

A First Course on Kinetics and Reaction Engineering

Unit 5. Empirical and Theoretical Rate Expressions

Overview

This course is divided into four parts, I through IV. Part II is focused upon modeling the rates of chemical reactions, that is, rate expressions. Rate expressions for a particular reaction are generated by fitting experimental reactor data to a reactor model that includes a mathematical function being tested for its suitability as a rate expression. Unit 5 begins by introducing power-law rate expressions, which are often used as empirical rate expressions, as long as they prove to be accurate. An elementary reaction is then defined, and two theories are presented that allow the mathematical form of the rate expression for an elementary reaction to be predicted. These theories are known as Collision Theory and Transition State Theory.

Learning Objectives

Upon completion of this unit, you should be able to define, in words, the following terms:

- empirical rate expression
- reaction order, overall and with respect to a given species
- elementary reaction
- collision cross section
- molecularity
- steric limitation
- steric factor
- potential energy surface
- activated complex
- transition state
- saddle point
- activation energy
- reaction coordinate
- transmission coefficient

Upon completion of this unit, you should be able to write the defining equation for the following quantities:

- power-law rate expression
- Monod equation
- general form of the rate expression for an elementary reaction as predicted
 - by collision theory
 - by transition state theory

Upon completion of this unit, you should be able to perform the following specific tasks and be able to recognize when they are needed and apply them correctly in the course of a more complex analysis:

- Determine the kinetic reaction order, both overall and with respect to any particular species, given a rate expression (see Example 6.1)

- Write a mathematical term by which any rate expression can be multiplied so that the resulting rate expression equals zero when it is evaluated at equilibrium conditions (see Example 5.1)
- Explain why the stoichiometric coefficients in an elementary reaction must be integers (see Example 5.2 and 5.3)
- State and apply the principle of microscopic reversibility (see Example 5.2 and 5.3)
- Describe the information contained in the Boltzmann distribution
- State the assumptions and outline the procedure used to derive a rate expression using collision theory (see Example 5.5)
- Calculate the steric factor for an elementary gas phase reaction, given the observed reaction rate and judge whether it is reasonable for the reaction in question
- State the assumptions and outline the procedure used to derive a rate expression using transition state theory (see Example 5.5)
- Calculate a rate coefficient using collision theory or transition state theory, given appropriate data (see Example 5.4)
- Identify and describe the limitations of simple collision theory and transition state theory

Information

It was pointed out in Unit 4 that rate expressions are generated by selecting mathematical functions and testing them using experimental data to determine whether they can accurately describe the variation of the rate with temperature, pressure and composition. Perhaps the simplest approach is to pick a function that is mathematically tractable. There is no theoretical basis in this type of selection, but for engineering purposes it is often the most attractive option. As long as the function that is selected displays the proper mathematical behavior (single valued and goes to zero at equilibrium conditions) and proves to be accurate, it should be acceptable for engineering purposes. This type of rate expression can be referred to as an *empirical rate expression*. “Empirical” means “based upon observation.” This is the situation here, the empirical rate expression is not selected on a theoretical basis, but instead for its combined convenience and accuracy.

Probably the most common empirical rate expression is the *power-law rate expression* given in equation (5.1) below.

$$r_j = k_j \prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{m_i} \quad (5.1)$$

In this equation, the square bracket denotes a composition variable (typically either the molar concentration or, in a gas phase system, the partial pressure). The exponent m_i is called the *reaction order* with respect to species i ; in a power-law rate expression it can have any value including decimal fractions, positive or negative in sign. If m_i is negative, the reaction rate is said to be inhibited by species i . If the values of m_i for every species i are summed, the result is the *overall reaction order*. The reaction orders with respect to the species are treated as parameters for fitting the rate expression to the

experimental rate data. The rate coefficient, k_j , also includes parameters. For example, if the Arrhenius expression is used to describe the rate coefficient, then the pre-exponential factor and the activation energy are parameters that can be used to fit the expression to experimental data.

The power-law expression given above might be suitable for an irreversible reaction, but generally it doesn't satisfy the mathematical behavior expected of rate expressions in that it will not evaluate to zero if evaluated at equilibrium conditions. There is a way to ensure that any rate expression selected for testing, including the power-law expression above, will equal zero if it is evaluated at equilibrium conditions. This is done by multiplying the rate expression by the term given in equation (5.2)

$$\left\{ 1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{v_{i,j}}}{K_{eq,j}(T)} \right\}^a \quad (5.2)$$

In this term, $K_{eq,j}$ is the equilibrium constant for reaction j for the concentration or pressure units used in the numerator; the temperature dependence of the equilibrium "constant" is explicitly included here as a reminder that the equilibrium constant varies with temperature. Thus, for example, if partial pressures are used as the $[i]$ terms, then $K_{eq,j}$ is the pressure form of the equilibrium constant. The exponent a is an additional parameter that can be used in fitting the rate expression to the experimental rate data. Notice that at compositions far away from the equilibrium composition, this term evaluates to 1 while at the equilibrium composition it evaluates to zero. Thus, at conditions far from equilibrium, the rate will default to whatever rate expression is being multiplied by this factor, but as the conditions approach equilibrium, this factor will cause the rate to go to zero.

Thus, a more complete power-law rate expression is given in equation (5.3). That equation includes the factor to ensure the rate will be zero at equilibrium and it also explicitly incorporates Arrhenius temperature dependence for the rate coefficient.

$$r_j = k_{0,j} \exp\left(\frac{-E_j}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{m_i} \left\{ 1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{v_{i,j}}}{K_{eq,j}(T)} \right\}^a \quad (5.3)$$

For cell growth kinetics, a very common empirical rate expression is the *Monod equation* (see Example 4.4). The Monod equation has a form similar to theory-based equations for enzymatic reactions. However, the theory used in the enzymatic reactions does not apply directly to cell growth processes. As such, the Monod equation (5.4) must be considered to be empirical.

$$\mu = \frac{\mu_{\max} C_S}{K_s + C_S} \quad (5.4)$$

In this form of the Monod equation, μ is the specific growth rate (see Unit 4), μ_{max} is an adjustable constant equal to the maximum growth rate, C_S is the *mass* concentration of the substrate (nutrient) that is limiting cell growth, and K_S is a constant called the saturation constant. In this form, the equation cannot be used to describe cell growth where there are inhibition effects, multiple substrates, etc.

There are other kinds of empirical expressions in addition to those covered here. For example, Hougen and Watson described a family of empirical rate expressions that can be used to describe the rates of heterogeneous catalytic reactions [1].

Empirical rate expressions are often useful for engineering purposes because their mathematical form is convenient. However, for scientific purposes, rate expressions grounded in theory are often more useful. There are theories for reaction kinetics, but unfortunately, they only apply to a special kind of chemical reaction that is called an elementary reaction. An *elementary reaction* is a chemical reaction where the reaction equation, as written, is an **exact** description of a single reaction event that takes place at the molecular level. Most reaction equations only convey the overall stoichiometry of the process; they do not describe the exact molecular event that takes place. It is very important to understand that one can not tell whether a reaction is elementary just by looking at the equation. The HBr formation reaction given in equation (5.5) looks very simple, and it is easy to imagine a single molecular event where an H₂ molecule and a Br₂ molecule collide with each other and two HBr molecules are formed. Nonetheless, the formation of HBr *does not* take place in a single molecular event. The equation below simply conveys the fact that overall, for every two HBr molecules produced, there will be one H₂ and one Br₂ molecule consumed. Note that *if* a reaction is elementary, then all of the stoichiometric coefficients **must** be integers since, at the molecular level, there's no such thing as a fraction of a molecule.



According to the *principle of microscopic reversibility*, elementary reactions are always reversible. That is, if an elementary reaction takes place in the forward direction, it must also be possible for that reaction to take place in the reverse direction as a single molecular event. The rate in the reverse direction may be very small, but it must be non-zero.

Because elementary reactions are exact descriptions of a single molecular event, it is possible to develop theories for how they occur. In this unit, two theories for the rates of elementary reactions will be considered. The first is the *collision theory* for the rate of an elementary gas phase reaction. It is based upon the *kinetic theory of gases*, so clearly, it applies to gas phase reactions. The kinetic theory of gases treats a gas as a large number of particles which are small compared to the distance between them. They are assumed to be in constant motion, with the full mass of each particle located at a point in space. Each kind of molecule has its own collision radius. Beyond their collision radii, the molecules exert no forces on each other, but when the distance between two molecules equals the sum of those molecules' collision radii, they exert an infinite repulsive force on each other. This is commonly described by saying the molecules behave as hard spheres when they collide, but there is a significant difference. Hard spheres can have angular momentum due to spin, and they can transfer angular momentum when they collide. Because the mass of these molecules is all located at a point, they cannot have angular momentum.

Collisions between these molecules are assumed to be perfectly elastic. This means that when two gas molecules collide there is no change in the total translational kinetic energy.

As the name implies, the basic assumption of collision theory is that reaction takes place as a result of collisions between molecules. The development of collision theory begins with the Boltzmann distribution (sometimes called the Maxwell-Boltzmann distribution) which describes how available energy is distributed amongst a collection of molecules. For a gas at a given temperature, the Boltzmann distribution tells how many molecules will have a velocity, u , which lies in the interval from u to $u + du$. For a system which contains both A molecules and B molecules, a Boltzmann distribution of the velocities of A molecules, relative to a B molecule, is given in equation (5.6). In equation (5.6) u is the velocity relative to a particular B molecule, dN_A is the number of A molecules which have a velocity between u and $u + du$, N_A^* is the number of A molecules per unit volume, μ is the reduced mass given in equation (5.7) and k_B is Boltzmann's constant ($1.3806 \times 10^{-23} \text{ J K}^{-1}$). In equation (5.7), m_A and m_B are the masses of the corresponding molecules.

$$dN_A = \left(4\pi N_A^* u^2\right) \left(\frac{\mu}{2\pi k_B T}\right)^{3/2} \exp\left(\frac{-\mu u^2}{2k_B T}\right) du \quad (5.6)$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad (5.7)$$

As Figure 5.1a shows, an A molecule and a B molecule will collide when the distance between their centers equals the sum of their collision radii. As noted, the kinetic theory of gases doesn't include any attractive or repulsive forces between molecules. As a consequence, when an A molecule travels through space (between collisions) its center traces out a straight line (not a curve), Figure 5.1b. This straight line can be used as the axis of a cylinder with a radius equal to the sum of the radii of an A molecule and a B molecule. Thus as the A molecule travels through space it sweeps out a cylindrical volume and a collision will occur if a B molecule has its center within this cylinder. The cross-sectional area of this cylinder is called the collision cross-section, σ_{AB} . The collision cross section is calculated using equation (5.8) where R_A is the radius of an A molecule and R_B is the radius of a B molecule.

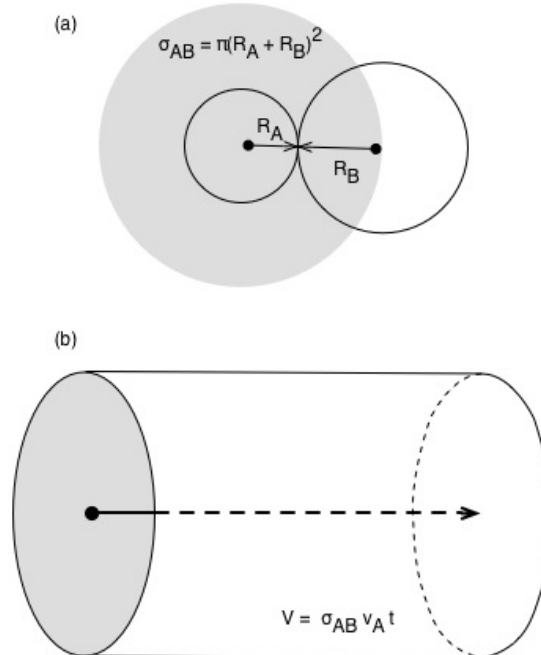


Figure 5.1. (a) Two point masses collide when the distance between them equals the sum of their collision radii. (b) As one point mass travels through space, it sweeps out a cylindrical volume.

$$\sigma_{AB} = \pi(R_A + R_B)^2 \quad (5.8)$$

It is next assumed that B molecules are uniformly distributed throughout space. If N_B^* equals the number of B molecules per unit volume, then on average there will be one B molecule in a volume, V_B^* , given by equation (5.9).

$$V_B^* = \frac{1}{N_B^*} \quad (5.9)$$

On average the cylindrical volume swept out by a single A molecule before it collides with a B molecule will equal V_B^* . Putting it another way, since on average there is one B molecule per volume V_B^* , then on average an A molecule will have to sweep out that volume in order to collide with a B molecule. The distance, L , traveled by the A molecule before it undergoes collision can then be found using equation (5.10) which comes from the formula for the volume of a cylinder.

$$L = \frac{V_B^*}{\sigma_{AB}} \quad (5.10)$$

The amount of time, t , it takes the A molecule to travel the distance L can be found from its velocity, u , relative to the B molecule with which it collides using equation (5.11) which is a simple rearrangement of the definition of a velocity.

$$t = \frac{L}{u} \quad (5.11)$$

Thus, equation (5.11) can be used to find how long it takes, on average, for an A molecule to collide with a B molecule. Substituting equation (5.10) into equation (5.11) leads to equation (5.12) for the amount of time required for an A molecule to have a single collision with a B molecule.

$$t_{\text{one collision}} = \frac{V_B^*}{u\sigma_{AB}} \quad (5.12)$$

The time calculated using equation (5.12) is the period of the collisions of the A molecule with B molecules. The frequency of collisions of a single A molecule with a B molecule is equal to the reciprocal of this period. This frequency is only for collisions between the single A molecule under consideration and a B molecule. If ν is used to represent frequency, the frequency of collisions of a single A molecule moving with a velocity u is then given by equation (5.13).

$$\nu_{\text{collisions of single A molecule with velocity } u} = \frac{u\sigma_{AB}}{V_B^*} \quad (5.13)$$

The frequency of collisions involving all A molecules that are moving with one particular velocity u is found by multiplying the frequency of collisions for a single A molecule moving with that velocity u (given

in equation (5.13)) by the total number of A molecules that are moving with that velocity (dN_A). This is expressed in equation (5.14).

$$\left(\begin{array}{l} \text{frequency of collisions} \\ \text{involving all A molecules} \\ \text{that have a velocity of } u \end{array} \right) = \left(\begin{array}{l} \text{frequency of collisions} \\ \text{of a single A molecule} \\ \text{that has a velocity } u \end{array} \right) \left(\begin{array}{l} \text{number of A} \\ \text{molecules that} \\ \text{have velocity } u \end{array} \right)$$

$$v_{\text{collisions of all A}} = \frac{u\sigma_{AB}}{V_B^*} dN_A^* \quad (5.14)$$

The frequency of all collisions between A molecules and B molecules (i. e. with any velocity) is found by summing equation (5.14) over all possible velocities. To do this, the Boltzmann distribution function, equation (5.6) is substituted into equation (5.14) along with substitution of equation (5.9). Since the velocity distribution is continuous, the summation takes the form of an integral over all possible velocities. The frequency of all collisions between A and B molecules is often called a collision number. The symbol Z'_{AB} is used here to represent the frequency of all collisions between A molecules and B molecules. Equation (5.15) gives an expression for the collision number, Z'_{AB} .

$$\left(\begin{array}{l} \text{frequency of collisions} \\ \text{involving all A molecules} \\ \text{that have velocity } u \end{array} \right) = \sum_{\text{all possible velocities } u} \left(\begin{array}{l} \text{frequency of collisions} \\ \text{involving all A molecules} \\ \text{that have velocity } u \end{array} \right)$$

$$Z'_{AB} = \sum_{\text{all possible velocities } u} v_{\text{all A molecules with velocity } u} = \sum_{\text{all possible velocities } u} \left(\frac{u\sigma_{AB}}{V_B^*} dN_A^* \right)$$

$$Z'_{AB} = \int_{u=0}^{u=\infty} (4\pi N_A^* N_B^* u^3 \sigma_{AB}) \left(\frac{\mu}{2\pi k_B T} \right)^{3/2} \exp\left(\frac{-\mu u^2}{2k_B T} \right) du$$

$$Z'_{AB} = N_A^* N_B^* \sigma_{AB} \sqrt{\frac{8k_B T}{\pi\mu}} \quad (5.15)$$

Some of the collisions between the A molecules and the B molecules will involve very small relative velocities, u . These are cases where the molecules just gently bump each other. Therefore, it is next assumed that there must be some minimum relative velocity associated with a collision if it is going to lead to reaction. Collisions which have at least this minimum velocity associated with them can be called reactive collisions, and their frequency can be represented by Z_{AB} (no prime). The frequency of collisions involving a velocity equal to or greater than some minimum, u_0 , can be found by replacing the lower limit of the integral above with u_0 , leading to equation (5.16) for Z_{AB} , where ϵ_0 is the energy corresponding to the relative velocity, u_0 .

$$Z_{AB} = N_A^* N_B^* \sigma_{AB} \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left(\frac{-\varepsilon_0}{k_B T}\right) \quad (5.16)$$

An analysis similar to the one just presented can be done for collisions between two A molecules. The primary difference is that one must be careful not to double-count the collisions. The resulting expression for the reactive collision frequency, Z_{AA} , is given in equation (5.17). The analysis of a collision between three molecules, A, B, and C, requires a slight modification. The probability that all three molecules are in contact simultaneously is extremely small. Therefore, a collision is considered to have occurred whenever the centers of all three molecules are within a distance l of each other. The resulting expression for the reactive three-body collision frequency, Z_{ABC} , is given in equation (5.18).

$$Z_{AA} = (N_A^*)^2 \sigma_{AA} \sqrt{\frac{2k_B T}{\pi \mu}} \exp\left(\frac{-\varepsilon_0}{k_B T}\right) \quad (5.17)$$

$$Z_{ABC} = 8N_A^* N_B^* N_C^* \sigma_{AB} \sigma_{BC} l \sqrt{\frac{2k_B T}{\pi}} \left(\frac{1}{\mu_{AB}} + \frac{1}{\mu_{BC}}\right) \exp\left(\frac{-\varepsilon_0}{k_B T}\right) \quad (5.18)$$

To this point, all the equations have been developed on the basis of molecules. Through the use of Avogadro's number, N_{Av} , each quantity appearing in the equations above can be converted to molar units. Equations (5.19) through (5.22) give the necessary relationships.

$$\varepsilon_0 = \frac{E}{N_{Av}} \quad (5.19)$$

$$k_B = \frac{R}{N_{Av}} \quad (5.20)$$

$$N_i^* = N_{Av} C_i \quad (5.21)$$

$$Z_{AB} = N_{Av} r_{j,f} \quad (5.22)$$

Substituting equations (5.19) through (5.22) into equations (5.16) through (5.18) gives equations (5.23) through (5.25) for the generalized *forward* rates of bimolecular A-B reactions, bimolecular A-A reactions, and termolecular A-B-C reactions, respectively. (The *molecularity* of an elementary reaction is equal to the number of species that participate as reactants.) It should be noted that these expressions only give the rate of the reaction in the forward direction, as indicated by the f appended to the subscript on the rate, r .

$$r_{AB,f} = N_{Av} \sigma_{AB} C_A C_B \sqrt{\frac{8k_B T}{\pi \mu}} \exp\left(\frac{-E_j}{RT}\right) \quad (5.23)$$

$$r_{AA,f} = N_{Av} \sigma_{AA} C_A^2 \sqrt{\frac{2k_B T}{\pi \mu}} \exp\left(\frac{-E_j}{RT}\right) \quad (5.24)$$

$$r_{ABC,f} = 8 N_{Av} \sigma_{AB} \sigma_{BC} I C_A C_B C_C \sqrt{\frac{2k_B T}{\pi}} \left(\frac{1}{\mu_{AB}} + \frac{1}{\mu_{BC}}\right) \exp\left(\frac{-E_j}{RT}\right) \quad (5.25)$$

Real molecules are not spheres. For an asymmetrical molecule, it may be necessary for the collision to take place in one part of the molecule in order to have reaction take place. If the colliding molecules are not oriented properly, necessary bonds can't form and reaction can't occur. The collision theory does not account for this kind of *steric* (geometric) *limitation*. If a reaction does have steric limitations, a constant is introduced into the rate expressions above. This constant, called a *steric factor*, is equal to the fraction of the collisions that have the orientation necessary for reaction to take place.

If the constants in the rate expressions above are unknown, they can be treated as adjustable parameters that are used to fit the rate expression to experimental data. In order to do so, groups of constants in the expressions above must be lumped together into single constants. Doing results in a single collision theory rate expression for the forward rate of an elementary reaction, equation (5.26). Note that the stoichiometric coefficients of the reactants in that equation, ν_{ij} , are negative numbers so the resulting exponents on the concentrations are positive.

$$r_{j,f} = k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{i,j}} \quad (5.26)$$

Generally the net rate of reaction is more useful than the rate in the forward direction only. It is straightforward to generate an expression for the net rate of reaction. The definition of forward and reverse is completely arbitrary, so equation (5.26) can be used to generate an expression for the rate in the reverse direction, too.

$$r_{j,r} = k_{0,j,r} \sqrt{T} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{products}}} C_i^{\nu_{i,j}} \quad (5.26)$$

When the reaction reaches thermodynamic equilibrium, its net rate will equal zero, and as a consequence, the rate in the forward direction will equal the rate in the reverse direction. Thus, the two uni-directional rates can be set equal to each other while simultaneously recognizing that this only true when the concentrations are equal to the equilibrium concentrations. Rearrangement of the resulting equation reveals that the ratio of the forward to the reverse rate coefficients must equal the equilibrium constant for the elementary reaction, equation (5.27).

$$r_{j,f} \Big|_{\text{equilibrium}} = r_{j,r} \Big|_{\text{equilibrium}}$$

$$\begin{aligned}
 k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{ij}} &= k_{0,j,r} \sqrt{T} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{products}}} C_i^{\nu_{ij}} \\
 \frac{k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right)}{k_{0,j,r} \sqrt{T} \exp\left(\frac{-E_{j,r}}{RT}\right)} &= \prod_{\substack{i=\text{all} \\ \text{species}}} C_i^{\nu_{ij}} \\
 \frac{k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right)}{k_{0,j,r} \sqrt{T} \exp\left(\frac{-E_{j,r}}{RT}\right)} &= K_{j,eq_c} \tag{5.27}
 \end{aligned}$$

An expression for the *net* rate of reaction according to collision theory is found by taking the difference between the forward and reverse rates. This can be written using the reverse rate coefficient, as in equation (5.28) or using the equilibrium constant, as in equation (5.29). The two forms are equivalent.

$$\begin{aligned}
 r_j &= r_{j,f} - r_{j,r} \\
 r_j &= k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{ij}} - k_{0,j,r} \sqrt{T} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{products}}} C_i^{\nu_{ij}} \tag{5.28}
 \end{aligned}$$

$$r_j = k_{0,j,f} \sqrt{T} \exp\left(\frac{-E_{j,f}}{RT}\right) \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{ij}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} C_i^{\nu_{ij}}}{K_{j,eq_c}} \right) \tag{5.29}$$

It is often convenient to use partial pressures as the composition variables in a gas phase reaction system. Equations (5.28) and (5.29) can be easily converted so that partial pressures replace the concentrations. Since equations (5.28) and (5.29) were derived assuming ideal gas type behavior, the concentrations and partial pressures are simply related via the ideal gas law as given in equation (5.30). Substitution of equation (5.30) into equation (5.28) or (5.29) leads, in a straightforward manner, to a rate expression in terms of partial pressures instead of concentrations.

$$C_i = \frac{n_i}{V} = \frac{P_i}{RT} \tag{5.30}$$

Collision theory as presented here is sometimes referred to as simple collision theory. It offers a simple molecular view of how reactions take place, and it can be useful for making rough approximations

of the values of pre-exponential factors. There are several shortcomings of simple collision theory. First, the point-mass assumption is very limiting; it ignores internal motions within molecules and the energy associated with those internal motions. A second shortcoming is the absence of attractive and repulsive forces between molecules. In a real system, a molecule that is passing close to a second molecule may be attracted by it, causing it to travel in a curved path and collide with that molecule instead of continuing past it on a straight line path. Another shortcoming is the absence of orientation requirements for reaction to occur. Simple collision theory does not offer an easy way to estimate the activation energy, it strictly applies only to gas phase reactions. There are also reactions for which the observed rate is higher than that predicted by the collision theory, and this can't be explained by steric effects because they should lower the reaction rate, not raise it. There are more advanced formulations of collision theory that address the shortcomings enumerated here. Since these advanced formulations use more accurate representations of the molecules, they are often referred to as molecular reaction dynamics models.

The second theory for elementary reaction rates considered in this unit is known as *transition state theory* or sometimes as the *theory of absolute reaction rates*. There are several ways to develop the transition state theory. Some use classical thermodynamics and some use statistical mechanics. Here the theory will be developed in the context of the hypothetical reaction between an AB molecule and a C atom, equation (5.31).



There are three atoms involved in reaction (5.31). Consider a system in space consisting of these three atoms. Each of the atoms may be located anywhere within the system. The arrangement of these three atoms in space can be specified using nine coordinates, namely the x , y , and z coordinates of each atom's center. Quantum chemistry could be used to calculate the energy, Φ , of the system for all possible combinations of these nine coordinates. The energy could then be plotted as a function of the nine coordinates; that is, the potential energy would be a ten dimensional surface.

Most people can't visualize a ten dimensional surface. Therefore consider an approximate three dimensional system where the centers of mass of all three atoms are constrained to lie on a common straight line, where the C atom is fixed at the origin, and where the C atom is not between the other two atoms. As shown in Figure 5.2, the geometry of this simplified system can be completely defined by two coordinates: the distance between the centers of the A and B atoms, D_{AB} , and the distance between the centers of the B and C atoms, D_{BC} . The energy for this simplified system can be represented as a three-dimensional surface.

Figure 5.3 is an example of how this *potential energy surface* might appear. It can be seen that there are valleys or wells on the surface. (The same would be true of the ten-dimensional potential surface originally considered.) Wells that are relatively deep represent geometric arrangements where stable compounds have formed. Figure 5.3 indicates two such wells. For one well in Figure 5.3 the D_{AB} distance is

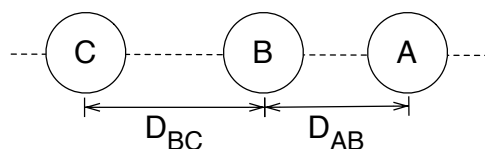


Figure 5.2. Constrained three atom system where all atoms lie on a common straight line. The geometry of the system is completely specified by the two distances D_{AB} and D_{BC} .

small and constant whereas the D_{BC} distance can take on any large value. This well corresponds to the existence of an AB molecule and a separate C atom. The other well in Figure 5.3 corresponds to the existence of a BC molecule and a separate A atom; D_{BC} is small and constant (equal to the bond length), and D_{AB} can take on any large value.

Figure 5.3 also shows a path (a-b-c-d-e) between the two potential wells. This path crosses over the smallest barrier separating the two wells. (That is, if one moved from one well to the other along any path other than the one shown, they would have to pass over a point where the energy was greater than the energy at point c.) Put another way, the point

c is a *saddle point* from which the potential energy increases in all directions except along the identified path. For the reaction as written in equation (5.31), the starting point, a, is the well corresponding to an AB molecule and a separate C atom. Assume the reaction takes place with the three atoms constrained to remain collinear, with the C atom fixed at the origin, and with the C atom not between the other two atoms. Then as the reaction takes place the system traces out the path a-b-c-d-e shown in Figure 5.3. The difference in energy between the bottom of the well where the system started (point a) and the highest point on the path (point c) is the *activation energy* for the reaction. Notice that as the system passes over the barrier, D_{AB} increases (the AB bond breaks) and D_{BC} begins to approach the normal BC bond length.

Thus, if it is assumed that the lowest energy path is followed, the potential surface can be used to determine that path. Each point on the path completely specifies the orientation of the entire system. Once this path has been determined, the potential diagram can be reduced from however many dimensions it originally had to a two dimensional plot. The abscissa of the plot is the distance along the path that has been determined from the full potential surface, and the ordinate is the potential energy of the system at that distance along the path. The distance along the identified path is often referred to as the *reaction coordinate*. Figure 5.4 shows this kind of two-dimensional potential energy diagram. The diagram in Figure 5.4 corresponds to Figure 5.3; the points a through e on the two diagrams also correspond.

The state of the system when it is at the highest point in Figure 5.4 is known as the *transition state*. Recall that each point on the path corresponds to a specific arrangement of the atoms. At the top of the activation barrier (i. e. in the transition state) all the atoms are in close proximity. The distances D_{AB} and D_{BC} are different than they would be in either stable molecule. The species formed from the three atoms

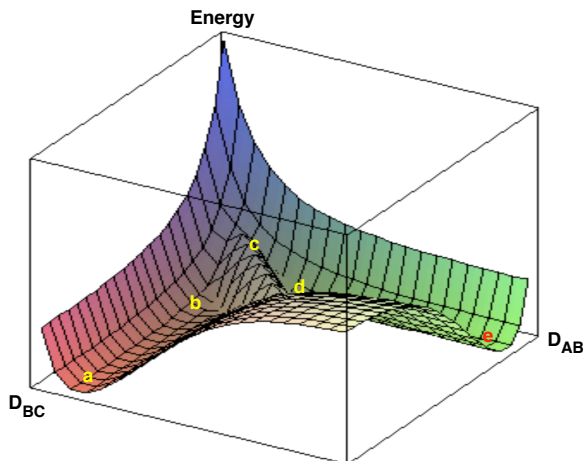


Figure 5.3. A schematic representation of a potential energy surface for the reaction given in equation (5.31). The path denoted by the points a-b-c-d-e is the reaction coordinate. At point c, the lowest point on the barrier between the two potential energy wells, the activated complex is in the transition state.

when they are in the orientation corresponding to the transition state is called the *activated complex*. The activated complex is neither reactants nor products; it is a hybrid of the two. To recap, the entity at the top of the activation barrier is called the activated complex and it is said to be in the transition state.

The activated complex is not a stable chemical species. It is a species in transition, and its lifetime is exceedingly short. Nonetheless, in transition state theory, it is assumed that the activated complex can be treated like a stable chemical species. Specifically, it is assumed that the activated complex can be assigned thermodynamic properties like any stable species. These thermodynamic properties can be estimated using the same techniques that are used to estimate the thermodynamic properties of stable species.

The most important assumption of transition state theory is that the reactants are in a special kind of equilibrium with those activated complexes that are in the process of transforming from reactants into products. (The reactants are only in equilibrium with those activated complexes that are in the process of becoming products and not with those that are in the process of becoming reactants.) One consequence of this is that *the theory will only apply when the reactant molecules are present in a Boltzmann distribution*. If the reaction process is so fast that the distribution of reactant molecules deviates from the Boltzmann distribution, the transition state theory cannot be used. Fortunately this situation is infrequently encountered.

The rationale for assuming that “forward moving” activated complexes are in equilibrium with the reactants begins by considering the situation where the chemical reaction has reached thermodynamic equilibrium. At this point the net rate of reaction equals zero, but there is still a significant absolute rate in the forward direction and an equal absolute rate in the reverse direction. Thus, at overall equilibrium the reactants are in equilibrium with the forward moving activated complexes, the products are in equilibrium with the “backward moving” activated complexes, and the number of forward moving activated complexes must just equal the number of backward moving activated complexes. Now suppose that by some unspecified means, all product molecules are instantaneously removed, and thereby the overall reaction is no longer at equilibrium. Since the products have all been removed, the absolute rate in the reverse direction will be zero, but there is no reason why the number of forward moving activated complexes should change. This thought experiment justifies the assumption that the reactants are always in a special kind of equilibrium with those activated complexes which are in the process of becoming products. If this was not true, then the rate coefficient would change as the reaction approached equilibrium. Such a change in the rate coefficient has not been observed experimentally.

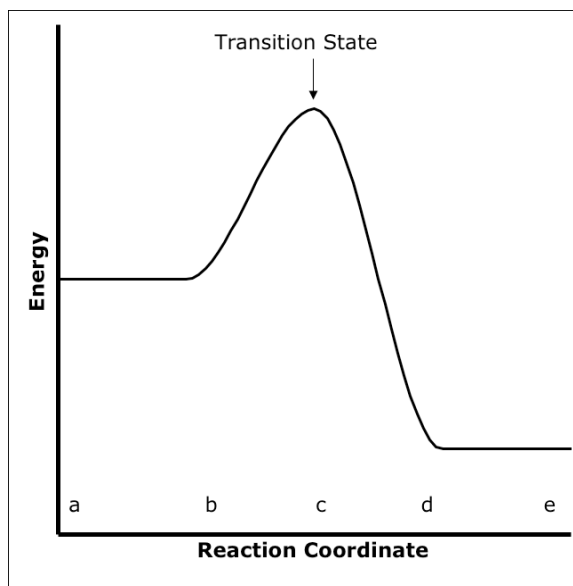


Figure 5.4. A two dimensional representation of the potential energy along the reaction coordinate. Points a through e correspond their counterparts in Figure 5.3.

Returning to Figure 5.4, the absolute rate of reaction in the forward direction is seen to be equal to the number of times activated complexes pass over the potential barrier from the reactant well to the product well. This, in turn, depends upon two factors: how many forward-moving activated complexes are present at a given time, and how fast do they proceed along the reaction coordinate. The first factor is determined using the assumptions just described. It is assumed that the reactants are in equilibrium with those activated complexes in the process of moving across the potential barrier in the forward direction. For the reaction as written in equation (5.32), this can be expressed using an equilibrium constant as shown in equation (5.33). The latter equation can be rearranged to give an expression for the concentration of the activated complexes, equation (5.34). In equations (5.33) and (5.34) the brackets denote molar concentrations of the species within, K^\ddagger is a concentration-based equilibrium constant for reaction (5.32), and the superscripted symbol, \ddagger , is used to denote that a given quantity is associated with a forward moving activated complex which is proceeding along the reaction coordinate.



$$K^\ddagger = \frac{[ABC^\ddagger]}{[AB][C]} \quad (5.33)$$

$$[ABC^\ddagger] = K^\ddagger [AB][C] \quad (5.34)$$

Equation (5.34) gives the number of moles of activated complexes in a unit volume. All that remains is to determine how rapidly each of these complexes travels along the reaction coordinate. In principle it would be possible to determine how rapidly the activated complex moves along the reaction coordinate using the original Cartesian coordinate system. Thus, progress along the reaction coordinate could be expressed in terms of the x , y , and z components of velocity of each of the three atoms in the activated complex. This would be very cumbersome because motion along the reaction coordinate involves simultaneous changes of all nine of the coordinates. It is easier (and customary) to use a different set of coordinates to describe the motion along the reaction coordinate. This does not change the potential surface in any way, it just changes the ease with which motion upon it can be described. (It is possible to describe a sphere using rectangular, cylindrical, or spherical coordinates. The sphere is the same in all three cases, but the equations describing it are much simpler if spherical coordinates are used). Thus, motion of the atoms making up the ABC^\ddagger activated complex as it moves along the reaction coordinate can then be described in terms of the following nine coordinates. Three coordinates correspond translational motion of the center of mass of the activated complex as a whole; one coordinate in each of the x , y , and z directions. For non-linear activated complexes, three additional coordinates describe the rotational motion of the whole complex about axes parallel to the x , y , and z directions. (If the activated complex is linear only two coordinates are used; one each to describe the rotational motion about the two axes perpendicular to the centerline of the complex itself.) The remaining coordinates correspond to different vibrations within the activated complex. In general, if there are N atoms making up the activated complex the total number of coordinates is $3N$. At first it may seem that little has been gained by changing

coordinate systems. However, it will be reasoned in what follows that as the activated complex approaches the top of the activation barrier, moving along the reaction coordinate becomes equivalent to changing just one vibrational mode. Hence the reaction coordinate becomes associated with a single coordinate of the system.

Consider now the equilibrium constant, K^\ddagger , in equation (5.34). Since it has been assumed that the activated complex can be treated as a stable species, this equilibrium constant can be analyzed from the viewpoint of statistical mechanics. *For an ideal gas* the equilibrium constant in terms of molar concentrations is given by equation (5.35).

$$K^\ddagger = \frac{N_{Av} q_{ABC^\ddagger}}{q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) \quad (5.35)$$

In Equation (5.35) K^\ddagger is the equilibrium constant for reaction (5.32) in terms of molar concentrations, q_i is the molecular partition function (omitting the electronic contribution) per unit volume for species i , $-\Delta E_0^0$ is the change in ground state electronic energy of the system when reaction (5.32) takes place stoichiometrically at the absolute zero of temperature, k_B is the Boltzmann constant, T is the temperature, and a superscripted \ddagger is used to denote that a particular quantity involves a forward moving activated complex. (Note: equation (5.35) assumes that essentially all species are in their electronic ground state during reaction.)

According to statistical mechanics, the energy available to a system is distributed, or partitioned, among the different possible states of the system. The partition function, q , is a measure of the availability of these states per unit volume. The partition function is made up of component terms for each different type of state available to the system, e. g. as given in equation (5.36), where q_{tr-i} is the partition function for the translational states of species i , q_{rot-i} is the rotational partition function and q_{vib-i} is the vibrational partition function.

$$q_i = q_{tr-i} q_{rot-i} q_{vib-i} \quad (5.36)$$

Each type of state may have more than one degree of freedom. For example, if ABC^\ddagger is a linear complex it will have three degrees of translational freedom, two degrees of rotational freedom, and four degrees of vibrational freedom. The partition functions for a certain type of motion can be broken down into terms for each of the available degrees of freedom. For example, if ABC^\ddagger is a linear complex, then its vibrational partition function can be broken into four component terms as indicated in equation (5.37). In equation (15.37) the terms q_{v1-i} , q_{v2-i} , q_{v3-i} , and q_{v4-i} are vibrational partition functions for each of the (in this case, four) vibrational degree of freedom of species i . Equation (5.38) is used to calculate the value of the partition function for any one particular vibrational degree of freedom of species i . In equation (5.38) ν_n is the characteristic vibrational frequency associated with the n^{th} degree of vibrational freedom and h is Planck's constant.

$$q_{vib-i} = q_{v_1-i} q_{v_2-i} q_{v_3-i} q_{v_4-i} \quad (5.37)$$

$$q_{v-i} = \frac{1}{1 - \exp\left(\frac{-h\nu_n}{k_B T}\right)} \quad (5.38)$$

Using equation (5.36) through (5.38) the partition function for the activated complex can be expanded as in equation (5.39), where N_{vib} is the number of vibrational degrees of freedom for the ABC^\ddagger activated complex.

$$q_{ABC^\ddagger} = q_{tr-ABC^\ddagger} q_{rot-ABC^\ddagger} \left\{ \prod_{n=1}^{N_{vib}} q_{v_n-ABC^\ddagger} \right\} \quad (5.39)$$

In an activated complex there are bonds which are in the process of breaking and/or forming. One way to view such a process is as a stretching/compressing vibration along the bond(s) in question. Referring back to Figure 5.2, one can imagine a kind of vibration where the central B atom moves back and forth horizontally while A and C remain relatively motionless. Clearly, at one end of this particular vibrational mode, the system would look more like AB + C, while at the other end of this mode it would look like A + BC. In other words, one half-cycle of this asymmetric stretching mode can easily be visualized as leading to the formation of a BC bond and the breaking of an AB bond. With this view, motion along the reaction coordinate in the vicinity of the transition state becomes equivalent to this one vibration. For present purposes this vibrational mode will be called the critical mode and its frequency will be denoted as ν_c . Since the bond(s) in question are not completely formed and/or broken in the activated complex, they are expected to be quite weak. The vibrational frequency of a weak bond is low, and this allows the partition function of this one vibrational mode to be approximated using equation (5.40). The partition function for this one weak bond can then be factored out of the total partition function, equation (5.39), for the ABC^\ddagger activated complex, resulting in equation (5.41).

$$\lim_{\nu_c \rightarrow 0} \frac{1}{1 - \exp\left(\frac{-h\nu_c}{k_B T}\right)} = \frac{k_B T}{h\nu_c} \quad (5.40)$$

$$q_{ABC^\ddagger} = q_{tr-ABC^\ddagger} q_{rot-ABC^\ddagger} \left\{ \prod_{\substack{n=1 \\ n \neq \text{critical} \\ \text{mode}}}^{N_{\text{vibrational}} \text{ modes}} q_{v_n-ABC^\ddagger} \right\} \left\{ \frac{k_B T}{h\nu_c} \right\} \quad (5.41)$$

Notice particularly that the continuous product in equation (5.41) excludes the partition function that was factored out. In addition, the approximation given in equation (5.40) has been used for the partition function of the critical vibration. The part of the total partition function which remains after factoring out the

term for the critical vibration is often denoted by the symbol q_{\ddagger}^{\dagger} , where the subscripted \ddagger denotes that one term has been factored out. This notation is formalized in equation (5.42).

$$q_{\ddagger}^{\dagger} = \frac{q_{ABC\ddagger}^{\dagger}}{\left\{ \frac{k_B T}{h \nu_c} \right\}} = q_{tr-ABC\ddagger}^{\dagger} q_{rot-ABC\ddagger}^{\dagger} \left\{ \prod_{\substack{n=1 \\ n \neq \text{critical mode}}}^{N_{\text{vibrational modes}}} q_{v_n-ABC\ddagger}^{\dagger} \right\} \quad (5.42)$$

Rearranging equation (5.42) gives equation (5.43), which can then be substituted into equation (5.35) giving equation (5.44). Then equation (5.44) can be rearranged to give an expression for the critical vibrational frequency, equation (5.45).

$$q_{ABC\ddagger}^{\dagger} = q_{\ddagger}^{\dagger} \left\{ \frac{k_B T}{h \nu_c} \right\} \quad (5.43)$$

$$K^{\ddagger} = \frac{N_{Av} q_{\ddagger}^{\dagger} \left\{ \frac{k_B T}{h \nu_c} \right\}}{q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) \quad (5.44)$$

$$\nu_c = \frac{N_{Av} q_{\ddagger}^{\dagger} \left\{ \frac{k_B T}{h} \right\}}{K^{\ddagger} q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) \quad (5.45)$$

The final assumption needed to complete the analysis is that the frequency of the critical vibration will in fact equal the frequency at which the activated complexes are transformed into products. The assumption is that the first time the activated complex attempts to go through the asymmetric stretching vibration just described, the AB bond will break and the BC bond will form. As mentioned previously, the rate of the elementary reaction (5.32) will be equal to the product of the concentration of forward-moving activated complexes and the frequency at which they decompose. This is expressed in equation (5.46), which makes use of this final assumption.

$$r_{j,f} = [ABC\ddagger] \nu_c \quad (5.46)$$

Equations (5.34) and (5.45) give expressions for the two terms on the right-hand side of equation (5.46). These can be substituted into equation (5.46) leading to equation (5.47) for the forward rate of the elementary reaction (5.31).

$$r_{j,f} = \left(K^{\ddagger} [AB][C] \right) \frac{N_{Av} q_{\ddagger}^{\dagger} \left\{ \frac{k_B T}{h} \right\}}{K^{\ddagger} q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right)$$

$$r_{j,f} = \frac{N_{Av} q_{\ddagger}^{\dagger} \left\{ \frac{k_B T}{h} \right\}}{q_{AB} q_C} \exp\left(\frac{-\Delta E_0^0}{k_B T}\right) [AB][C] \quad (5.47)$$

The first few terms on the right-hand side of equation (5.47) are the rate coefficient according to the transition state theory. This is given in equation (5.48). Notice that the transition state theory rate coefficient contains an exponential dependence upon reciprocal temperature, but in addition the total partition functions include temperature dependence and temperature also appears directly.

$$k_{j,f} = \frac{N_{Av} q_{\ddagger}}{q_{AB} q_C} \left\{ \frac{k_B T}{h} \right\} \exp\left(\frac{-\Delta E_0^0}{k_B T} \right) \quad (5.48)$$

The same analysis can be applied to find the rate in the reverse direction. As was done above for collision theory, an expression can then be found for the net rate of reaction. The result is given by equations (5.49) and (5.50).

$$r_j = k_{0,j,f} T \exp\left(\frac{-E_{j,f}}{RT} \right) \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{ij}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} C_i^{\nu_{ij}}}{K_{j,eq_c}} \right) \quad (5.49)$$

$$k_{0,j,f} = \left(\frac{q_{\ddagger}}{N_{Av}} \right) \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} \left(\frac{q_i}{N_{Av}} \right)^{\nu_{ij}} \right) \left(\frac{k_B}{h} \right) \quad (5.50)$$

This simple formulation of transition state theory does have some shortcomings. It ignores the possibility of quantum mechanical tunneling through the barrier. Tunneling does not affect the rate coefficient for the vast majority of chemical reactions; it is most important when light elements are involved. A *transmission coefficient* can be added to account for tunneling in a manner similar to the way the steric factor accounts for orientation effects in simple collision theory. The assumption that all modes remain in thermodynamic equilibrium is the source for another shortcoming. Reaction typically takes place within 10^{-12} s, and that is often not enough time for all modes of motion to reach equilibrium, but the treatment given here ignores the dynamics of moving energy into the forming bond and into the leaving entity are not included. A third shortcoming of simple transition state theory is that it assumes all reaction events pass through the saddle point. Experimental and computational studies indicate that many times, the reacting molecules follow a reaction coordinate that passes over the barrier at a location other than the saddle point.

Comparing simple collision and transition state theory, they both predict that the form of the rate expression for an elementary reaction is given by equation (5.51) or (5.52). They differ in the temperature dependence they predict for the pre-exponential factors, $k_{0,j,f}$ and $k_{0,j,r}$. Neither of the theories predicts the pre-exponential factors to be independent of temperature, as in the Arrhenius expression. In practice, however, it turns out to be very difficult to detect the variations due to the temperature dependence of the pre-exponential factors because it is weaker than the exponential temperature dependence shown explicitly in equations (5.51) and (5.52). As such, it is very common to treat the pre-exponential factors as

constants when writing theory-based rate expressions for elementary reactions. When this is done, the theories predict the same mathematical form for the rate expression and the rate coefficients conform to the Arrhenius expression.

$$r_j = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{i,j}} - k_{0,j,r} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{products}}} C_i^{\nu_{i,j}} \quad (5.51)$$

$$r_j = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} C_i^{-\nu_{i,j}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} C_i^{\nu_{i,j}}}{K_{j,eq_c}} \right) \quad (5.52)$$

Finally, when dealing with gas phase reactants, it is often more convenient to use partial pressures instead of concentrations. For an ideal gas, the partial pressure is related to the concentration as shown in equation (5.53). Substitution of equation (5.53) into equation (5.51), introduces the reciprocal of the quantity RT raised to an integer power into both terms in equation (5.51). This added term is again a weak temperature dependence compared to the exponential term, and as a consequence, it is quite common to include it within the pre-exponential factor while still assuming the pre-exponential factor to be a constant. The same is done when equation (5.53) is substituted into the concentrations in the first continuous product of equation (5.52). However, when equation (5.53) is substituted into the second continuous product of equation (5.52), it can be included in the equilibrium constant. This simply changes the equilibrium constant from a concentration equilibrium constant to a partial pressure equilibrium constant. The overall consequence of this is that both the simple collision theory and transition state theory then predict equation (5.54) or equation (5.55), they are equivalent, for the rate expression for an elementary reaction. In these equations, the pre-exponential factors are constants, the square brackets can denote either concentration or (for gases) partial pressure, and the equilibrium constant is either a concentration equilibrium constant or a partial pressure equilibrium constant, depending on whether concentrations or partial pressures are used for the square brackets.

$$C_i = \frac{P_i}{RT} \quad (5.53)$$

$$r_j = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} - k_{0,j,r} \exp\left(\frac{-E_{j,r}}{RT}\right) \prod_{\substack{i=\text{all} \\ \text{products}}} [i]^{\nu_{i,j}} \quad (5.54)$$

$$r_j = k_{0,j,f} \exp\left(\frac{-E_{j,f}}{RT}\right) \left(\prod_{\substack{i=\text{all} \\ \text{reactants}}} [i]^{-\nu_{i,j}} \right) \left(1 - \frac{\prod_{\substack{i=\text{all} \\ \text{species}}} [i]^{\nu_{i,j}}}{K_{j,eq}} \right) \quad (5.55)$$

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