

# Chapter 6

## Fundamentals of Reaction Rates

In the preceding chapters, we are primarily concerned with an empirical macroscopic description of reaction rates, as summarized by rate laws. This is without regard for any description of reactions at the molecular or microscopic level. In this chapter and the next, we focus on the fundamental basis of rate laws in terms of theories of reaction rates and reaction "mechanisms."

We first introduce the idea of a reaction mechanism in terms of elementary reaction steps, together with some examples of the latter. We then consider various aspects of molecular energy, particularly in relation to energy requirements in reaction. This is followed by the introduction of simple forms of two theories of reaction rates, the *collision theory* and the *transition state theory*, primarily as applied to gas-phase reactions. We conclude this chapter with brief considerations of reactions in condensed phases, surface phenomena, and photochemical reactions.

### PRELIMINARY CONSIDERATIONS

#### Relating to Reaction-Rate Theories

As a model of real behavior, the role of a theory is twofold: (1) to account for observed phenomena in relatively simple terms (hindsight), and (2) to predict hitherto unobserved phenomena (foresight).

What do we wish to account for and predict? Consider the form of the rate law used for the model reaction  $A + \dots \rightarrow \text{products}$  (from equations 3.1-8 and 4.1-3):

$$(-r_A) = A \exp(-E_A/RT) \prod_{i=1}^N c_i^{\alpha_i} \quad (6.1-1)$$

We wish to account for (i.e., interpret) the Arrhenius parameters  $A$  and  $E_A$ , and the form of the concentration dependence as a product of the factors  $c_i^{\alpha_i}$  (the order of reaction). We would also like to predict values of the various parameters, from as simple and general a basis as possible, without having to measure them for every case. The first of these two tasks is the easier one. The second is still not achieved despite more than a century of study of reaction kinetics; the difficulty lies in quantum mechanical

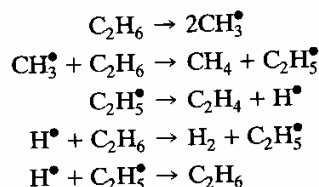
calculations—not in any remaining scientific mystery. However, the current level of theoretical understanding has improved our ability to estimate many kinetics parameters and has sharpened our intuition in the search for improved chemical processes.

In many cases, reaction rates cannot be adequately represented by equation 6.1 but are more complex functions of temperature and composition. Theories of reaction kinetics should also explain the underlying basis for this phenomenon.

### 6.1.2 Relating to Reaction Mechanisms and Elementary Reactions

Even a “simple” reaction usually takes place in a “complex” manner involving multiple steps making up a reaction mechanism. For example, the formation of ammonia, represented by the simple reaction  $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ , does not take place in the manner implied by this chemical statement, that is, by the simultaneous union of one molecule of  $\text{N}_2$  and three molecules of  $\text{H}_2$  to form two of  $\text{NH}_3$ . Similarly, the formation of ethylene, represented by  $\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2$ , does not occur by the disintegration of a molecule of  $\text{C}_2\text{H}_6$  to form one of  $\text{C}_2\text{H}_4$  and one of  $\text{H}_2$  directly.

The original reaction mechanism (Rice and Herzfeld, 1934) proposed for the formation of  $\text{C}_2\text{H}_4$  from  $\text{C}_2\text{H}_6$  consists of the following five steps:<sup>1</sup>



where the “dot” denotes a free-radical species.

We use this example to illustrate and define several terms relating to reaction fundamentals:

**Elementary reaction:** a chemical reaction step that takes place in a single molecular counter (each of the five steps above is an elementary reaction); it involves one, or (rarely) three molecular entities (atoms, molecules, ions, radicals, etc.). Only a small number of chemical bonds is rearranged.

**Reaction mechanism:** a postulated sequence of elementary reactions that is consistent with the observed stoichiometry and rate law; these are necessary but not sufficient conditions for the correctness of a mechanism, and are illustrated in Chapter 7.

**Reactive intermediate:** a transient species introduced into the mechanism but not appearing in the stoichiometric equation or the rate law; the free atomic and free radical species  $\text{H}^\bullet$ ,  $\text{CH}_3^\bullet$ , and  $\text{C}_2\text{H}_5^\bullet$  are reactive intermediates in the mechanism above. Such species must ultimately be identified experimentally to justify their inclusion.

**Molecularity of a reaction:** the number of reacting partners in an elementary reaction: unimolecular (one), bimolecular (two), or termolecular (three); in the mechanism above, the first and third steps are unimolecular as written, and the remainder are bimolecular. Molecularity (a mechanistic concept) is to be distinguished from order (algebraic). Molecularity must be integral, but order need not be; there is no necessary correlation between molecularity and order, except for an elementary reaction: the numbers describing molecularity, order, and stoichiometry of an elementary reaction are the same.

<sup>1</sup>In the dehydrogenation of  $\text{C}_2\text{H}_6$  to produce  $\text{C}_2\text{H}_4$ ,  $\text{CH}_4$  is a minor coproduct; this is also reflected in the first step of the mechanism; hence, both the overall reaction and the proposed mechanism do not strictly represent a simple system.

It is the combination of individual elementary reaction steps, each with its own rate law, that determines the overall kinetics of a reaction. Elementary reactions have simple rate laws of the form

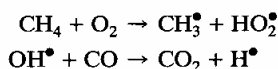
$$r = k(T) \prod_i^{N_R} c_i^{\alpha_i} \quad (6.1-2)$$

where the temperature dependence of rate constant  $k$  is Arrhenius-like, and the reaction orders  $\alpha_i$  are equal to the absolute values of the stoichiometric coefficients  $|\nu_i|$  of the *reactants* (number  $N_R$ ).

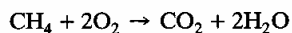
This chapter presents the underlying fundamentals of the rates of elementary chemical reaction steps. In doing so, we outline the essential concepts and results from physical chemistry necessary to provide a basic understanding of how reactions occur. These concepts are then used to generate expressions for the rates of elementary reaction steps. The following chapters use these building blocks to develop intrinsic rate laws for a variety of chemical systems. Rather complicated, nonseparable rate laws for the overall reaction can result, or simple ones as in equation 6.1-1 or -2.

## 2 DESCRIPTION OF ELEMENTARY CHEMICAL REACTIONS

An elementary step must necessarily be simple. The reactants are together with sufficient energy for a very short time, and only simple rearrangements can be accomplished. In addition, complex rearrangements tend to require more energy. Thus, almost all elementary steps break and/or make one or two bonds. In the combustion of methane, the following steps (among many others) occur as elementary reactions:



These two steps are simple rearrangements. The overall reaction



cannot occur in a single step; too much would have to transpire in a single encounter.

### 2.1 Types of Elementary Reactions

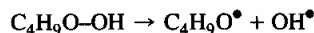
The following list of elementary reactions, divided into various categories, allows us to understand and build rate laws for a wide variety of chemical systems.

#### 6.2.1.1 Elementary Reactions Involving Neutral Species (Homogeneous Gas or Liquid Phase)

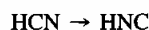
This is the most common category of elementary reactions and can be illustrated by unimolecular, bimolecular, and termolecular steps.

##### Unimolecular Steps:

- Fragmentation/dissociation—the molecule breaks into two or more fragments:



- Rearrangements—the internal bonding of a molecule changes:

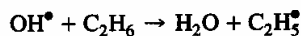


**Bimolecular Steps:**

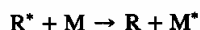
- Bimolecular association/recombination—two species combine:



- Bimolecular exchange reactions—atoms or group of atoms transferred:



- Energy transfer—this is not actually a reaction; there is no change in bonding; but is nevertheless an important process involving another molecule M:



The asterisk denotes an excited state—a molecule with excess energy (more than enough energy to enable it to undergo a specific reaction step).

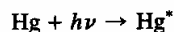
**Termolecular Steps:**

- Termolecular steps are rare, but may appear to arise from two rapid bimolecular steps in sequence.

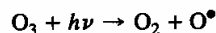
**6.2.1.2 Photochemical Elementary Reactions**

Light energy (absorbed or emitted in a quantum or photon of energy,  $h\nu$ , where  $h$  is Planck's constant ( $6.626 \times 10^{-34}$  J s), and  $\nu$  is the frequency of the light,  $\text{s}^{-1}$ ) can change the energy content of a molecule enough to produce chemical change.

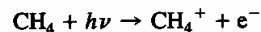
- Absorption of light (photon):



- Photodissociation:



- Photoionization (electron ejected from molecule):

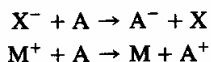


- Light (photon) emission (reverse of absorption):

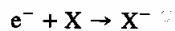
**6.2.1.3 Elementary Reactions Involving Charged Particles (Ions, Electrons)**

These reactions occur in plasmas, or other high-energy situations.

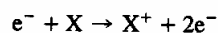
- Charge exchange:



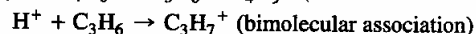
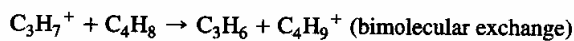
- Electron attachment:



- Electron-impact ionization:



- Ion-molecule reactions:



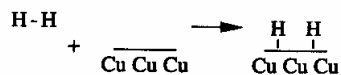
#### 6.2.1.4 Elementary Reactions on Surfaces

Surface reactions are important in heterogeneous reactions and catalysis.

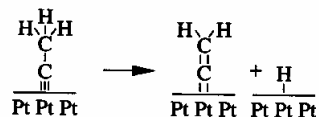
- Adsorption/desorption—molecules or fragments from gas or liquid bond to solid surface.
- Simple adsorption—molecule remains intact.



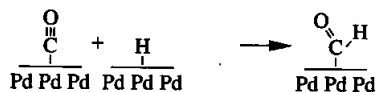
- Dissociative adsorption—molecule forms two or more surface-bound species.



- Site hopping—surface-bound intermediates move between binding sites on surface.
- Surface reactions—similar to gas-phase arrangements, but occur while species bonded to a solid surface.
- Dissociation:



- Combination:



Rearrangements of the adsorbed species are also possible.

### 6.2.2 General Requirements for Elementary Chemical Reactions

The requirements for a reaction to occur are:

- (1) The reaction partners must encounter one another.
- (2) The encounter must be successful. This in turn requires:
  - (i) the geometry of the encounter to be correct (e.g., the atoms in the proper position to form the new bonds) and,
  - (ii) sufficient energy to be available to overcome any energy barriers to this transformation.

The simple theories of reaction rates involve applying basic physical chemistry knowledge to calculate or estimate the rates of successful molecular encounters. In Section 6.3 we present important results from physical chemistry for this purpose; in subsequent sections, we show how they are used to build rate theories, construct rate laws, and estimate the values of rate constants for elementary reactions.

## 6.3 ENERGY IN MOLECULES

Energy in molecules, as in macroscopic objects, can be divided into potential energy (the energy which results from their position at rest) and kinetic energy (energy associated with motion). Potential energy in our context deals with the energy associated with chemical bonding. The changes in bond energy often produce energy barriers to reaction as the atoms rearrange. The kinetic energy of a group of molecules governs (1) how rapidly reactants encounter one another, and (2) how much energy is available in the encounter to surmount any barriers to reaction. Research has led to a detailed understanding of how these factors influence the rates of elementary reactions, and was recognized by the award of the Nobel prize in chemistry to Lee, Herschbach, and Polanyi in 1986.

### 6.3.1 Potential Energy in Molecules—Requirements for Reaction

#### 6.3.1.1 Diatomic Molecules

The potential energy of a pair of atoms (A and B) is shown schematically in Figure 6.1 as a function of the distance between them,  $r_{AB}$ . As the atoms approach one another, the associated electron orbitals form a bonding interaction which lowers the potential energy (i.e., makes the system more stable than when the two atoms are far apart).

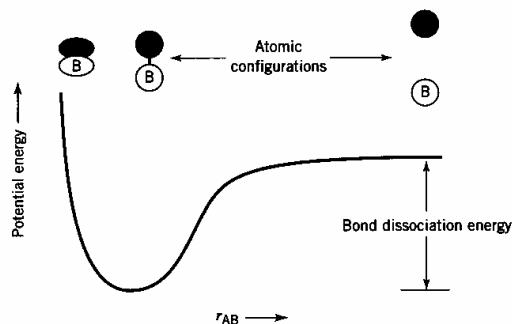


Figure 6.1 Potential energy of a two-atom system

The minimum energy on the curve corresponds to the most stable configuration where the bonding is most effective, and thus to the stable A–B diatomic molecule. In the specific case of a pair of iodine atoms, this minimum is  $149 \text{ kJ mol}^{-1}$  below that of the separated atoms. Therefore, to dissociate an isolated  $\text{I}_2$  molecule at rest,  $\text{I}_2 \rightarrow 2\text{I}^\bullet$ ,  $149 \text{ kJ mol}^{-1}$  must be supplied from outside the molecule. This elementary reaction is said to be endoergic (energy absorbing) by this amount, also known as the bond dissociation energy. This energy can be supplied by absorption of light energy, or by transfer of kinetic energy from other molecules. This energy can also be thought of as the height of an energy barrier to be scaled in order for reaction to occur. The path along the potential energy curve can be thought of as a path or trajectory leading to reaction, which is described as the “reaction coordinate”.

Now consider the reverse reaction,  $2\text{I}^\bullet \rightarrow \text{I}_2$ . The reaction coordinate in this case is just the reverse of that for the dissociation reaction. The reaction is exoergic (energy releasing), and for the  $\text{I}_2$  molecule to come to rest in its most stable configuration, an amount of energy equal to the bond energy must be given off to the rest of the system. If not, the molecule has enough energy (converted to internal kinetic energy) to dissociate again very quickly. This requirement to “offload” this excess energy (usually through collisions with other molecules) is important in the rates of these bimolecular association reactions. The input of additional energy is not required along the reaction coordinate for this reaction to occur; the two atoms only have to encounter each other; that is, there is no energy barrier to this reaction. These concepts form a useful basis for discussing more complicated systems.

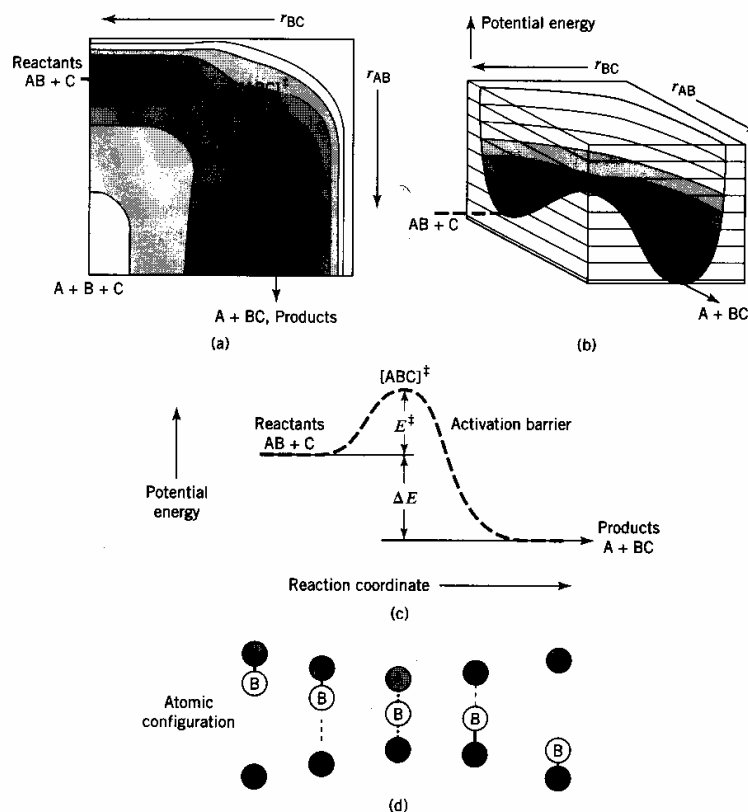
### 6.3.1.2 Triatomic Systems: Potential Energy Surface and Transition State

Consider a system made up of the atoms A, B, and C. Whereas the configuration of a diatomic system can be represented by a single distance, the internal geometry of a triatomic system requires three independent parameters, such as the three interatomic distances  $r_{AB}$ ,  $r_{BC}$ , and  $r_{CA}$ , or  $r_{AB}$ ,  $r_{BC}$ , and the angle  $\phi_{ABC}$ . These are illustrated in Figure 6.2.

The potential energy is a function of all three parameters, and is a surface (called the potential energy surface) in three-dimensional (3-D) space. If we simplify the system by constraining the atoms to remain in a straight line in the order A–B–C, the potential energy depends only on two parameters (i.e.,  $r_{AB}$  and  $r_{BC}$ ), and we can conveniently represent it as a 2-D “topographical map” in Figure 6.3(a), or as a 3-D perspective drawing in Figure 6.3(b). At the lower-left corner of Figure 6.3(a), all three atoms are far apart: there are no bonding interactions. As A approaches B while C remains distant (equivalent to moving up the left edge of Figure 6.3(a)), a stable AB molecule is formed (like the  $\text{I}_2$  case). Similarly, a B–C bond is formed if B approaches C with A far away (moving right along the bottom edge of Figure 6.3(a)). When all three atoms are near each other, the molecular orbitals involve all three atoms. If additional bonding is possible, the energy is lowered when this happens, and a stable triatomic molecule can be formed. This is not the case shown in Figure 6.3(a), since in all configurations where A, B, and C are close together, the system is less stable than  $\text{AB} + \text{C}$  or  $\text{A} + \text{BC}$ . This is typical for many systems where AB (and BC) are stable molecules with saturated bonding. The two partial bonds A–B and B–C are weaker than either complete bond.



Figure 6.2 Representation of configuration of three-atom system



**Figure 6.3** Potential energy surface for colinear reaction  $AB + C \rightarrow A + BC$ ; (a) 2-D topographical representation; (b) 3-D representation; (c) potential energy along reaction coordinate; (d) atomic configurations along reaction coordinate

Now consider the reaction



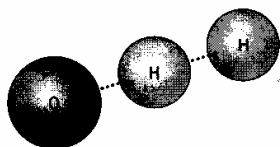
For the reaction to occur, the atoms must trace out a path on this surface from the configuration, in Figure 6.3(a), labeled “reactants” ( $AB + C$ ), to the point labeled “products” ( $A + BC$ ). The path which requires the minimum energy is shown by the dashed line. In this example, the energy rises as  $C$  approaches  $A-B$  and there is an energy barrier (marked “ $\ddagger$ ”). As a result, for the reaction to occur, the reactants must have at least enough additional (kinetic) energy to “get over the pass” at “ $\ddagger$ ”. This critical configuration of the atoms,  $[ABC]^\ddagger$ , is called the “transition state” of the system (or “activated complex”). This minimum energy path describes the most likely path for reaction, and is the reaction coordinate, although other paths are possible with additional energy. Plotting the potential energy  $E$  as a function of distance along this reaction coordinate, we obtain Figure 6.3(c) (corresponding to Figure 6.1 for the diatomic case). This figure shows the energy barrier  $E^\ddagger$  at the transition state and that the reaction is exothermic. The height of the energy barrier,  $E^\ddagger$ , corresponds approximately to the Arrhenius

activation energy,  $E_A$ , of the reaction. Figure 6.3(d) indicates atomic configurations along the reaction coordinate.

In the elementary reaction



which is part of the reaction mechanism in hydrogen flames and the space shuttle main rocket engine, the transition state would resemble:



The energy barrier for this reaction is quite low,  $37 \text{ kJ mol}^{-1}$ . There are many schemes for the estimation of the barrier height,  $E^\ddagger$ . The simplest of these are based on empirical correlations. For details see Steinfeld et al., 1989, p. 231.

The reverse reaction ( $\text{BC} + \text{A} \rightarrow \text{AB} + \text{C}$ ) follows the same reaction coordinate in the opposite direction. The barrier for the reverse reaction occurs at the same place. The barrier height in the reverse direction is related to the barrier height in the forward direction by

$$E^\ddagger(\text{reverse}) = E^\ddagger(\text{forward}) - \Delta E(\text{forward}) \quad (6.3-2)$$

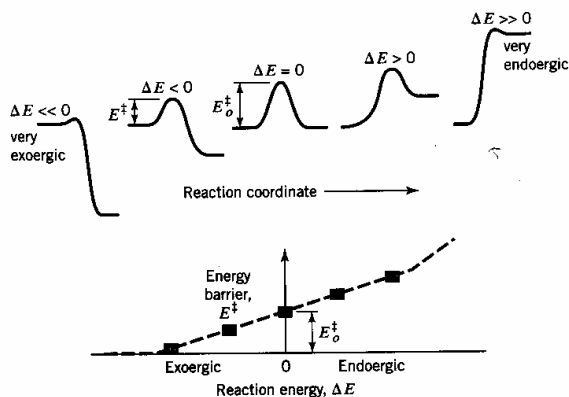
where  $\Delta E$  (forward) is the reaction energy change in the forward direction. For example, reaction 6.3-1a is endoergic by approximately  $9 \text{ kJ mol}^{-1}$ , and so the energy barrier for the reverse reaction is  $37 - 9 = 28 \text{ kJ mol}^{-1}$ .

### 6.3.1.3 Relationship Between Barrier Height and Reaction Energy

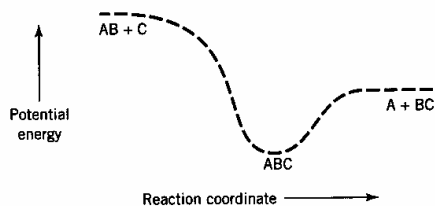
In reaction 6.3-1, the A–B bond weakens as the B–C bond is formed. If there is a barrier, these two effects do not cancel. However, if the B–C bond is much stronger than the A–B bond (very exoergic reaction), even partial B–C bond formation compensates for the weakening of the A–B bond. This explains the observation that for a series of similar reactions, the energy barrier (activation energy) is lower for the more exoergic reactions. A correlation expressing this has been given by Evans and Polanyi (1938):

$$E^\ddagger = E_o^\ddagger + q\Delta E(\text{reaction}) \quad (6.3-3)$$

where  $E_o^\ddagger$  is the barrier for an energetically neutral reaction (such as  $\text{CH}_3^\bullet + \text{CD}_4 \rightarrow \text{CH}_3\text{D} + \text{CD}_3^\bullet$ ). The correlation predicts the barriers ( $E^\ddagger$ ) for similar exoergic/endoergic reactions to be smaller/larger by a fraction,  $q$ , of the reaction energy ( $\Delta E$  (reaction)). For one set of H transfer reactions, the best value of  $q$  is 0.4. This correlation holds only until the barrier becomes zero, in the case of sufficiently exoergic reactions; or until the barrier becomes equal to the endoergicity, in the case of sufficiently endoergic reactions. Figure 6.4 shows reaction coordinate diagrams for a hypothetical series of reactions, and the “data” for these reactions are indicated in Figure 6.4, along with the Evans-Polanyi correlation (dashed line). This and other correlations allow unknown rate constant parameters to be estimated from known values.



**Figure 6.4** Reaction coordinate diagrams showing various types of energy-barrier behavior

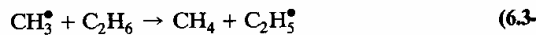


**Figure 6.5** Potential energy diagram for stable ABC molecule

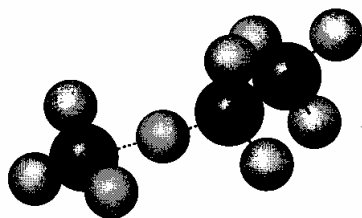
If a stable ABC molecule exists, the reaction coordinate may appear as in Figure 6.5. In this case, there is no barrier to formation of the ABC molecule in either direction. Just like the diatomic case, energy must be removed from this molecule, because not only does it have enough internal energy to form reactants again, it has more than enough to form products. In the reverse direction, additional energy must be carried into the reaction if the system is to form AB + C. There can also be barriers to formation of triatomic molecules, particularly if the AB bond must be broken, for example to form the molecule ACB. The reactions of ions with molecules rarely have intrinsic barriers because of the long-range attractive force (ion-induced dipole) between the species.

#### 6.3.1.4 Potential Energy Surface and Transition State in More Complex Systems

For a system containing a larger number of atoms, the general picture of the potential energy surface and the transition state also applies. For example, in the second reaction step in the mechanism of ethane pyrolysis in Section 6.1.2,



the transition state should resemble:



Here, the  $\text{CH}_3\text{-H}$  bond is formed as the  $\text{C}_2\text{H}_5\text{-H}$  bond is broken. For this system, the other bond lengths and angles also affect the potential energy, and the potential energy surface therefore depends on all other coordinates ( $3N - 6$  or 30 in all). This system, however, is similar to the triatomic case above, where  $\text{A} = \text{C}_2\text{H}_5^\ddagger$ ,  $\text{B} = \text{H}^\ddagger$ , and  $\text{C} = \text{CH}_3^\ddagger$ . Again note that the transition state for the reverse reaction is the same.

The notion of the transition state is central to both theories discussed in this chapter. The transition state is the atomic configuration that must be reached for reaction to occur, and the bonding dictates the *energy* required for the reaction. The configuration or shape of the transition state indicates how probable it is for the reactants to “line up” properly or have the correct *orientation* to react. *The rate of a reaction is the rate at which these requirements are achieved.* A quantitative interpretation of both these issues, as treated by the two theories, is the subject of Sections 6.4 and 6.5.

In reactions which occur on solid surfaces, it is acceptable to think of the surface as a large molecule capable of forming bonds with molecules or fragments. Because of the large number of atoms involved, this is theoretically complicated. However, the binding usually occurs at specific sites on the surface, and very few surface atoms have their bonding coordination changed. Therefore, the same general concepts are useful in the discussion of surface reactions. For example, the nondissociated adsorption of CO on a metal surface (Section 6.2.1.4) can be thought of as equivalent to bimolecular association reactions, which generally have no barrier. Desorption is similar to unimolecular dissociation reactions, and the barrier equals the bond strength to the surface. Some reactions involving bond breakage, such as the dissociative adsorption of  $\text{H}_2$  on copper surfaces, have energy barriers.

### 6.3.1.5 Other Electronic States

If the electrons occupy orbitals different from the most stable (ground) electronic state, the bonding between the atoms also changes. Therefore, an entirely different potential energy surface is produced for each new electronic configuration. This is illustrated in Figure 6.6 for a diatomic molecule.

The most stable (ground state) potential energy curve is shown (for AB) along with one for an electronically excited state ( $\text{AB}^*$ ) and also for a positive molecular ion ( $\text{AB}^+$ , with one electron ejected from the neutral molecule). Both light absorption and electron-transfer reactions produce a change in the electronic structure. Since electrons move so much faster than the nuclei in molecules, the change in electronic state is complete before the nuclei have a chance to move, which in turn means that the initial geometry of the final electronic state in these processes must be the same as in the initial state. This is shown by the arrow symbolizing the absorption of light to produce an electronically excited molecule. The  $r_{\text{AB}}$  distance is the same after the transition as before, although this is not the most stable configuration of the excited-state molecule. This has the practical implication that the absorption of light to promote a molecule from its stable bonding configuration to an excited state often requires more energy

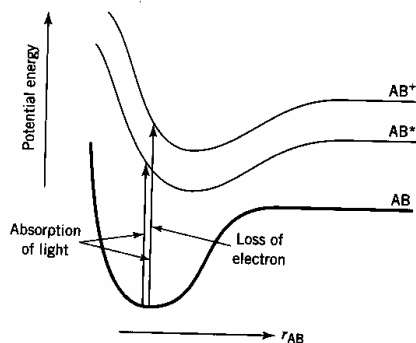


Figure 6.6 Potential energy diagrams for various electronic configurations

than is required to make the most stable configuration of the excited state. Similarly, charge-exchange reactions, in which an electron is transferred between molecules, often require more energy than the minimum required to make the products. This is one of the reasons for overpotentials in electrochemical reactions. The extra energy in the new molecule appears as internal energy of motion (vibration), or, if there is enough energy to dissociate the molecule, as translational energy.

### 6.3.2 Kinetic Energy in Molecules

Energy is also stored in the motion of atoms, and for a molecule, this takes the form of translational motion, where the whole molecule moves, and internal motion, where the atoms in the molecule move with respect to each other (vibration and rotation). These modes are illustrated in Figure 6.7.

All forms of kinetic energy, including relative translational motion, can be used to surmount potential energy barriers during reaction. In Figure 6.3, C can approach AB with sufficient kinetic energy to “roll up the barrier” near the transition state. Alternatively, A–B vibrational motion can scale the barrier from a different angle. The actual trajectories must obey physical laws (e.g., momentum conservation), and the role of different forms of energy in reactions has been investigated in extensive computer calculations for a variety of potential energy surfaces. In addition to its role in topping the energy barrier, translational motion governs the rate that reactants encounter each other.

#### 6.3.2.1 Energy States

All forms of energy are subject to the rules of quantum mechanics, which allow only certain (discrete) energy levels to exist. Therefore, an isolated molecule cannot contain

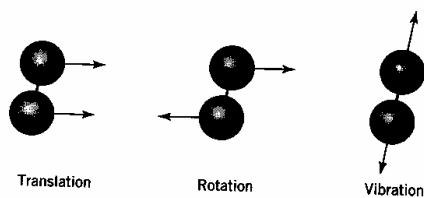


Figure 6.7 Modes of molecular motion

any arbitrary amount of vibrational energy, but must have one of a relatively small number of discrete quantities of vibrational energy. This is also true for rotational energy, although many more states are available. For translational energy, there are usually so many allowed translational energy states that a continuous distribution is assumed. Extra energy can also be stored in the electrons, by promoting an electron from an occupied orbital to an unoccupied orbital. This changes the bonding interactions and can be thought of as an entirely separate potential energy surface at higher energy. These energy states are not usually encountered in thermal reactions, but are an important part of photochemistry and high-energy processes which involve charged species.

### 6.3.2.2 Distribution of Molecular Energy

In a group of molecules in thermal equilibrium at temperature  $T$ , the distribution of energy among the various modes of energy and among the molecules is given by the Boltzmann distribution, which states that the probability of finding a molecule within a narrow energy range around  $\epsilon$  is proportional to the number of states in that energy range times the "Boltzmann factor,"  $e^{-\epsilon/k_B T}$ :

$$P(\epsilon) = g(\epsilon)e^{-\epsilon/k_B T} \quad (6.3-5)$$

where  $k_B$  is the Boltzmann constant:

$$k_B = R/N_{Av} = 1.381 \times 10^{-23} \text{ J K}^{-1} \quad (6.3-6)$$

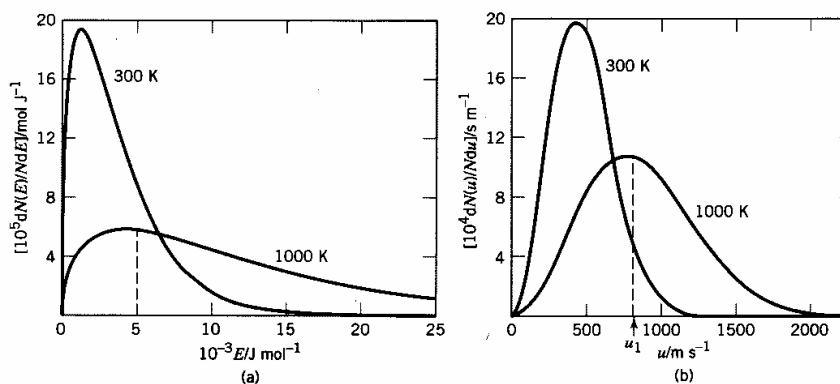
and  $g(\epsilon)$ , the number of states in the energy range  $\epsilon$  to  $\epsilon + d\epsilon$ , is known as the "density of states" function. This function is derived from quantum mechanical arguments, although when many levels are accessible at the energy (temperature) of the system, classical (Newtonian) mechanics can also give satisfactory results. This result arises from the concept that energy is distributed randomly among all the types of motion, subject to the constraint that the total energy and the number of molecules are conserved. This relationship gives the probability that any molecule has energy above a certain quantity (like a barrier height), and allows one to derive the distribution of molecular velocities in a gas. The randomization of energy is accomplished by energy exchange in encounters with other molecules in the system. Therefore, each molecule spends some time in high-energy states, and some time with little energy. The energy distribution over time of an individual molecule is equal to the instantaneous distribution over the molecules in the system. We can use molar energy ( $E$ ) in 6.3-5 to replace molecular energy ( $\epsilon$ ), if  $R$  is substituted for  $k_B$ .

### 6.3.2.3 Distribution of Molecular Translational Energy and Velocity in a Gas

In an ideal gas, molecules spend most of the time isolated from the other molecules in the system and therefore have well defined velocities. In a *liquid*, the molecules are in a constant state of collision. The derivation of the translational energy distribution from equation 6.3-5 (which requires obtaining  $g(\epsilon)$ ) gives the distribution (expressed as  $dN/N$ , the fraction of molecules with energy between  $\epsilon$  and  $\epsilon + d\epsilon$ ):

$$dN(\epsilon)/N = 2\pi^{-1/2}(k_B T)^{-3/2} \epsilon^{1/2} e^{-\epsilon/k_B T} d\epsilon \quad (6.3-7)$$

which is Boltzmann's law of the distribution of energy (Moelwyn-Hughes, 1957, p. 37). The analogous velocity distribution in terms of molecular velocity,  $u = (2\epsilon/m)^{1/2}$ , where  $m$  is the mass per molecule, is:



**Figure 6.8** (a) Translational kinetic energy distribution for an ideal gas (equation 6.3-7); (b) velocity distribution for  $N_2$  molecules (equation 6.3-8)

$$dN(u)/N = (2/\pi)^{1/2} (m/k_B T)^{3/2} u^2 e^{-mu^2/2k_B T} du \quad (6.3-8)$$

$$= g(u) du \quad (6.3-9)$$

which is Maxwell's law of the distribution of velocities (Moelwyn-Hughes, 1957, p. 38).

These distributions are shown in Figure 6.8. The energy distribution, Figure 6.8(a), is independent of the molecular mass and is shown for  $T = 300$  K and 1000 K. The fraction of molecules with translational kinetic energy in excess of a particular value increases as  $T$  increases. The increase is more dramatic for energies much higher than the average. By comparing the scale in Figure 6.8(a) with values for even modest energy barriers (e.g.,  $10 \text{ kJ mol}^{-1}$ ), we see that a very small fraction of the molecules at either temperature has enough translational energy to overcome such a barrier. The average translational energy is

$$\bar{\epsilon} = (3/2)k_B T \quad (6.3-10)$$

The velocity distribution for  $N_2$  at these two temperatures is shown in Figure 6.8(b). The average velocity is (Moelwyn-Hughes, 1957, p. 38):

$$\bar{u} = (8k_B T/\pi m)^{1/2} \quad (6.3-11)$$

## 6.4 SIMPLE COLLISION THEORY OF REACTION RATES

The collision theory of reaction rates in its simplest form (the "simple collision theory" or SCT) is one of two theories discussed in this chapter. Collision theories are based on the notion that only when reactants encounter each other, or *collide*, do they have the chance to react. The reaction rate is therefore based on the following expressions:

$$\text{reaction rate} \equiv \text{number of effective collisions } m^{-3} s^{-1} \quad (6.4-1)$$

or, reaction rate =

$$(\text{number of collisions } m^{-3} s^{-1}) \times (\text{probability of success (energy, orientation, etc.)}) \quad (6.4-2)$$

The notion of a collision implies at least two collision partners, but collision-based theories are applicable for theories of unimolecular reactions as well.

### 6.4.1 Simple Collision Theory (SCT) of Bimolecular Gas-Phase Reactions

#### 6.4.1.1 Frequency of Binary Molecular Collisions

In this section, we consider the total rate of molecular collisions without considering whether they result in reaction. This treatment introduces many of the concepts used in collision-based theories; the criteria for success are included in succeeding sections.

Consider a volume containing  $c'_A$  molecules of A (mass  $m_A$ ) and  $c'_B$  molecules of B (mass  $m_B$ ) per unit volume. A simple estimate of the frequency of A-B collisions can be obtained by assuming that the molecules are hard spheres with a finite size, and that, like billiard balls, a collision occurs if the center of the B molecule is within the "collision diameter"  $d_{AB}$  of the center of A. This distance is the arithmetic mean of the two molecular diameters  $d_A$  and  $d_B$ :

$$d_{AB} = (d_A + d_B)/2 \quad (6.4-3)$$

and is shown in Figure 6.9(a). The area of the circle of radius  $d_{AB}$ ,  $\sigma = \pi d_{AB}^2$ , is the collision target area (known as the collision "cross-section"). If the A molecules move at average velocity  $\bar{u}$  (equation 6.3-11) and the B molecules are assumed to be stationary, then each A sweeps out a volume  $\sigma\bar{u}$  per unit time (Figure 6.9(b)) such that every B molecule inside is hit. The frequency of A-B collisions for each A molecule is then  $\sigma\bar{u}c'_B$ . By multiplying by the concentration of A, we obtain the frequency of A-B collisions per unit volume:

$$Z_{AB} = \sigma\bar{u}c'_A c'_B \quad (6.4-4)$$

This simple calculation gives a result close to that obtained by integrating over the three-dimensional Maxwell velocity distributions for both A and B. In this case, the same expression is obtained with the characteristic velocity of approach between A and B given by

$$\bar{u} = (8k_B T/\pi\mu)^{1/2} \quad (6.4-5)$$

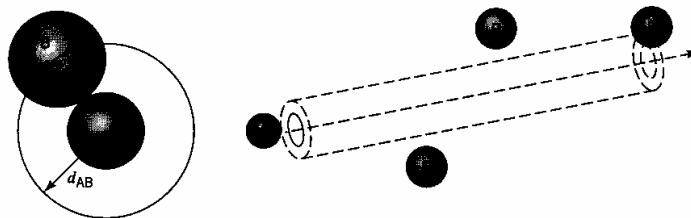


Figure 6.9 (a) Collision diameter  $d_{AB}$ ; (b) simplified basis for calculating frequency of A-B collisions

where  $\mu$  is the reduced molecular mass defined by:

$$\mu = m_A m_B / (m_A + m_B) \quad (6.4-6)$$

The collision frequency of like molecules,  $Z_{AA}$ , can be obtained similarly, but the collision cross-section is  $\sigma = \pi d_A^2$ , the reduced mass is  $\mu = m_A/2$ , and we must divide by 2 to avoid counting collisions twice:

$$Z_{AA} = (1/2)\sigma \bar{u} (c'_A)^2 \quad (6.4-7)$$

- (a) Calculate the rate of collision ( $Z_{AB}$ ) of molecules of  $N_2$  (A) and  $O_2$  (B) in air (21 mol %  $O_2$ , 78 mol %  $N_2$ ) at 1 bar and 300 K, if  $d_A = 3.8 \times 10^{-10}$  m and  $d_B = 3.6 \times 10^{-10}$  m.
- (b) Calculate the rate of collision ( $Z_{AA}$ ) of molecules of  $N_2$  (A) with each other in air.

### SOLUTION

- (a) From equations 6.4-4 and -5, with  $\sigma = \pi d_{AB}^2$ ,

$$Z_{AB} = d_{AB}^2 c'_A c'_B (8\pi k_B T / \mu)^{1/2} \quad (6.4-4a)$$

with

$$d_{AB} = (3.8 + 3.6) \times 10^{-10} / 2 = 3.7 \times 10^{-10} \text{ m}$$

From equation 4.2-3a,

$$\begin{aligned} c'_A &= N_{Av} c_A = N_{Av} p_A / RT = 6.022 \times 10^{23} (0.78) 10^5 / 8.314 (300) \\ &= 1.88 \times 10^{25} \text{ molecules m}^{-3} \end{aligned}$$

Similarly,

$$\begin{aligned} c'_B &= 0.507 \times 10^{25} \text{ molecules m}^{-3} \\ \mu &= m_A m_B / (m_A + m_B) = 28.0(32.0) / (28.0 + 32.0) (6.022 \times 10^{23}) 1000 \\ &= 2.48 \times 10^{-26} \text{ kg} \\ Z_{AB} &= (3.7 \times 10^{-10})^2 (1.88 \times 10^{25}) (0.507 \times 10^{25}) [8\pi (1.381 \times 10^{-23}) 300 / 2.48 \times 10^{-26}]^{1/2} \\ &= 2.7 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1} \end{aligned}$$

- (b) From equation 6.4-7, together with 6.4-5 and -6 (giving  $\mu = m_A/2$ ), and with  $\sigma = \pi d_A^2$ ,

$$Z_{AA} = \frac{1}{2} \pi d_A^2 (c'_A)^2 (\pi k_B T / m_A)^{1/2} \quad (6.4-7a)$$

From (a),

$$\begin{aligned}
 c_A' &= 1.88 \times 10^{25} \text{ molecules m}^{-3} \\
 m_A &= 28.0 / (6.022 \times 10^{23}) 1000 = 4.65 \times 10^{-26} \text{ kg molecule}^{-1} \\
 Z_{AA} &= 2(3.8 \times 10^{-10})^2 (1.88 \times 10^{25})^2 [\pi(1.381 \times 10^{-23}) 300 / 4.65 \times 10^{-26}]^{1/2} \\
 &= 5.4 \times 10^{34} \text{ m}^{-3} \text{ s}^{-1}
 \end{aligned}$$

Both parts (a) and (b) of Example 6-1 illustrate that rates of molecular collisions are extremely large. If "collision" were the only factor involved in chemical reaction, the rates of all reactions would be virtually instantaneous (the "rate" of  $\text{N}_2\text{-O}_2$  collisions in air calculated in Example 6-1(a) corresponds to  $4.5 \times 10^7 \text{ mol L}^{-1} \text{ s}^{-1}$ ). Evidently, the energy and orientation factors indicated in equation 6.4-2 are important, and we now turn attention to them.

#### 6.4.1.2 Requirements for Successful Reactive Collision

The rate of reaction in collision theories is related to the number of "successful" collisions. A successful reactive encounter depends on many things, including (1) the speed at which the molecules approach each other (relative translational energy), (2) how close they are to a head-on collision (measured by a miss distance or impact parameter,  $b$ , Figure 6.10), (3) the internal energy states of each reactant (vibrational ( $v$ ), rotational ( $J$ )), (4) the timing (phase) of the vibrations and rotations as the reactants approach, and (5) orientation (or steric aspects) of the molecules (the H atom to be abstracted in reaction 6.3-4 must be pointing toward the radical center).

Detailed theories include all these effects in the reaction cross-section, which is then a function of all the various dynamic parameters:

$$\sigma_{\text{reaction}} = \sigma(\bar{u}, b, v_A, J_A, \dots) \quad (6.4-8)$$

The SCT treats the reaction cross-section as a separable function,

$$\sigma_{\text{reaction}} = \sigma_{\text{hard sphere}} f(E) p \quad (6.4-9)$$

$$= \pi d_{AB}^2 f(E) p \quad (6.4-10)$$

where the energy requirements,  $f(E)$ , and the steric requirements,  $p$ , are multiplicative factors.

#### 6.4.1.3 Energy Requirements

The energy barrier  $E^\ddagger$  is the minimum energy requirement for reaction. If only this amount of energy is available, only one orientation out of all the possible collision orientations is successful. The probability of success rises rapidly if extra energy is

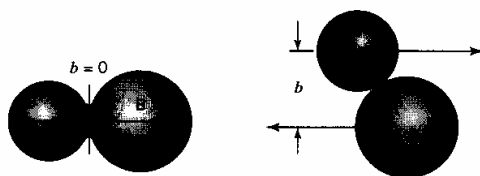


Figure 6.10 Illustration of (a) a head-on collision ( $b = 0$ ), and (b) a glancing collision ( $0 < b < d_{AB}$ )

available, since other configurations around the transition state (at higher energy) can be reached, and the geometric requirements of the collision are not as precise. Therefore, the best representation of the “necessary” amount of energy is somewhat higher than the barrier height. Because the Boltzmann factor decreases rapidly with increasing energy, this difference is not great. Nevertheless, in the simplified theory, we call this “necessary” energy  $E^*$  to distinguish it from the barrier height. The simplest model for the collision theory of rates assumes that the molecules are hard spheres and that only the component of kinetic energy between the molecular centers is effective. As illustrated in Figure 6.10, in a head-on collision ( $b = 0$ ), all of the translational energy of approach is available for internal changes, whereas in a grazing collision ( $b = d_{AB}$ ) none is. By counting only collisions where the intermolecular component at the moment of collision exceeds the “necessary” energy  $E^*$ , we obtain a simple expression from the tedious, but straightforward, integration over the joint Maxwell velocity distributions and  $b$  (Steinfeld et al., 1989, pp. 248–250). Thus, for the reaction  $A + B \rightarrow$  products, if there are no steric requirements, the rate of reaction is

$$r \equiv (-r_A) = Z_{AB} e^{-E^*/RT} \quad (6.4-11)$$

that is, the function  $f(E)$  in equation 6.4-9 (in molar units) is  $\exp(-E^*/RT)$ .

Similarly, for the reaction  $2A \rightarrow$  products,

$$r \equiv (-r_A)/2 = Z_{AA} e^{-E^*/RT} \quad (6.4-12)$$

#### 6.4.1.4 Orientation or Steric Factors

The third factor in equation 6.4-9,  $p$ , contains any criteria other than energy that the reactants must satisfy to form products. Consider a hydrogen atom and an ethyl radical colliding in the fifth step in the mechanism in Section 6.1.2. If the hydrogen atom collides with the wrong ( $\text{CH}_3$ ) end of the ethyl radical, the new C–H bond in ethane cannot be formed; a fraction of the collisions is thus ineffective. Calculation of the real distribution of successful collisions is complex, but for simplicity, we use the steric factor approach, where all orientational effects are represented by  $p$  as a constant. This factor can be estimated if enough is known about the reaction coordinate: in the case above, an estimate of the fraction of directions given by the H– $\text{CH}_2$ – $\text{CH}_3$  bond angle which can form a C–H bond. A reasonable, but uncertain, estimate for  $p$  in this case is 0.2. Alternatively, if the value of the rate constant is known, the value of  $p$ , and therefore some information about the reaction coordinate, can be estimated by comparing the measured value to that given by theory. In this case  $p(\text{derived}) = r(\text{observed})/r(\text{theory})$ . Reasonable values of  $p$  are equal to or less than 1; however, in some cases the observed rate is much greater than expected ( $p \gg 1$ ); in such cases a chain mechanism is probably involved (Chapter 7), and the reaction is not an elementary step.

#### 6.4.1.5 SCT Rate Expression

We obtain the SCT rate expression by incorporating the steric factor  $p$  in equation 6.4-11 or -12. Thus,

$$r_{SCT}/\text{molecules m}^{-3} \text{ s}^{-1} = pZ e^{-E^*/RT} \quad (6.4-13)$$

where  $Z = Z_{AB}$  for  $A + B \rightarrow$  products, or  $Z = Z_{AA}$  for  $A + A \rightarrow$  products. We develop the latter case in more detail at this point; a similar treatment for  $A + B \rightarrow$  products is left to problem 6-3.

For the bimolecular reaction  $2A \rightarrow \text{products}$ , by combining equations 6.4-12 and -13, using equation 6.4-7a to eliminate  $Z_{AA}$ , and converting completely to a molar basis, with  $(r_{SCT})$  in  $\text{mol L}^{-1} \text{s}^{-1}$ ,  $c'_A = 1000 N_{Av} c_A$ , where  $c_A$  is in  $\text{mol L}^{-1}$ , and  $k_B/m_A = R/M_A$ , where  $M_A$  is the molar mass of A, we obtain

$$\text{where } r_{SCT} = 2000 p N_{Av} d_A^2 (\pi R/M_A)^{1/2} T^{1/2} e^{-E^*/RT} c_A^2 \equiv k_{SCT} c_A^2 \quad (6.4-14)$$

$$k_{SCT} = 2000 p N_{Av} d_A^2 (\pi R/M_A)^{1/2} T^{1/2} e^{-E^*/RT} \quad (6.4-15)$$

We may compare these results with a second-order rate law which exhibits Arrhenius temperature dependence:

$$r_{obs} = k_{obs} c_A^2 = A e^{-E_A/RT} c_A^2 \quad (6.1-1)$$

We note that the concentration dependence ( $c_A^2$ ) is the same, but that the temperature dependence differs by the factor  $T^{1/2}$  in  $r_{SCT}$ . Although we do not have an independent value for  $E^*$  in equations 6.4-14 and -15, we may compare  $E^*$  with  $E_A$  by equating  $r_{SCT}$  and  $r_{obs}$ ; thus,

$$\begin{aligned} k_{obs} &= k_{SCT} \\ d \ln k_{obs}/dT &= d \ln k_{SCT}/dT \end{aligned}$$

and, from the Arrhenius equation, 3.1-6,

$$E_A/RT^2 = 1/2T + E^*/RT^2$$

or

$$E_A = \frac{1}{2}RT + E^* \quad (6.4-16)$$

Similarly, the pre-exponential factor  $A_{SCT}$  can be obtained by substitution of  $E^*$  from 6.4-16 into 6.4-15:

$$A_{SCT} = 2000 p N_{Av} d_A^2 (\pi R/M_A)^{1/2} e^{1/2} T^{1/2} \quad (6.4-16a)$$

According to equations 6.4-16 and -16a,  $E_A$  and  $A$  are somewhat dependent on  $T$ . The calculated values for  $A_{SCT}$  usually agree with measured values within an order of magnitude, which, considering the approximations made regarding the cross-sections, is satisfactory support for the general concepts of the theory. SCT provides a basis for the estimation of rate constants, especially where experimental values exist for related reactions. Then, values of  $p$  and  $E^*$  can be estimated by comparison with the known system.

For the reaction  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$ , the observed rate constant ( $2k$  in  $r_{\text{HI}} = 2kc_{\text{HI}}^2$ ) is  $2.42 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$  at 700 K, and the observed activation energy,  $E_A$ , is  $186 \text{ kJ mol}^{-1}$  (Moelwyn-Hughes, 1957 p. 1109). If the collision diameter,  $d_{\text{HI}}$ , is  $3.5 \times 10^{-10} \text{ m}$  for HI ( $M = 128$ ), calculate the value of the ("steric")  $p$  factor necessary for agreement between the observed rate constant and that calculated from the SCT.

**SOLUTION**

From equation 6.4-15, with  $E^*$  given by equation 6.4-17, and  $M_A = (128/1000) \text{ kg mol}^{-1}$ ,

$$k_{SCT}/p = 2.42 \times 10^{-3} \text{ L mol}^{-1} \text{ s}^{-1}$$

This is remarkably coincident with the value of  $k_{obs}$ , with the result that  $p = 1$ . Such closeness of agreement is rarely the case, and depends on, among other things, the correctness and interpretation of the values given above for the various parameters.

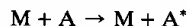
For the bimolecular reaction  $A + B \rightarrow \text{products}$ , as in the reverse of the reaction in Example 6-2, equation 6.4-15 is replaced by

$$k_{SCT} = 1000 p N_A v_{AB}^2 [8\pi R(M_A + M_B)/M_A M_B]^{1/2} T^{1/2} e^{-E^*/RT} \quad (6.4-17)$$

The proof of this is left to problem 6-3.

**6.4.1.6 Energy Transfer in Bimolecular Collisions**

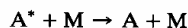
Collisions which place energy into, or remove energy from, internal modes in one molecule without producing any chemical change are very important in some processes. The transfer of this energy into reactant A is represented by the bimolecular process



where  $A^*$  is a molecule with a critical amount of internal energy necessary for a subsequent process, and M is any collision partner. For example, the dissociation of  $I_2$  discussed in Section 6.3 requires  $149 \text{ kJ mol}^{-1}$  to be deposited into the interatomic bond. The SCT rate of such a process can be expressed as the rate of collisions which meet the energy requirements to deposit the critical amount of energy in the reactant molecule:

$$r = Z_{AM} \exp(-E^*/RT) = k_{ET} c_A c_M$$

where  $E^*$  is approximately equal to the critical energy required. However, this simple theory underestimates the rate constant, because it ignores the contribution of internal energy distributed in the A molecules. Various theories which take this into account provide more satisfactory agreement with experiment (Steinfeld et al., 1989, pp. 352-357). The deactivation step



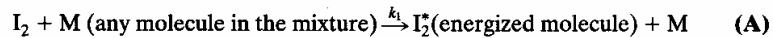
is assumed to happen on every collision, if the critical energy is much greater than  $k_B T$ .

**6.4.2 Collision Theory of Unimolecular Reactions**

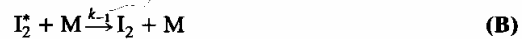
For a unimolecular reaction, such as  $I_2 \rightarrow 2I^*$ , there are apparently no collisions necessary, but the overwhelming majority of molecules do not have the energy required for this dissociation. For those that have enough energy ( $> 149 \text{ kJ mol}^{-1}$ ), the reaction occurs in the time for energy to become concentrated into motion along the reaction coordinate, and for the rearrangement to occur (about the time of a molecular vibration,  $10^{-13} \text{ s}$ ). The internal energy can be distributed among all the internal modes, and so the time required for the energy to become concentrated in the critical reaction coordinate is greater for complex molecules than for smaller ones. Those that do not have

enough energy must wait until sufficient energy is transferred by collision, as in Section 6.4.1.6. Therefore, as Lindemann (1922) recognized, three separate basic processes are involved in this reaction:

- (1) Collisions which transfer the critical amount of energy:



- (2) The removal of this energy (deactivation) by subsequent collisions (reverse of (A)):



- (3) The dissociation reaction:



Steps (A), (B), and (C) constitute a reaction mechanism from which a rate law may be deduced for the overall reaction. Thus, if, in a generic sense, we replace  $I_2$  by the reactant A,  $I_2^*$  by  $A^*$ , and  $2I^*$  by the product P, the rate of formation of  $A^*$  is

$$r_{A^*} = -k_2 c_{A^*} + k_1 c_A c_M - k_{-1} c_{A^*} c_M \quad (\text{6.4-18})$$

and the rate of reaction to form product P,  $r_P$ , is:

$$r_P = k_2 c_{A^*} = \frac{k_2 (k_1 c_A c_M - r_{A^*})}{k_2 + k_{-1} c_M} \quad (\text{6.4-19})$$

if we use equation 6.4-18 to eliminate  $c_{A^*}$ . Equation 6.4-19 contains the unknown  $r_{A^*}$ . To eliminate this we use the *stationary-state hypothesis* (SSH): an approximation used to simplify the derivation of a rate law from a reaction mechanism by eliminating the concentration of a reactive intermediate (RI) on the assumption that its rate of formation and rate of disappearance are equal (i.e., net rate  $r_{RI} = 0$ ).

By considering  $A^*$  as a reactive intermediate, we set  $r_{A^*} = 0$  in equations 6.4-18 and -19, and the latter may be rewritten as

$$r_P = \left( \frac{k_1 k_2 c_M}{k_2 + k_{-1} c_M} \right) c_A \quad (\text{6.4-20})$$

$$\equiv k_{uni} c_A \quad (\text{6.4-20a})$$

where  $k_{uni}$  is an effective first-order rate constant that depends on  $c_M$ . There are two limiting cases of equation 6.4-20, corresponding to relatively high  $c_M$  ("high pressure" for a gas-phase-reaction),  $k_{-1} c_M \gg k_2$ , and low  $c_M$  ("low pressure"),  $k_2 \gg k_{-1} c_M$ :

$$r_P = (k_1 k_2 / k_{-1}) c_A \quad (\text{"high-pressure" limit}) \quad (\text{6.4-21})$$

$$r_P = k_1 c_M c_A \quad (\text{"low-pressure" limit}) \quad (\text{6.4-22})$$

Thus, according to this (Lindemann) mechanism, a unimolecular reaction is first-order at relatively high concentration ( $c_M$ ) and second-order at low concentration. There is a

transition from first-order to second-order kinetics as  $c_M$  decreases. This is referred to as the “fall-off regime,” since, although the order increases,  $k_{uni}$  decreases as  $c_M$  decreases (from equations 6.4-20 and -20a).

This mechanism also illustrates the concept of a *rate-determining step* (*rd*s) to designate a “slow” step (relatively low value of rate constant; as opposed to a “fast” step), which then controls the overall rate for the purpose of constructing the rate law.

At low  $c_M$ , the rate-determining step is the second-order rate of activation by collision, since there is sufficient time between collisions that virtually every activated molecule reacts; only the rate constant  $k_1$  appears in the rate law (equation 6.4-22). At high  $c_M$ , the rate-determining step is the first-order disruption of  $A^*$  molecules, since both activation and deactivation are relatively rapid and at virtual equilibrium. Hence, we have the additional concept of a *rapidly established equilibrium* in which an elementary process and its reverse are assumed to be at equilibrium, enabling the introduction of an equilibrium constant to replace the ratio of two rate constants.

In equation 6.4-21, although all three rate constants appear, the ratio  $k_1/k_{-1}$  may be considered to be a virtual equilibrium constant (but it is not usually represented as such).

A test of the Lindemann mechanism is normally applied to observed apparent first-order kinetics for a reaction involving a single reactant, as in  $A \rightarrow P$ . The test may be used in either a differential or an integral manner, most conveniently by using results obtained by varying the initial concentration,  $c_{A_0}$  (or partial pressure for a gas-phase reaction). In the differential test, from equations 6.4-20 and -20a, we obtain, for an initial concentration  $c_{A_0} \equiv c_M$ , corresponding to the initial rate  $r_{P_0}$ ,

$$k_{uni} = \frac{k_1 k_2 c_{A_0}}{k_2 + k_{-1} c_{A_0}}$$

or

$$\frac{1}{k_{uni}} = \frac{k_{-1}}{k_1 k_2} + \frac{1}{k_1 c_{A_0}} = \frac{1}{k_\infty} + \frac{1}{k_1 c_{A_0}} \quad (6.4-23)$$

where  $k_\infty$  is the asymptotic value of  $k_{uni}$  as  $c_{A_0} \rightarrow \infty$ . Thus  $k_{uni}^{-1}$  should be a linear function of  $c_{A_0}^{-1}$ , from the intercept and slope of which  $k_\infty$  and  $k_1$  can be determined. This is illustrated in the following example. The integral method is explored in problem 6-4.

For the gas-phase unimolecular isomerization of cyclopropane (A) to propylene (P), values of the observed first-order rate constant,  $k_{uni}$ , at various initial pressures,  $P_0$ , at 470° C in a batch reactor are as follows:

$P_0/\text{kPa}$	14.7	28.2	51.8	101.3
$10^5 k_{uni}/\text{s}^{-1}$	9.58	10.4	10.8	11.1

- Show that the results are consistent with the Lindemann mechanism.
- Calculate the rate constant for the energy transfer (activation) step.
- Calculate  $k_\infty$ .
- Suggest a value of  $E_A$  for the deactivation step.

### SOLUTION

(a) In this example,  $P_0$  is the initial pressure of cyclopropane (no other species present), and is a measure of  $c_{A_0}$ . Expressing  $c_{A_0}$  in terms of  $P_0$  by means of the ideal-gas law,

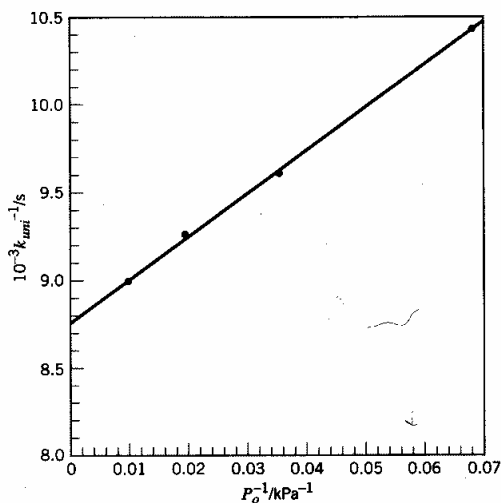


Figure 6.11 Test of Lindemann mechanism in Example 6-3

equation 4.2.3a, we rewrite equation 6.4-23 as:

$$\frac{1}{k_{uni}} = \frac{1}{k_{\infty}} + \frac{1}{k_1} \frac{RT}{P_o} \quad (6.4-23a)$$

The linear relation is shown in Figure 6.11.

(b) From the slope of the fitted linear form,  $k_1 = 0.253 \text{ L mol}^{-1} \text{ s}^{-1}$ .

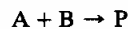
(c) Similarly, from the intercept,  $k_{\infty} = 11.4 \times 10^{-5} \text{ s}^{-1}$

(d)  $E_A$  (deactivation)  $\rightarrow 0$ , since  $A^*$  is an activated state (energetically), and any collision should lead to deactivation.

### 6.4.3 Collision Theory of Bimolecular Combination Reactions; Termolecular Reactions

A treatment similar to that for unimolecular reactions is necessary for recombination reactions which result in a single product. An example is the possible termination step for the mechanism for decomposition of  $C_2H_6$ ,  $H^{\bullet} + C_2H_5^{\bullet} \rightarrow C_2H_6$  (Section 6.1.2). The initial formation of ethane in this reaction can be treated as a bimolecular event. However, the newly formed molecule has enough energy to redissociate, and must be stabilized by transfer of some of this energy to another molecule.

Consider the recombination reaction



A three-step mechanism is as follows:

(I) Reaction to form  $P^*$  (an activated or energized form of P):



(2) Unimolecular dissociation of  $P^*$  (reverse of (A)):(3) Stabilization of  $P^*$  by collision with M (any other molecule):

Treatment of steps (A), (B), and (C) similar to that for the steps in a unimolecular reaction, including application of the SSH to  $P^*$ , results in

$$r_P = \left( \frac{k_1 k_2 c_M}{k_{-1} + k_2 c_M} \right) c_A c_B \quad (6.4-24)$$

$$\equiv k_{bi} c_A c_B \quad (6.4-25)$$

where  $k_{bi}$  is an effective second-order rate constant that depends on  $c_M$ . Just as for a unimolecular reaction, there are two limiting cases for equation 6.4-24, corresponding to relatively high and low  $c_M$ :

$$r_P = k_1 c_A c_B \quad (\text{"high-pressure" limit}) \quad (6.4-26)$$

$$r_P = (k_1 k_2 / k_{-1}) c_M c_A c_B \quad (\text{"low-pressure" limit}) \quad (6.4-27)$$

Thus, according to this three-step mechanism, a bimolecular recombination reaction is second-order at relatively high concentration ( $c_M$ ), and third-order at low concentration. There is a transition from second- to third-order kinetics as  $c_M$  decreases, resulting in a "fall-off" regime for  $k_{bi}$ .

The low-pressure third-order result can also be written as a termolecular process:



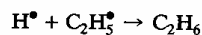
which implies that all three species must collide with one another at the same time. In the scheme above, this is pictured as taking place in two sequential bimolecular events, the second of which must happen within a very short time of the first. In the end, the distinction is a semantic one which depends on how collision is defined. There are few termolecular elementary reactions of the type



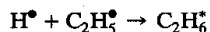
and the kinetics of these can also be thought of as sequences of bimolecular events.

The "fall-off" effects in unimolecular and recombination reactions are important in modern low-pressure processes such as chemical vapor deposition (CVD) and plasma-etching of semiconductor chips, and also for reactions in the upper atmosphere.

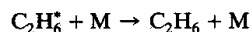
The importance of an "energized" reaction complex in bimolecular reactions is illustrated by considering in more detail the termination step in the ethane dehydrogenation mechanism of Section 6.1.2:



The formation of  $C_2H_6$  must first involve the formation of the "energized" molecule  $C_2H_6^*$ :



which is followed by collisional deactivation:

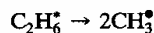


However,  $C_2H_6^*$  may convert to other possible sets of products:

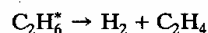
- (1) Redissociation to  $H^\bullet$  and  $C_2H_5^\bullet$ :



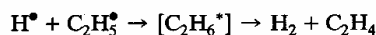
- (2) Dissociation into two methyl radicals:



- (3) Formation of stable products:



The overall process for this last possibility



can be thought of as a bimolecular reaction with a stable molecule on the reaction coordinate ( $C_2H_6^*$ ), as illustrated in Figure 6.5. The competition of these other processes with the formation of ethane can substantially influence the overall rate of ethane dehydrogenation. These and similar reactions have a substantial influence in reactions at low pressures and high temperatures.

## 6.5 TRANSITION STATE THEORY (TST)

### 6.5.1 General Features of the TST

While the collision theory of reactions is intuitive, and the calculation of encounter rates is relatively straightforward, the calculation of the cross-sections, especially the steric requirements, from such a dynamic model is difficult. A very different and less detailed approach was begun in the 1930s that sidesteps some of the difficulties. Variously known as *absolute rate theory*, *activated complex theory*, and *transition state theory* (TST), this class of model ignores the rates at which molecules encounter each other, and instead lets thermodynamic/statistical considerations predict how many combinations of reactants are in the transition-state configuration under reaction conditions.

Consider three atomic species A, B, and C, and reaction represented by



The TST considers this reaction to take place in the manner



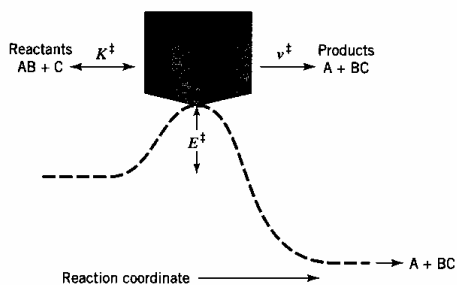


Figure 6.12 Potential energy along the reaction coordinate for reaction 6.5-2

in which  $ABC^\ddagger$  represents the transition state described in Section 6.3. The potential energy along the reaction coordinate, showing the energy barrier, is illustrated in Figure 6.12 (cf. Figure 6.3(c)).

The two main assumptions of the TST are:

- (1) The transition state is treated as an unstable molecular species in equilibrium with the reactants, as indicated by the equilibrium constant for its formation,  $K_c^\ddagger$ , where, for reaction 6.5-2,

$$K_c^\ddagger = c_{ABC^\ddagger}/c_{AB}c_C \quad (6.5-3)$$

and  $c_{ABC^\ddagger}$  is the concentration of these "molecules"; it is implied in this assumption that the transition state and the reactants are in thermal equilibrium (i.e., their internal energy distributions are given by the Boltzmann distribution).

- (2) The frequency with which the transition state is transformed into products,  $\nu^\ddagger$ , can be thought of as a typical unimolecular rate constant; no barrier is associated with this step. Various points of view have been used to calculate this frequency, and all rely on the assumption that the internal motions of the transition state are governed by thermally equilibrated motions. Thus, the motion along the reaction coordinate is treated as thermal translational motion between the product fragments (or as a vibrational motion along an unstable potential). Statistical theories (such as those used to derive the Maxwell-Boltzmann distribution of velocities) lead to the expression:

$$\nu^\ddagger = k_B T/h \quad (6.5-4)$$

where  $k_B$  is the Boltzmann constant and  $h$  is Planck's constant. In some variations of TST, an additional factor (a transmission coefficient,  $\kappa$ ) is used to allow for the fact that not all decompositions of the transition state lead to products, but this is seldom used in the estimation of rate constants by the TST.

Thus, from equations 6.5-3 and -4, the rate of formation of products (P) in reaction 6.5-2 is written as

$$r_P = \nu^\ddagger c_{ABC^\ddagger} = (k_B T/h) K_c^\ddagger c_{AB} c_C \quad (6.5-5)$$

If we compare equation 6.5-5 with the usual form of rate law, then the rate constant is given by

$$k = (k_B T/h) K_c^\ddagger \quad (6.5-6)$$

In the TST, molecularity ( $m$ ) is the number of reactant molecules forming one molecule of the transition state. In reaction 6.5-2,  $m = 2$  (AB and C); that is, the formation is bimolecular. Other possibilities are  $m = 1$  (unimolecular) and  $m = 3$  (termolecular). The molecularity of formation of the transition state affects the form of  $K_c^\ddagger$ , and the order of the reaction equals  $m$ .

### 6.5.2 Thermodynamic Formulation

The reaction isotherm of classical thermodynamics applied to the formation of the transition state relates  $K_c^\ddagger$  to  $\Delta G^{\circ\ddagger}$ , the standard Gibbs energy of formation of the activated complex:

$$\Delta G^{\circ\ddagger} = -RT \ln K_c^\ddagger \quad (6.5-7)$$

Also

$$\Delta G^{\circ\ddagger} = \Delta H^{\circ\ddagger} - T\Delta S^{\circ\ddagger} \quad (6.5-8)$$

where  $\Delta H^{\circ\ddagger}$  and  $\Delta S^{\circ\ddagger}$  are, respectively, the (standard) enthalpy of activation and (standard) entropy of activation. Combining equations 6.5-6 to -8, we obtain

$$k = (k_B T/h) e^{\Delta S^{\circ\ddagger}/R} e^{-\Delta H^{\circ\ddagger}/RT} \quad (6.5-9)$$

for the rate constant according to the TST. As with the SCT, we may compare this expression with observed behavior

$$k_{obs} = A e^{-E_A/RT} \quad (3.1-8)$$

to obtain interpretations of the Arrhenius parameters  $A$  and  $E_A$  in terms of the TST quantities.

We first relate  $E_A$  to  $\Delta H^{\circ\ddagger}$ . From equation 6.5-6,

$$\frac{d \ln k}{dT} = \frac{1}{T} + \frac{d \ln K_c^\ddagger}{dT} = \frac{1}{T} + \frac{\Delta U^{\circ\ddagger}}{RT^2} \quad (6.5-10)$$

where  $\Delta U^{\circ\ddagger}$  is the internal energy of activation, and we have used the analogue of the van't Hoff equation (3.1-5) for the temperature-dependence of  $K_c^\ddagger$  (Denbigh, 1981, p.147). For the activation step as a gas-phase reaction of molecularity  $m$  involving ideal gases, from the definition  $H = U + PV$ ,

$$\Delta H^{\circ\ddagger} = \Delta U^{\circ\ddagger} + (1 - m)RT. \quad (6.5-11)$$

From equations 3.1-8 (i.e., from 3.1-6), and 6.5-10 and -11,

$$E_A = \Delta H^{\circ\ddagger} + mRT \quad (6.5-12)$$

We next relate the pre-exponential factor  $A$  to  $\Delta S^{\circ\ddagger}$ . From equations 6.5-9 and 6.5-12,

$$k = (k_B T/h) e^{\Delta S^{\circ\ddagger}/R} e^m e^{-E_A/RT} \quad (6.5-13)$$

**Table 6.1** Expected (approximate) values of  $\Delta S^{\ddagger}$  for different values of molecularity ( $m$ ) at 500 K

$m$	$A/(\text{L mol}^{-1})^{m-1} \text{ s}^{-1}$	$\Delta S^{\ddagger}/\text{J mol}^{-1} \text{ K}^{-1}$
1	$10^{13}$ to $10^{14}$	0
2	$10^{11}$ to $10^{12}$	-45
3	$10^9$ to $10^{10}$	-90

Comparing equations 6.5-13 and 3.1-8, we obtain

$$A = (k_B T/h) e^{\Delta S^{\ddagger}/R} e^m \quad (6.5-14)$$

or

$$\Delta S^{\ddagger} = R[\ln(Ah/k_B T) - m] \quad (6.5-15)$$

$$= 8.314(-23.76 + \ln A - \ln T - m) \text{ J mol}^{-1} \text{ K}^{-1} \quad (6.5-15a)$$

on substitution of numerical values for the constants.

From equation 6.5-15a and typical experimental values of  $A$ , we may estimate expected values for  $\Delta S^{\ddagger}$ . The results are summarized in Table 6.1.

If the Arrhenius parameters for the gas-phase unimolecular decomposition of ethyl chloride ( $\text{C}_2\text{H}_5\text{Cl}$ ) to ethylene ( $\text{C}_2\text{H}_4$ ) and  $\text{HCl}$  are  $A = 4 \times 10^{14} \text{ s}^{-1}$  and  $E_A = 254 \text{ kJ mol}^{-1}$ , calculate the entropy of activation ( $\Delta S^{\ddagger}/\text{J mol}^{-1} \text{ K}^{-1}$ ), the enthalpy of activation ( $\Delta H^{\ddagger}/\text{J mol}^{-1}$ ), and the Gibbs energy of activation ( $\Delta G^{\ddagger}/\text{J mol}^{-1}$ ) at 500 K. Comment on the value of  $\Delta S^{\ddagger}$  in relation to the normally "expected" value for a unimolecular reaction.

### SOLUTION

From equation 6.5-15,

$$\begin{aligned} \Delta S^{\ddagger} &= R \left( \ln \frac{Ah}{k_B T} - m \right) \\ &= 8.314 \left[ \ln \left( \frac{4 \times 10^{14} \times 6.626 \times 10^{-34}}{1.381 \times 10^{-23} \times 500} \right) - 1 \right] \\ &= 22 \text{ J mol}^{-1} \text{ K}^{-1} \end{aligned}$$

From equation 6.5-12,

$$\begin{aligned} \Delta H^{\ddagger} &= E_A - mRT \\ &= 254,000 - 1(8.314)500 \\ &= 250,000 \text{ J mol}^{-1} \end{aligned}$$

$$\begin{aligned}
 \Delta G^{\ddagger} &= \Delta H^{\ddagger} - T\Delta S^{\ddagger} & (6.5-8) \\
 &= 250,000 - 500(22) \\
 &= 239,000 \text{ J mol}^{-1}
 \end{aligned}$$

(Comment: the normally expected value of  $\Delta S^{\ddagger}$  for a unimolecular reaction, based on  $A \approx 10^{13}$  to  $10^{14}$ , is  $\approx 0$  (Table 6.1); the result here is greater than this.)

A method for the estimation of thermodynamic properties of the transition state and other unstable species involves analyzing parts of the molecule and assigning separate properties to functional groups (Benson, 1976). Another approach stemming from statistical mechanics is outlined in the next section.

### 6.5.3 Quantitative Estimates of Rate Constants Using TST with Statistical Mechanics

Quantitative estimates of  $E_0^{\ddagger}$  are obtained the same way as for the collision theory, from measurements, or from quantum mechanical calculations, or by comparison with known systems. Quantitative estimates of the  $A$  factor require the use of statistical mechanics, the subject that provides the link between thermodynamic properties, such as heat capacities and entropy, and molecular properties (bond lengths, vibrational frequencies, etc.). The transition state theory was originally formulated using statistical mechanics. The following treatment of this advanced subject indicates how such estimates of rate constants are made. For more detailed discussion, see Steinfeld et al. (1989).

Statistical mechanics yields the following expression for the equilibrium constant,  $K_c^{\ddagger}$ ,

$$K_c^{\ddagger} = (Q^{\ddagger}/Q_r) \exp(-E_0^{\ddagger}/RT) \quad (6.5-16)$$

The function  $Q^{\ddagger}$  is the *partition function* for the transition state, and  $Q_r$  is the product of the partition functions for the reactant molecules. The partition function essentially counts the number of ways that thermal energy can be "stored" in the various modes (translation, rotation, vibration, etc.) of a system of molecules, and is directly related to the number of quantum states available at each energy. This is related to the freedom of motion in the various modes. From equations 6.5-7 and -16, we see that the entropy change is related to the ratio of the partition functions:

$$\Delta S^{\ddagger} = R \ln(Q^{\ddagger}/Q_r) \quad (6.5-17)$$

An increase in the number of ways to store energy increases the entropy of a system. Thus, an estimate of the pre-exponential factor  $A$  in TST requires an estimate of the ratio  $Q^{\ddagger}/Q_r$ . A common approximation in evaluating a partition function is to separate it into contributions from the various modes of energy storage, translational (tr), rotational (rot), and vibrational (vib):

$$Q = Q_{tr} Q_{rot} Q_{vib} Q(\text{electronic, symmetry}) \quad (6.5-18)$$

This approximation is valid if the modes of motion are completely independent—an assumption that is often made. The ratio in equation 6.5-17 can therefore be written as a product of ratios:

$$(Q^{\ddagger}/Q_r) = (Q_{tr}^{\ddagger}/Q_{tr}) (Q_{rot}^{\ddagger}/Q_{rot}) (Q_{vib}^{\ddagger}/Q_{vib}) \dots \quad (6.5-19)$$

Furthermore, each  $Q$  factor in equation 6.5-18 can be further factored for each individual mode, if the motions are independent; for example,

**Table 6.2** Forms for translational, rotational, and vibrational contributions to the molecular partition function

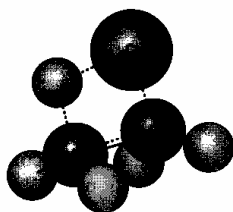
Mode	Partition function	Model
$Q_{tr}/V =$ translational (per unit volume)	$(2\pi mk_B T/h^2)^{3/2}$	particle of mass $m$ in 3D box of volume $V$ ; increases if mass increases
$Q_{rot} =$ rotational	$(8\pi^2 I k_B T/h^2)^{1/2}$	rigid rotating body with moment of inertia $I$ per mode; increases if moment of inertia increases
$Q_{vib} =$ vibrational	$(1 - \exp(-hc\nu/k_B T))^{-1}$	harmonic vibrator with frequency $\nu$ per mode; increases if frequency decreases (force constant decreases)

$$Q_{vib} = Q_{vib, mode 1} Q_{vib, mode 2} \dots \quad (6.5-20)$$

with a factor for each normal mode of vibration. The  $A$  factor can then be evaluated by calculating the individual ratios. For the translational, rotational, and vibrational modes of molecular energy, the results obtained from simplified models for the contributions to the molecular partition function are shown in Table 6.2.

Generally,  $Q_{tr} > Q_{rot} > Q_{vib}$ , reflecting the decreasing freedom of movement in the modes. Evaluating the partition functions for the reactants is relatively straightforward, since the molecular properties (and the related thermodynamic properties) can be measured. The same parameters for the transition state are not available, except in a few simple systems where the full potential energy surface has been calculated. The problem is simplified by noting that if a mode is unchanged in forming the transition state, the ratio for that mode is equal to 1. Therefore, only the modes that change need to be considered in calculating the ratio. The following two examples illustrate how estimates of rate constants are made, for unimolecular and bimolecular reactions.

For the unimolecular reaction in Example 6-4,  $C_2H_3Cl \rightarrow HCl + C_2H_4$ , the transition state should resemble the configuration below, with the C-Cl and C-H bonds almost broken, and HCl almost formed:



The ratio of translational partition functions ( $Q_{tr}^\ddagger/Q_{tr}$ ) is 1 here, and for all unimolecular reactions, because the mass and number of molecules of the reactants is the same as for the transition state. The rotational ratio ( $Q_{rot}^\ddagger/Q_{rot}$ ) is given by the ratio of the moments of inertia:  $(I_1^\ddagger I_2^\ddagger I_3^\ddagger / I_1 I_2 I_3)^{1/2}$ . The moments of inertia are probably slightly higher in the

transition state because the important Cl–C bond is stretched. The increased C–C–Cl bond angle also increases the value of the smallest moment of inertia. Thus, the ratio  $Q_{rot}^\ddagger/Q_{rot}$  is greater than 1. An exact calculation requires a quantitative estimate of the bond lengths and angles. The transition state has the same number of vibrational modes, but several of the vibrational frequencies in the transition state are expected to be somewhat lower, particularly those involving both the weakened C–Cl bond stretch and the affected C–H bond. It is also possible to form the transition state with any of the three hydrogen atoms on the  $\text{CH}_3$  group, and so a symmetry number of 3 accrues to the transition state. The internal rotation around the C–C bond is inhibited in the transition state, which decreases the contribution of this model to  $Q^\ddagger$ , but the rest of the considerations increase it, and the net effect is that  $(Q^\ddagger/Q_r) > 1$ . From the value of the  $A$  factor in Example 6-4,  $A/(kT/h) = (Q^\ddagger/Q_r) = 38.4$ . As with many theories, the information flows two ways: (1) measured rate constants can be used to study the properties of transition states, and (2) information about transition states gained in such studies, as well as in calculations, can be used to estimate rate constants.

Consider a bimolecular reaction,  $A + B \rightarrow \text{products}$ . Confining two molecules  $A$  and  $B$  to be together in the transition state in a bimolecular reaction always produces a loss of entropy. This is dominated by the ratio of the translational partition functions:

$$\begin{aligned} (Q_{tr}^\ddagger/V)/(Q_{trA}/V)(Q_{trB}/V) &= (2\pi m_{A+B} k_B T/h^2)^{3/2} / [2\pi m_A k_B T/h^2]^{3/2} (2\pi m_B k_B T/h^2)^{3/2}] \\ &= (2\pi \mu k_B T/h^2)^{-3/2} \end{aligned}$$

where  $\mu$  is the reduced mass, equation 6.4-6. This ratio introduces the volume units to the rate constant, and is always less than 1 for a bimolecular (and termolecular) reaction. At 500 K, and for a reduced mass of  $30 \text{ g mol}^{-1}$ , this factor is  $1.7 \times 10^{-6} \text{ L mol}^{-1} \text{ s}^{-1}$ , and corresponds to an entropy change of  $-110 \text{ J mol}^{-1} \text{ K}^{-1}$ . The number of internal modes (rotation and vibration) is increased by 3, which partly compensates for this loss of entropy.

If  $A$  and  $B$  are atoms, the two rotational modes in the transition state add  $70 \text{ J mol}^{-1} \text{ K}^{-1}$  to the entropy of the transition state. The total  $\Delta S^\ddagger$  is therefore approximately  $-40 \text{ J mol}^{-1} \text{ K}^{-1}$ , a value in agreement with the typical value given in Table 6.1. For each of the two rotational modes, the moment of inertia cited in Table 6.2 is  $I = \mu d_{AB}^2$ ; the value above is calculated using  $d_{AB} = 3 \times 10^{-10} \text{ m}$ .

#### 6.5.4 Comparison of TST with SCT

Qualitatively, both the TST and the SCT are in accord with observed features of kinetics:

- (1) Both theories yield laws for elementary reactions in which order, molecularity, and stoichiometry are the same (Section 6.1.2).
- (2) The temperature dependence of the reaction rate constant closely (but not exactly) obeys the Arrhenius equation. Both theories, however, predict non-Arrhenius behavior. The deviation from Arrhenius behavior can usually be ignored over a small temperature range. However, non-Arrhenius behavior is common (Steinfeld et al., 1989, p. 321). As a consequence, rate constants are often fitted to the more general expression  $k = BT^n \exp(-E/RT)$ , where  $B$ ,  $n$ , and  $E$  are empirical constants.

The activation energy in both theories arises from the energy barrier at the transition state, and is treated similarly in both. The relationship between the pre-exponential factors in the two theories is not immediately obvious, since many of the terms which arise

from the intuitive dynamical picture in SCT are “hidden” in the partition functions in TST. Nevertheless, the ratio of partition functions (thermodynamics) tells how easy (probable) the achievement of the transition state is. This ratio contains many of the notions in collision theories, for example, (1) how close the reactants must approach to react (equivalent to the hard-sphere cross-section in SCT), and (2) the precision of alignment of the atoms in the transition state (equivalent to the  $p$  factor in SCT). The combination of a smaller cross-section and more demanding configuration is equivalent to a smaller entropy in the transition state. All of the dynamics in TST is contained in  $kT/h$ , which in turn is contained in the velocity of approach in bimolecular reactions in SCT. The assumption that the transition state is in thermal equilibrium with the reactants is central to a discussion of the merits of TST. On the one hand, this assumption allows a relatively simple statistical (thermodynamic) calculation to replace the detailed dynamics. This has made transition state theory the more useful of the two for the estimation of unmeasured rate constants. This considerable advantage of TST is also its main weakness, and TST must fail when the assumption of thermal equilibrium is grossly wrong. Such an example is the behavior of unimolecular reactions at low pressure, where the supply of energy is rate limiting. Both theories have been very useful in the understanding of kinetics, and in building detailed mechanisms of important chemical processes.

## 6.6 ELEMENTARY REACTIONS INVOLVING OTHER THAN GAS-PHASE NEUTRAL SPECIES

The two simple theories SCT and TST have been developed in the context of neutral gas-phase reactions. In this section, we consider other types of elementary reactions listed in Section 6.2.1, and include reactions in condensed phases. The rates of this diverse set of reactions, including photochemistry, can be understood with the concepts developed for gas-phase reactions.

### 6.6.1 Reactions in Condensed Phases

Reactions in solution proceed in a similar manner, by elementary steps, to those in the gas phase. Many of the concepts, such as reaction coordinates and energy barriers, are the same. The two theories for elementary reactions have also been extended to liquid-phase reactions. The TST naturally extends to the liquid phase, since the transition state is treated as a thermodynamic entity. Features not present in gas-phase reactions, such as solvent effects and activity coefficients of ionic species in polar media, are treated as for stable species. Molecules in a liquid are in an almost constant state of collision so that the collision-based rate theories require modification to be used quantitatively. The energy distributions in the jostling motion in a liquid are similar to those in gas-phase collisions, but any reaction trajectory is modified by interaction with neighboring molecules. Furthermore, the frequency with which reaction partners approach each other is governed by diffusion rather than by random collisions, and, once together, multiple encounters between a reactant pair occur in this molecular traffic jam. This can modify the rate constants for individual reaction steps significantly. Thus, several aspects of reaction in a condensed phase differ from those in the gas phase:

- (1) *Solvent interactions*: Because all species in solution are surrounded by solvent, the solvation energies can dramatically shift the energies of the reactants, products, and the transition state. The most dramatic changes in energies are for ionic species, which are generally unimportant in gas-phase chemistry, but are prominent in polar solvents. Solvation energies for other species can also be large enough to change the reaction mechanism. For example, in the alkylation of

naphthol by methyl iodide, changes in solvent can shift the site of alkylation from oxygen to carbon. The TST is altered by allowing the thermodynamic properties to be modified by activity coefficients.

- (2) *Encounter frequency*: Between two reactive species in solution, the encounter frequency is slower than in the gas phase at the same concentration. The motion in a liquid is governed by diffusion, and in one version, which assumes that there are no long-range forces between the reactants (too simple for ionic species), the collision rate is given by  $Z_{AB} = 4\pi Dd_{AB}c'_A c'_B$ , where  $D$  is the sum of the diffusion coefficients of the two species. If reaction occurs on every collision, then the rate constant is lower in solution (even with no appreciable solvent interactions) than in the gas phase. If reaction does not occur on every collision, but is quite slow, then the probability of finding the two reactants together is similar to that in the gas phase, and the rate constants are also similar. One way to think of this is that diffusion in the liquid slows the rate at which the reactants move away from each other to the same degree that it slows the rate of encounters, so that each encounter lasts longer in a liquid. This "trapping" of molecules near each other in condensed phases is sometimes referred to as the "cage effect," and is important in photochemical reactions in liquids, among others.
- (3) *Energy transfer*: Because the species are continually in collision, the rate of energy transfer is never considered to be the rate-limiting step, unlike in unimolecular gas-phase reactions.
- (4) *Pressure effects*: The diffusion through liquids is governed by the number of "defects" or atomic-sized holes in the liquid. A high external pressure can reduce the concentration of holes and slow diffusion. Therefore, in a liquid, a diffusion-controlled rate constant also depends on the pressure.

## 6.6.2 Surface Phenomena

Elementary reactions on solid surfaces are central to heterogeneous catalysis (Chapter 8) and gas-solid reactions (Chapter 9). This class of elementary reactions is the most complex and least understood of all those considered here. The simple quantitative theories of reaction rates on surfaces, which begin with the work of Langmuir in the 1920s, use the concept of "sites," which are atomic groupings on the surface involved in bonding to other atoms or molecules. These theories treat the sites as if they are stationary gas-phase species which participate in reactive collisions in a similar manner to gas-phase reactants.

### 6.6.2.1 Adsorption

Adsorption can be considered to involve the formation of a "bond" between the surface and a gas-phase or liquid-phase molecule. The surface "bond" can be due to physical forces, and hence weak, or can be a chemical bond, in which case adsorption is called chemisorption. Adsorption is therefore like a bimolecular combination reaction:



where "s" is an "open" surface site without a molecule bonded to it, and  $A \bullet s$  is a surface-bound molecule of A. By analogy with gas-phase reactions, the collision rate of molecules of A with a site with a reaction cross-section  $\sigma$  on a flat surface,  $Z_A$ , can be calculated by integration of the Maxwell-Boltzmann velocity distributions over the possible angles of impingement:

$$Z_A/\text{molecules site}^{-1} \text{ s}^{-1} = (1/4)\sigma\bar{u}c'_A \quad (6.6-2)$$

where  $\bar{u}$  is the average velocity  $(8k_B T/\pi m_A)^{1/2}$ . If the reaction requires a direct impingement on an open surface site (one with no molecules bonded to it), then the rate of adsorption per unit area on the surface should be proportional to the number of open sites on the surface:

$$r_a/\text{mol m}^{-2}\text{s}^{-1} = Z_A N \theta_{\square}/N_{Av} = (2.5 \times 10^{-4} \sigma \bar{u} N) \theta_{\square} c_A \equiv k_a \theta_{\square} c_A \quad (6.6-3)$$

where  $N$  is the number of sites  $\text{m}^{-2}$  of surface,  $\theta_{\square}$  is the fraction of sites which are open, and  $c_A$  is the gas-phase concentration in  $\text{mol L}^{-1}$ . This "bimolecular" type of adsorption kinetics, where the cross-section does not depend on the amount of adsorbed material, is said to obey Langmuir adsorption kinetics. The factor in parentheses is the SCT expression for the adsorption rate constant  $k_a$ . Like bimolecular combination reactions, no activation energy is expected, unless bond-breaking must take place in the solid or in the adsorbing molecule.

### 6.6.2.2 Desorption

Desorption, the reverse of reaction 6.6-1, that is,



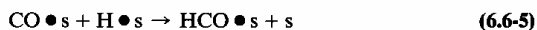
is a unimolecular process, which, like gas-phase analogues, requires enough energy to break the bond to the surface. Similar to reactions in liquids, energy is transferred through the solid, making collisions unnecessary to supply energy to the adsorbed molecule. If the sites are independent, the rate is proportional to the amount of adsorbed material:

$$r_d/\text{mol m}^{-2}\text{s}^{-1} = k_d \theta_A$$

where  $k_d$  is the unimolecular desorption rate constant, which is expected to have an activation energy similar to the adsorption bond strength, and  $\theta_A$  is the fraction of the sites which have A adsorbed on them, often called the "coverage" of the surface by A.

### 6.6.2.3 Surface Reactions

The simplest theories of reactions on surfaces also predict surface rate laws in which the rate is proportional to the amount of each adsorbed reactant raised to the power of its stoichiometric coefficient, just like elementary gas-phase reactions. For example, the rate of reaction of adsorbed carbon monoxide and hydrogen atoms on a metal surface to produce a formyl species and an open site,



is assumed to exhibit the following rate law:

$$r/\text{mol m}^{-2}\text{s}^{-1} = k \theta_{\text{CO}} \theta_{\text{H}} \quad (6.6-6)$$

This behavior arises, as in the gas phase, from assuming statistical encounter rates of the reactants on the surface. Because the motion of adsorbed species on surfaces is not well understood, however, quantitative prediction of this encounter rate is not generally possible.

**6.6.2.4 General Observations**

Simple theories provide useful rate expressions for reactions involving solid surfaces (Chapter 8). In fundamental studies, there are examples of adsorption kinetics which obey the simple Langmuir rate expressions. However, many others are more complex and do not show first-order dependence on the number of open sites. These variations can be appreciated, if we accept the notion that a solid can be thought of as a giant molecule which presents a large number of locations where bonds can be made, and that changes in the bonding at one site on this molecule can change the bonding at other locations. As a result, the site properties can depend on whether molecules are adsorbed on neighboring sites. Furthermore, molecules can "pre-adsorb" weakly even on occupied sites and "hunt" for an open site. The desorption rate constant can vary with the amount of adsorbed material, if, for instance, the surface bond strength depends on the amount of adsorbed material. For these reasons, and because of the difficulty in obtaining reliable information on the structure of surface-adsorbed reaction intermediates, quantitative theories of surface reactions are not generally available.

**6.6.3 Photochemical Elementary Reactions**

Light energy interacts with matter in quantum units called photons which contain energy  $E = h\nu$  (Section 6.2.1.2). The frequency  $\nu$  is related to the wavelength  $\lambda$  by

$$\lambda = c/\nu \quad (6.6-7)$$

where  $c$  is the speed of light ( $3 \times 10^8 \text{ m s}^{-1}$ ). The energy of photons can be expressed in units, such as  $\text{J mol}^{-1}$ , to compare with chemical energies:

$$E/\text{J mol}^{-1} = N_A h \nu = N_A h c / \lambda = 0.1196/\lambda \quad (6.6-8)$$

where  $\lambda$  is in m. Low-energy photons (infrared wavelengths and longer,  $\lambda > \approx 0.8 \mu\text{m}$ ,  $E_{\text{photon}} < 150 \text{ kJ mol}^{-1}$ ) are generally only capable of exciting *vibrational* levels in the molecules. In photochemistry, we are usually concerned with photons with enough energy to produce changes in *electronic* states (visible wavelengths and shorter,  $\lambda < \approx 0.8 \mu\text{m}$ ,  $E_{\text{photon}} > 150 \text{ kJ mol}^{-1}$ ), and therefore to disrupt chemical bonds.

**6.6.3.1 Light Absorption**

Although light behaves like both waves and particles, photons can be thought of as particles which participate in elementary reactions analogous to those for neutral molecules. Furthermore, the language of collision theories is often used to describe the rates of these reactions. For example, the absorption of light can be treated in a collision theory as a "bimolecular" process in which light particles (photons) collide with the molecules, and are absorbed to produce a higher-energy "excited" state in the molecule:



There is a cross-section for absorption,  $\sigma$ , which characterizes the size of the "target" a photon has to hit to be absorbed. The rate of absorption is given a little differently, since the photons travel much faster than the A molecules (which can be treated as stationary). If the flux of photons (number traversing a given area per unit time) is  $I$ , then the rate of absorption per unit volume is

$$r/\text{events m}^{-3} \text{ s}^{-1} = (I/(\text{photons m}^{-2} \text{ s}^{-1})) \times (c'_A/\text{molecules m}^{-3}) \times (\sigma/\text{m}^2) \quad (6.6-10)$$

The attenuation of a light beam as it traverses a volume of light-absorbing material of thickness  $dl$  can be expressed as

$$r = -dI/dl = I\sigma c'_A \quad (6.6-11)$$

The integration of equation 6.6-11 with the boundary condition that  $I = I_o$  at  $l = 0$  gives the Beer-Lambert law (with  $c_A/\text{mol L}^{-1} = c'_A/N_{Av}$ ):

$$I = I_o \exp(-ac_A l) \quad (6.6-12)$$

where  $a (= \sigma N_{Av}/1000)$  is called the molar extinction coefficient of the medium. The cross-section is highly energy dependent and produces characteristic absorption spectra for each molecule.

### 6.6.3.2 Elementary Reactions of Molecules in Excited States

An electronically excited molecule can undergo several subsequent reaction steps. In addition to dissociation and rearrangements, there are processes involving light. These are:

*Light emission (fluorescence):* The reverse of reaction 6.6-9



is called fluorescence and can be thought of as another unimolecular reaction, with a first-order rate expression:

$$r = k_e c_A^* \quad (6.6-14)$$

The rate constant  $k_e$  corresponds to the reciprocal of the lifetime of the excited state. *Internal conversion:* The excited state can do other things, such as convert some of the original electronic excitation to a mixture of vibration and a different electronic state. These are also treated as unimolecular processes with associated rate constants:



Often, the second state formed this way is longer-lived, thus giving the excited molecule a longer time to undergo other reactions.

*Stimulated emission:* Another form of photon emission is called stimulated emission, where a photon of the right energy can cause an excited state to emit an additional identical photon, that is,



The waves of the two "product" photons are in phase; this process is the basis of laser operation.

## 6.6.4 Reactions in Plasmas

In specialized processes associated with the materials science industry, a reactive atmosphere is generated by reactions in which charged species are participants. A gaseous system wherein charged particles (electrons, ions) are important species is called a *plasma*, and the response of charged particles to an external field is used to increase

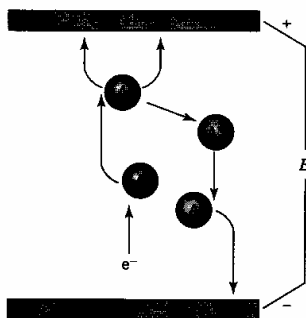


Figure 6.13 Illustration of collisional processes in a plasma

their translational energy. Consider a gas which has an electric field  $E$  ( $\text{V cm}^{-1}$ ) applied across it, as illustrated in Figure 6.13.

An electron (or ion) in the gas is accelerated (gains kinetic energy) in the electric field until it collides with a gas molecule (A). In this collision, kinetic energy is transferred to the collision partner and eventually randomized to the rest of the gas. The electron is again accelerated until the next collision, and so on. The average energy attained before each collision is

$$E_{kin} = E\lambda \quad (6.6-17)$$

where  $\lambda$  is the mean free path (average distance between collisions). For illustration, consider a gas at one bar ( $P$ ) and an applied electric field  $E$  of  $1000 \text{ V cm}^{-1}$ :  $\lambda \approx 1 \mu\text{m}$ , and the average kinetic energy of the electrons is  $0.1 \text{ eV}$  (electron volt) or about  $10 \text{ kJ mol}^{-1}$ . This is not enough to disrupt any chemical bonds and only serves to increase the gas temperature. The average energy can be increased by increasing the field strength or the mean free path (by decreasing  $P$ ). As the average energy rises, more can be accomplished in the collisions. At an average energy of a few hundred  $\text{kJ mol}^{-1}$ , bonds can be broken and electronic excitations achieved in the collisions:



The reactive species produced in these reactions can then participate in chemical processes. At slightly higher energy, it is possible to ionize the neutral species in the gas in the collisions:



Figure 6.13 schematically shows this event. The control of a plasma then relies on control of pressure and voltage/current. Although plasma chemistry takes place in the gas phase, the reactive intermediates are often used to accomplish the production or etching of solid materials, as in chemical vapor deposition (CVD).

## 6.7 SUMMARY

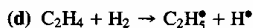
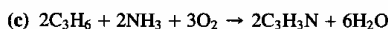
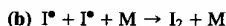
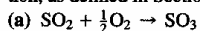
This chapter contains basic information for at least partial understanding of reaction kinetics. Some main points are summarized as follows:

- (1) Almost all chemical reactions involve a sequence of elementary steps, and do not occur in a single step.
- (2) The elementary steps in gas-phase reactions have rate laws in which reaction order for each species is the same as the corresponding molecularity. The rate constants for these elementary reactions can be understood quantitatively on the basis of simple theories. For our purpose, reactions involving photons and charged particles can be understood in the same way.
- (3) Elementary steps on surfaces and in condensed phases are more complex because the environment for the elementary reactions can change as the composition of the reaction mixture changes, and, in the case of surface reactions, there are several types of reactive sites on solid surfaces. Therefore, the rate constants of these elementary steps are not really constant, but can vary from system to system. Despite this complexity, the approximation of a single type of reaction step is useful and often generally correct.

In the following chapter, rate laws based on reaction mechanisms are developed. Although some of these are of the simple "generic" form described in Chapters 3 and 4, others are more complex. In some cases of reactor design, only an approximate fit to the real reaction kinetics is required, but more often the precision of the correct law is desirable, and the underlying mechanistic information can be useful for the rational improvement of chemical processes.

## 6.8 PROBLEMS FOR CHAPTER 6

**6-1** In each of the following cases, state whether the reaction written could be an elementary reaction, as defined in Section 6.1.2; explain briefly.



**6-2** Calculate the fraction of ideal-gas molecules with translational kinetic energy equal to or greater than  $5000 \text{ J mol}^{-1}$  (a) at 300 K, and (b) at 1000 K.

**6-3** Show that, for the bimolecular reaction  $\text{A} + \text{B} \rightarrow \text{products}$ ,  $k_{\text{SCR}}$  is given by equation 6.4-17.

**6-4** Some of the results obtained by Hinshelwood and Askey (1927) for the decomposition of dimethyl ether,  $(\text{CH}_3)_2\text{O}$  (A), to  $\text{CH}_4$ ,  $\text{CO}$  and  $\text{H}_2$  at 777.2 K in a series of experiments in a constant-volume batch reactor are as follows:

$P_o/\text{kPa}$	7.7	12.1	22.8	34.8	52.5	84.8
$t_{31}/\text{s}$	1500	1140	824	670	590	538

Each pair of points,  $P_o$  and  $t_{31}$ , refers to one experiment.  $P_o$  is the initial pressure of ether (no other species present initially), and  $t_{31}$  is the time required for 31% of the ether to decompose.

- (a) If the reaction is first-order, calculate the value of the rate constant  $k_{\text{uni}}/\text{s}^{-1}$  for each experiment.
  - (b) Test, using the differential method, whether the experimental data conform to the Lindemann hypothesis for a unimolecular reaction, and, if appropriate, calculate the values of the rate constants in the unimolecular mechanism as far as possible; use units of L, mol, s.
- 6-5** Repeat problem 6-4 using an integral method. For this purpose, substitute the rate law into the material balance for a constant-volume BR, and integrate the resulting expression to relate  $f_A$  and  $t$ . Then, with  $c_{A0}$  as a parameter (corresponding to  $P_o$  in problem 6-4), show that, for a

constant value of  $f_A$  (0.31 in problem 6-4),  $t_{f_A}$  ( $t_{31}$  above) is a linear function of  $1/c_{A_0}$ , from the slope and intercept of which  $k_1$  and  $k_\infty$  can be determined. Compare the values with those obtained in problem 6-4.

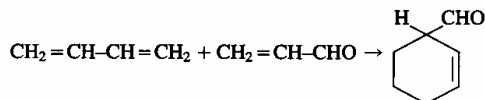
- 6-6 (a) Is the experimental quantity  $E_A$  in the Arrhenius equation intensive or extensive? Does its numerical value depend on the way in which the stoichiometry of reaction is expressed (cf.  $\Delta H$  of reaction)?  
 (b) The dimensions of  $E_A$  are energy  $\text{mol}^{-1}$ . To what does "mol" refer?
- 6-7 The isomerization of cyclopropane to propylene has Arrhenius parameters  $A = 1.6 \times 10^{15} \text{ s}^{-1}$  and  $E_A = 270 \text{ kJ mol}^{-1}$ .  
 (a) Calculate the entropy of activation,  $\Delta S^{\ddagger}/\text{J mol}^{-1} \text{ K}^{-1}$ , at 500 K.  
 (b) Comment on the answer in (a) in comparison with the "expected" result for a unimolecular reaction.  
 (c) Calculate the enthalpy of activation,  $\Delta H^{\ddagger}/\text{kJ mol}^{-1}$ , at 500 K.
- 6-8 Rowley and Steiner (1951) have obtained the result

$$k = A \exp(-E_A/RT) = 3.0 \times 10^7 \exp(-115,000/RT),$$

where  $A$  is in  $\text{L mol}^{-1} \text{ s}^{-1}$  and  $E_A$  is in  $\text{J mol}^{-1}$ , for the rate constant for the reaction



- (a) Calculate the entropy of activation for this reaction at 800 K.  
 (b) Comment on the answer in (a) in comparison with the "expected" result for a bimolecular reaction.  
 (c) Calculate the enthalpy of activation in  $\text{kJ mol}^{-1}$ .
- 6-9 (a) If the Arrhenius parameters for the gas-phase reaction



are  $A = 1.5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$  and  $E_A = 82.8 \text{ kJ mol}^{-1}$ , calculate, at 500 K,

- (i) the entropy of activation ( $\Delta S^{\ddagger}/\text{J mol}^{-1} \text{ K}^{-1}$ ), and  
 (ii) the enthalpy of activation ( $\Delta H^{\ddagger}/\text{kJ mol}^{-1}$ ).
- (b) Comment on the value of  $\Delta S^{\ddagger}$  calculated.  
 (c) Corresponding to the value of  $\Delta S^{\ddagger}$  calculated in (a) for the transition state theory, would you expect the value of the steric factor  $p$  in the simple collision theory to be  $\approx 1$ ,  $> 1$ , or  $< 1$ ? Explain briefly—detailed calculations or proofs are not necessary.
- 6-10 Show that, for the bimolecular reaction  $A + B \rightarrow P$ , where  $A$  and  $B$  are hard spheres,  $k_{TST}$  is given by the same result as  $k_{SCT}$ , equation 6.4-17.  $A$  and  $B$  contain no internal modes, and the transition state is the configuration in which  $A$  and  $B$  are touching (at distance  $d_{AB}$  between centers). The partition functions for the reactants contain only translational modes (one factor in  $Q_r$  for each reactant), while the transition state has one translation mode and two rotational modes. The moment of inertia ( $I$  in Table 6.2) of the transition state (the two spheres touching) is  $\mu d_{AB}^2$ , where  $\mu$  is reduced mass (equation 6.4-6).