH_3CHO into CH_4 and CO , which is believed to take place in the steps

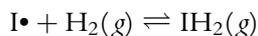


Use the steady state approximation to derive the rate law for the formation of CH_4 . What would the rate of formation of CO be?

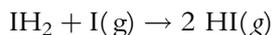
4. The rate of the reaction



is increased by electromagnetic radiation. Assuming that the radiation rapidly separates I_2 into $\text{I}\bullet$ and that the equilibrium



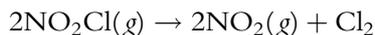
is reached rapidly, the slow step in the process is believed to be



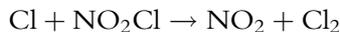
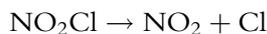
Show that this mechanism is consistent with a rate law of the form

$$\text{Rate} = k[\text{H}_2][\text{I}_2]$$

5. For the reaction

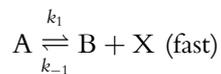


one possible mechanism is

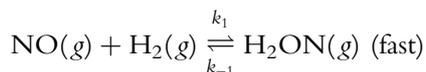


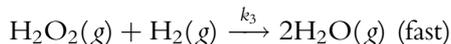
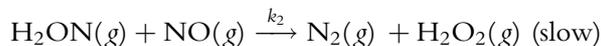
The observed rate law is $\text{Rate} = k[\text{NO}_2\text{Cl}]$. What does this tell about the mechanism?

6. Derive the rate law for the process represented by the following mechanism.



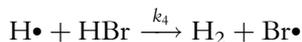
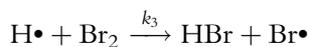
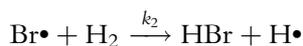
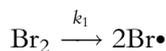
7. Consider the reaction scheme





Write the rate law for the overall reaction in terms of the steps just given. Apply the steady state approximation and obtain the final rate law.

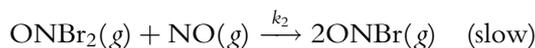
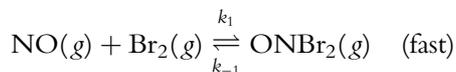
8. The reaction between H_2 and Br_2 has been described in terms of these steps:



Write the rate laws for the change in concentration of $\text{H}\bullet$, $\text{Br}\bullet$, and HBr with time. Apply the steady state approximation and show that the rate of formation of HBr is

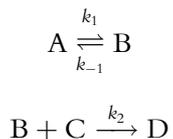
$$\frac{d[\text{HBr}]}{dt} = \left(\frac{k_1}{k_{-1}} \right)^{1/2} \frac{2k_2[\text{H}_2][\text{Br}_2]^{1/2}}{1 + \frac{k_4}{k_3} \frac{[\text{HBr}]}{[\text{Br}_2]}}$$

9. For each of the following, use the Langmuir isotherm and provide an interpretation for the observation. (a) The decomposition of gas X on solid S is zero-order. (b) The decomposition of gas Y on solid S is first-order. (c) The decomposition of NH_3 on a platinum surface is inversely proportional to the pressure of H_2 and directly proportional to the pressure of NH_3 .
10. The reaction of $\text{NO}(g)$ with $\text{Br}_2(g)$ produces $\text{ONBr}(g)$ and may take place in the steps



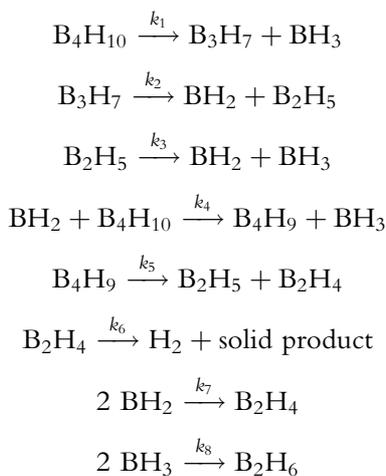
Assuming that $\text{ONBr}_2(g)$ establishes a steady state concentration, derive the rate law for the production of $\text{ONBr}(g)$.

11. Suppose a gaseous reaction takes place in the steps



Derive the rate law for the formation of D and show the limiting forms at high pressure and low pressure.

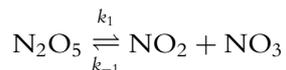
12. The decomposition of tetraborane-10, B_4H_{10} , is thought to take place in the following steps (Bond, A. C., Pinsky, M. L., *J. Am. Chem. Soc.* 1970, 92, 32).

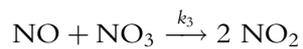
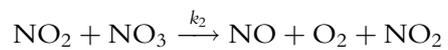


Make the steady state assumption regarding $\text{BH}_2, \text{BH}_3, \text{B}_2\text{H}_4, \text{B}_2\text{H}_5, \text{B}_3\text{H}_7$, and B_4H_9 , and show that the rate law is

$$-\frac{d[\text{B}_4\text{H}_{10}]}{dt} = k_1[\text{B}_4\text{H}_{10}] + \frac{k_4(2k_1)^{1/2}}{k_7^{1/2}}[\text{B}_4\text{H}_{10}]^{3/2}$$

13. The decomposition of N_2O_5 is believed to involve the following steps.





By making use of the steady state approximation with regard to the concentrations of the intermediates NO_3 and NO , derive the rate law for this process.