Rate Laws   **3**
and Stoichiometry

> Success is measured not so much by the position
> one has reached in life, as by the obstacles one has
> overcome while trying to succeed.
>
> Booker T. Washington

Overview. In Chapter 2, we showed that if we had the rate of reaction as a function of conversion, $-r_A = f(X)$, we could calculate reactor volumes necessary to achieve a specified conversion for flow systems and the time to achieve a given conversion in a batch system. Unfortunately, one is seldom, if ever, given $-r_A = f(X)$ directly from raw data. Not to fear, in this chapter we will show how to obtain the rate of reaction as a function of conversion. This relationship between reaction rate and conversion will be obtained in two steps. In Step 1, Part 1 of this chapter, we define the rate law, which relates the rate of reaction to the concentrations of the reacting species and to temperature. In Step 2, Part 2 of this chapter, we define concentrations for flow and batch systems and develop a stoichiometric table so that one can write concentrations as a function of conversion. Combining Steps 1 and 2, we see that one can then write the rate as a function conversion and use the techniques in Chapter 2 to design reaction systems.

After completing this chapter, you will be able to write the rate of reaction as a function of conversion for both liquid-phase and gas-phase reacting systems.

PART 1   RATE LAWS

3.1 Basic Definitions

A *homogeneous reaction* is one that involves only one phase. A *heterogeneou reaction* involves more than one phase, and the reaction usually occurs at th interface between the phases. An *irreversible reaction* is one that proceeds i only one direction and continues in that direction until the reactants ar

Types of reactions   exhausted. A *reversible reaction*, on the other hand, can proceed in eithe direction, depending on the concentrations of reactants and products relative t the corresponding equilibrium concentrations. An irreversible reaction behave as if no equilibrium condition exists. Strictly speaking, no chemical reaction i completely irreversible. However, for many reactions, the equilibrium poin lies so far to the product side that these reactions are treated as irreversibl reactions.

The *molecularity* of a reaction is the number of atoms, ions, or molecule involved (colliding) in a reaction step. The terms *unimolecular, bimolecula* and *termolecular* refer to reactions involving, respectively, one, two, or thre atoms (or molecules) interacting or colliding in any one reaction step. Th most common example of a *unimolecular* reaction is radioactive decay, such a: the spontaneous emission of an alpha particle from uranium-238 to give tho rium and helium:

$$_{92}U^{238} \rightarrow {}_{90}Th^{234} + {}_2He^4$$
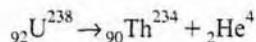
The rate of disappearance of uranium (U) is given by the rate law

$$-r_U = kC_U$$

The true *bimolecular* reactions that exist are reactions involving free radicals such as

$$Br \bullet + C_2H_6 \rightarrow HBr + C_2H_5 \bullet$$
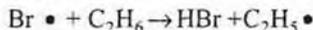
with the rate of disappearance of bromine given by the rate law

$$-r_{Br\bullet} = kC_{Br\bullet}C_{C_2H_6}$$

The probability of a *termolecular* reaction occurring is almost nonexistent, and in most instances the reaction pathway follows a series of *bimolecular* reactions as in the case of the reaction

$$2NO + O_2 \rightarrow 2NO_2$$
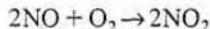
The reaction pathway for this "Hall of Fame" reaction is quite interesting and is discussed in Chapter 7 along with similar reactions that form active interme- diate complexes in their reaction pathways.

3.1.1 Relative Rates of Reaction

The relative rates of reaction of the various species involved in a reaction can be obtained from the ratio of stoichiometric coefficients. For Reaction (2-2),

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2-2}$$

we see that for every mole of A that is consumed, c/a moles of C appear. In other words,
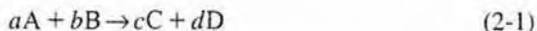
$$\text{Rate of formation of C} = \frac{c}{a} \text{ (Rate of disappearance of A)}$$

$$r_C = \frac{c}{a}(-r_A) = -\frac{c}{a}\,r_A$$

Similarly, the relationship between the rates of formation of C and D is

$$r_C = \frac{c}{d}\,r_D$$

The relationship can be expressed directly from the stoichiometry of the reaction,
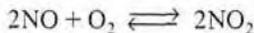
$$aA + bB \rightarrow cC + dD \tag{2-1}$$

for which

$$\boxed{\frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}} \tag{3-1}$$

Reaction   or
stoichiometry

$$\boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

For example, in the reaction

$$2NO + O_2 \rightleftharpoons 2NO_2$$

we have

$$\frac{r_{NO}}{-2} = \frac{r_{O_2}}{-1} = \frac{r_{NO_2}}{2}$$

If NO_2 is being formed at a rate of 4 mol/m³/s, i.e.,

$$r_{NO_2} = 4 \text{ mol/m}^3/\text{s}$$

then the rate of formation of NO is

$2NO + O_2 \rightarrow 2NO_2$
$r_{NO_2} = 4 \text{ mol/m}^3/\text{s}$
$-r_{NO} = 4 \text{ mol/m}^3/\text{s}$
$-r_{O_2} = 2 \text{ mol/m}^3/\text{s}$

$$r_{NO} = \frac{-2}{2} \, r_{NO_2} = -4 \text{ mol/m}^3/\text{s}$$

the rate of disappearance of NO is

$$-r_{NO} = 4 \text{ mol/m}^3/\text{s}$$

and the rate of disappearance of oxygen, O_2, is

$$-r_{O_2} = \frac{-1}{-2} \, r_{NO_2} = 2 \text{ mol/dm}^3/\text{s}$$

3.2 The Reaction Order and the Rate Law

In the chemical reactions considered in the following paragraphs, we take as the basis of calculation a species A, which is one of the reactants that is disappearing as a result of the reaction. The limiting reactant is usually chosen as our basis for calculation. The rate of disappearance of A, $-r_A$, depends on temperature and composition. For many reactions, it can be written as the product of a *reaction rate constant* k_A and a function of the concentrations (activities) of the various species involved in the reaction:

$$\boxed{-r_A = [k_A(T)][\text{fn}(C_A, C_B,....]} \tag{3-2}$$

The rate law gives the relationship between reaction rate and concentration.

The algebraic equation that relates $-r_A$ to the species concentrations is called the kinetic expression or **rate law**. The specific rate of reaction (also called the rate constant), k_A, like the reaction rate $-r_A$, always refers to a particular species in the reaction and normally should be subscripted with respect to that species. However, for reactions in which the stoichiometric coefficient is 1 for all species involved in the reaction, for example,

$$1NaOH + 1HCl \rightarrow 1NaCl + 1\,H_2O$$
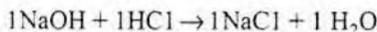
we shall delete the subscript on the specific reaction rate, (e.g., A in k_A), to let

$$k = k_{NaOH} = k_{HCl} = k_{NaCl} = k_{H_2O}$$

3.2.1 Power Law Models and Elementary Rate Laws

The dependence of the reaction rate, $-r_A$, on the concentrations of the species present, $\text{fn}(C_j)$, is almost without exception determined by experimental observation. Although the functional dependence on concentration may be postulated from theory, experiments are necessary to confirm the proposed form. One of the most common general forms of this dependence is the power law model. Here the rate law is the product of concentrations of the individual reacting species, each of which is raised to a power, for example,

$$-r_A = k_A C_A^\alpha C_B^\beta \qquad (3\text{-}3)$$

The exponents of the concentrations in Equation (3-3) lead to the concept of *reaction order*. The **order of a reaction** refers to the powers to which the concentrations are raised in the kinetic rate law.[1] In Equation (3-3), the reaction is α *order with respect to reactant A, and* β *order with respect to reactant B.* The overall order of the reaction, *n*, is

Overall
reaction
order

$$n = \alpha + \beta$$

The units of $-r_A$ are always in terms of concentration per unit time while the units of the specific reaction rate, k_A, will vary with the order of the reaction. Consider a reaction involving only one reactant, such as

$$A \rightarrow \text{Products}$$
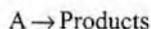
with a reaction order *n*. The units of the specific reaction rate constant are

$$k = \frac{(\text{Concentration})^{1-n}}{\text{Time}}$$

Consequently, the rate laws corresponding to a zero-, first-, second-, and third-order reaction, together with typical units for the corresponding rate constants, are:

Zero-order ($n = 0$): $\qquad\qquad\qquad -r_A = k_A:$

$$\{k\} = \text{mol/dm}^3 \cdot \text{s} \qquad (3\text{-}4)$$

First-order ($n = 1$): $\qquad\qquad\qquad -r_A = k_A C_A:$

$$\{k\} = \text{s}^{-1} \qquad (3\text{-}5)$$

Second-order ($n = 2$): $\qquad\qquad\qquad -r_A = k_A C_A^2:$

$$\{k\} = \text{dm}^3/\text{mol} \cdot \text{s} \qquad (3\text{-}6)$$

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[1] Strictly speaking, the reaction rates should be written in terms of the activities, a_i, ($a_i = \gamma_i C_i$, where γ_i is the activity coefficient). Kline and Fogler, *JCIS*, 82, 93 (1981); ibid., p. 103; and *Ind. Eng. Chem Fundamentals* 20, 155 (1981).

$$-r_A = k_A' a_A^\alpha a_B^\beta$$

However, for many reacting systems, the activity coefficients, γ_i, do not change appreciably during the course of the reaction, and they are absorbed into the specific reaction rate:
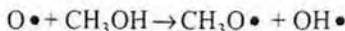
$$-r_A = k_A' a_A^\alpha a_B^\beta = -k_A' (\gamma_A C_A)^\alpha (\gamma_B C_B)^\beta = \overbrace{\left(k_A' \gamma_A^\alpha \gamma_B^\beta\right)}^{k_A} C_A^\alpha C_B^\beta = k_A C_A^\alpha C_B^\beta$$

Third-order ($n = 3$): $-r_A = k_A C_A^3$:

$$\{k\} = (dm^3/mol)^2 \cdot s^{-1} \tag{3-7}$$

An *elementary reaction* is one that evolves a single step such as the bimolecular reaction between oxygen and methanol

$$O \bullet + CH_3OH \rightarrow CH_3O \bullet + OH \bullet$$

The stoichiometric coefficients in this reaction are *identical* to the powers in the rate law. Consequently, the rate law for the disappearance of molecular oxygen is

$$-r_{O\bullet} = k C_{O\bullet} C_{CH_3OH}$$

The reaction is first order in molecular oxygen and first order in methanol therefore, we say both the reaction and the rate law are elementary. This form of the rate law can be derived from *Collision Theory* as shown in the Profes- sion Reference Shelf 3A on the CD-ROM. There are many reactions where the stoichiometric coefficients in the reaction are identical to the reaction orders, but the reactions are not elementary owing to such things as pathways involv- ing active intermediates and series reactions. For these reactions that are not elementary but whose stoichiometric coefficients are identical to the reaction orders in the rate law, we say the reaction *follows an elementary rate law*. For example, the oxidation reaction of nitric oxide discussed earlier,
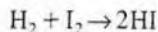
$$2NO + O_2 \rightarrow 2NO_2$$
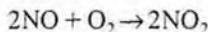
is not elementary but follows the elementary rate law

$$-r_{NO} = k_{NO} C_{NO}^2 C_{O_2}$$

Another nonelementary reaction that follows an elementary rate law is the gas-phase reaction between hydrogen and iodine

$$H_2 + I_2 \rightarrow 2HI$$

with

$$-r_{H_2} = k_{H_2} C_{H_2} C_{I_2}$$

In summary, for many reactions involving multiple steps and pathways, the powers in the rate laws surprisingly agree with the stoichiometric coefficients. Conse- quently, to facilitate describing this class of reactions, we say a reaction *follows an elementary rate law* when the reaction orders are identical with the stoichiometric coefficients of the reacting species for the reaction *as written*. It is important to remember that the rate laws **are determined by experimental observation!** They are a function of the reaction chemistry and not the type of reactor in which the reactions occur. Table 3-1 gives examples of rate laws for a number of reactions.

Reference Shelf

Collision theory

Note: the rate con- stant, k, is defined with respect to NO.
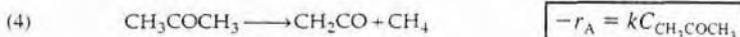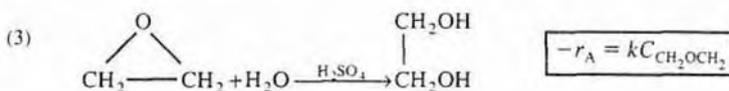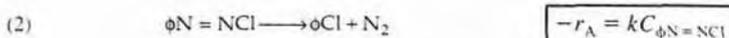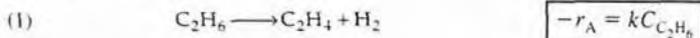
Web Hint

The values of specific reaction rates for these and a number of other reactions can be found in the *Data Base* found on the CD-ROM and on the web.
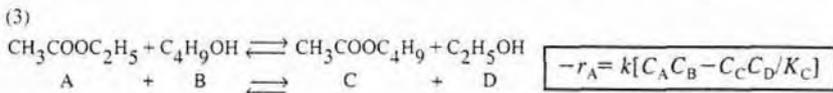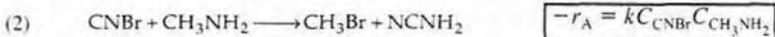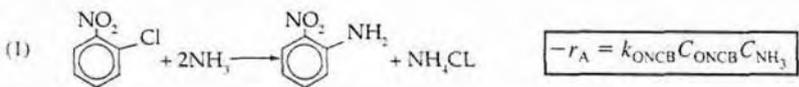
Where do you find rate laws?

The activation energy, frequency factor, and reaction orders for a large number of gas- and liquid-phase reactions can be found in the National Bureau of Standards' circulars and supplements.[2] Also consult the journals listed at the end of Chapter 1.

TABLE 3-1.   EXAMPLES OF REACTION RATE LAWS

A. First-Order Rate Laws

(1) $C_2H_6 \longrightarrow C_2H_4 + H_2$

$$-r_A = kC_{C_2H_6}$$

(2) $\phi N = NCl \longrightarrow \phi Cl + N_2$

$$-r_A = kC_{\phi N = NCl}$$

(3)

$$-r_A = kC_{CH_2OCH_2}$$

(4) $CH_3COCH_3 \longrightarrow CH_2CO + CH_4$

$$-r_A = kC_{CH_3COCH_3}$$

(5) $nC_4H_{10} \rightleftarrows iC_4H_{10}$

$$-r_n = k[C_{nC_4} - C_{iC_4}/K_C]$$

B. Second-Order Rate Laws

(1)

$$-r_A = k_{ONCB}C_{ONCB}C_{NH_3}{}^*$$

(2) $CNBr + CH_3NH_2 \longrightarrow CH_3Br + NCNH_2$

$$-r_A = kC_{CNBr}C_{CH_3NH_2}$$

(3)

$CH_3COOC_2H_5 + C_4H_9OH \rightleftarrows CH_3COOC_4H_9 + C_2H_5OH$

　　　A　　　+　　B　　$\rightleftarrows$　　C　　+　　D

$$-r_A = k[C_AC_B - C_CC_D/K_C]$$

† See Problem P3-13$_B$ and Section 9.2.

TABLE 3-1.   EXAMPLES OF REACTION RATE LAWS (CONTINUED)

C. Nonelementary Rate Laws

(1) $CH_3CHO \longrightarrow CH_4 + CO$

$$\boxed{-r_{CH_3CHO} = kC_{CH_3CHO}^{3/2}}$$

(2)

CH(CH$_3$)$_2$

$\longrightarrow$ $+ C_3H_6$

$$\boxed{-r_C = \frac{k[(P_C - P_B P_P)K_P]}{1 + K_B P_B + K_C P_C}}$$

Cumene (C) $\longrightarrow$ Benzene (B) + Propylene (P)
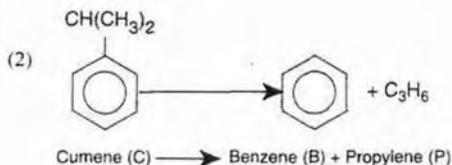
D. Enzymatic Reactions (Urea (U) + Urease (E))

$$NH_2CONH_2 + Urease \overset{+H_2O}{\rightarrow} 2NH_3 + CO_2 + Urease$$
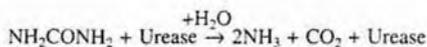
$$\boxed{-r_U = \frac{kC_U}{K_M + C_U}}$$

E. Biomass Reactions

Substrate (S) + Cells (C) $\rightarrow$ More Cells + Product
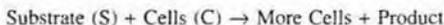
$$\boxed{-r_U = \frac{kC_S C_C}{K_S + C_S}}$$

Note: The rate constant, k, and activation energies for a number of the reactions in these examples are given in the Data Base on the CD-ROM and Summary Notes.

3.2.2 Nonelementary Rate Laws

A large number of both homogeneous and heterogeneous reactions do not follow simple rate laws. Examples of reactions that don't follow simple elementary rate laws are discussed below.

Homogeneous Reactions The overall order of a reaction does not have to be an integer, nor does the order have to be an integer with respect to any individual component. As an example, consider the gas-phase synthesis of phosgene,

$$CO + Cl_2 \rightarrow COCl_2$$
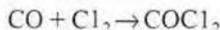
in which the kinetic *rate law* is

$$-r_{CO} = kC_{CO}C_{Cl_2}^{3/2}$$

This reaction is first order with respect to carbon monoxide, three-halves order with respect to chlorine, and five-halves order overall.

Sometimes reactions have complex rate expressions that cannot be separated into solely temperature-dependent and concentration-dependent portions. In the decomposition of nitrous oxide,

$$2N_2O \rightarrow 2N_2 + O_2$$
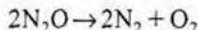
the kinetic *rate law* is

$$-r_{N_2O} = \frac{k_{N_2O} C_{N_2O}}{1 + k' C_{O_2}}$$

Both k_{N_2O} and k' are strongly temperature-dependent. When a rate expression such as the one given above occurs, we cannot state an overall reaction order. Here we can only speak of reaction orders under certain limiting conditions. For example, at very low concentrations of oxygen, the second term in the denominator would be negligible wrt 1 ($1 \gg k' C_{O_2}$), and the reaction would be "apparent" first order with respect to nitrous oxide and first order overall. However, if the concentration of oxygen were large enough so that the number 1 in the denominator were insignificant in comparison with the second term, $k' C_{O_2}$ ($k' C_{O_2} \gg 1$), the apparent reaction order would be -1 with respect to oxygen and first order with respect to nitrous oxide an overall *apparent* zero order. Rate expressions of this type are very common for liquid and gaseous reactions promoted by solid catalysts (see Chapter 10). They also occur in homogeneous reaction systems with reactive intermediates (see Chapter 7).

Apparent reaction orders

Important resources for rate laws

It is interesting to note that although the reaction orders often correspond to the stoichiometric coefficients as evidenced for the reaction between hydrogen and iodine, the rate expression for the reaction between hydrogen and another halogen, bromine, is quite complex. This nonelementary reaction

$$H_2 + Br_2 \rightarrow 2HBr$$
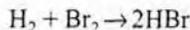
proceeds by a free-radical mechanism, and its reaction rate law is

$$-r_{HBr} = \frac{k_1 C_{H_2} C_{Br_2}^{1/2}}{k_2 + C_{HBr}/C_{Br_2}} \tag{3-8}$$

In Chapter 7, we will discuss reaction mechanisms and pathways that lead to nonelementary rate laws such as rate of formation of HBr shown in Equation (3-8).

Heterogeneous Reactions In many gas-solid catalyzed reactions, it historically has been the practice to write the rate law in terms of partial pressures rather than concentrations. An example of a heterogeneous reaction and corresponding rate law is the hydrodemethylation of toluene (T) to form benzene (B) and methane (M) carried out over a solid catalyst.

$$C_6H_5CH_3 + H_2 \xrightarrow[cat]{} C_6H_6 + CH_4$$
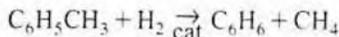
The rate of disappearance of toluene per mass of catalyst, $-r'_T$, follow Langmuir-Hinshelwood kinetics (Chapter 10), and the rate law was foun experimentally to be

$$-r'_T = \frac{kP_{H_2}P_T}{1 + K_BP_B + K_TP_T}$$

where K_B and K_T are the adsorption constants with units of kPa^{-1} (or atm^{-1} and the specific reaction rate has units of

$$[k] = \frac{\text{mol toluene}}{\text{kg cat} \cdot \text{s} \cdot \text{kPa}^2}$$

To express the rate of reaction in terms of concentration rather than partia pressure, we simply substitute for P_i using the ideal gas law

$$P_i = C_iRT \qquad (3-9$$

The rate of reaction per unit weight catalyst, $-r'_A$ (e.g., $-r'_T$), and the rate of reaction per unit volume, $-r_A$, are related through the bulk density ρ (mass of solid/volume) of the *catalyst particles* in the fluid media:

$$-r_A = \rho_b(-r'_A)$$

$$\frac{\text{moles}}{\text{time} \cdot \text{volume}} = \left(\frac{\text{mass}}{\text{volume}}\right)\left(\frac{\text{moles}}{\text{time} \cdot \text{mass}}\right)$$

In fluidized catalytic beds, the bulk density is normally a function of the volu-metric flow rate through the bed.

In summary on reaction orders, they **cannot** be deduced from reaction stoichiometry. Even though a number of reactions follow elementary rate laws, at least as many reactions do not. One **must** determine the reaction order from the literature or from experiments.

3.2.3 Reversible Reactions

All rate laws for reversible reactions *must* reduce to the thermodynamic rela-tionship relating the reacting species concentrations at equilibrium. At equilib-rium, the rate of reaction is identically zero for all species (i.e., $-r_A \equiv 0$). That is, for the general reaction

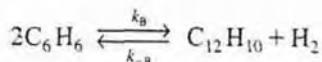$$aA + bB \; \rightleftharpoons \; cC + dD \qquad (2-1)$$
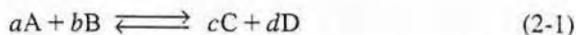
the concentrations at equilibrium are related by the thermodynamic relation-ship for the equilibrium constant K_C (see Appendix C).
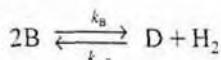
Thermodynamic
Equilibrium
Relationship

$$K_C = \frac{C_{Ce}^c C_{De}^d}{C_{Ae}^a C_{Be}^b} \qquad (3-10)$$

The units of the thermodynamic equilibrium constant, K_C, are K_C, are $(mol/dm^3)^{d+c-b-a}$.

To illustrate how to write rate laws for reversible reactions, we will use the combination of two benzene molecules to form one molecule of hydrogen and one of diphenyl. In this discussion, we shall consider this gas-phase reaction to be elementary and reversible:
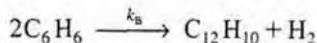
$$2C_6H_6 \underset{k_{-B}}{\overset{k_B}{\rightleftarrows}} C_{12}H_{10} + H_2$$

or, symbolically,

$$2B \underset{k_{-B}}{\overset{k_B}{\rightleftarrows}} D + H_2$$

The specific reaction rate, k_i, must be defined wrt a particular species.

The forward and reverse specific reaction rate constants, k_B and k_{-B}, respectively, will *be defined with respect to benzene.*

Benzene (B) is being depleted by the forward reaction

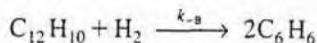$$2C_6H_6 \overset{k_B}{\longrightarrow} C_{12}H_{10} + H_2$$

in which the rate of disappearance of benzene is

$$-r_{B,forward} = k_B C_B^2$$

If we multiply both sides of this equation by -1, we obtain the expression for the rate of formation of benzene for the forward reaction:

$$r_{B,forward} = -k_B C_B^2 \tag{3-11}$$

For the reverse reaction between diphenyl (D) and hydrogen (H_2),

$$C_{12}H_{10} + H_2 \overset{k_{-B}}{\longrightarrow} 2C_6H_6$$

the rate of formation of benzene is given as

$$r_{B,reverse} = k_{-B} C_D C_{H_2} \tag{3-12}$$

Again, both the rate constants k_B and k_{-B} are *defined with respect to benzene!!!*

The net rate of formation of benzene is the sum of the rates of formation from the forward reaction [i.e., Equation (3-11)] and the reverse reaction [i.e., Equation (3-12)]:

$$r_B \equiv r_{B,net} = r_{B,forward} + r_{B,reverse}$$

$$r_B = -k_B C_B^2 + k_{-B} C_D C_{H_2} \tag{3-13}$$

Multiplying both sides of Equation (3-13) by -1, we obtain the rate law for the rate of disappearance of benzene, $-r_B$:

Elementary
reversible
$A \rightleftarrows B$

$$-r_B = k_B C_B^2 - k_{-B} C_D C_{H_2} = k_B \left(C_B^2 - \frac{k_{-B}}{k_B} C_D C_{H_2} \right)$$

$-r_A = k \left(C_A - \frac{C_B}{K_c} \right)$ Replacing the ratio of the reverse to forward rate law constants by the equilibrium constant, we obtain

$$\boxed{-r_B = k_B \left(C_B^2 - \frac{C_D C_{H_2}}{K_C} \right)} \qquad (3\text{-}14)$$

where

$$\frac{k_B}{k_{-B}} = K_C = \text{Concentration equilibrium constant}$$

The equilibrium constant decreases with increasing temperature for exothermic reactions and increases with increasing temperature for endothermic reactions.

Let's write the rate of formation of diphenyl, r_D, in terms of the concentrations of hydrogen, H_2, diphenyl, D, and benzene, B. The rate of formation of diphenyl, r_D, **must** have the same functional dependence on the reacting species concentrations as does the rate of disappearance of benzene, $-r_B$. The rate of formation of diphenyl is

$$r_D = k_D \left[C_B^2 - \frac{C_D C_{H_2}}{K_C} \right] \qquad (3\text{-}15)$$

Using the relationship given by Equation (3-1) for the general reaction

This is just
stoichiometry.

$$\boxed{\frac{r_A}{-a} = \frac{r_B}{-b} = \frac{r_C}{c} = \frac{r_D}{d}} \qquad (3\text{-}1)$$

we can obtain the relationship between the various specific reaction rates, k_B, k_D:

$$\frac{r_D}{1} = \frac{r_B}{-2} = \frac{k_B}{2} \left[C_B^2 - \frac{C_D C_{H_2}}{K_C} \right] \qquad (3\text{-}16)$$

Comparing Equations (3-15) and (3-16), we see the relationship between the specific reaction rate with respect to diphenyl and the specific reaction rate with respect to benzene is

$$k_D = \frac{k_B}{2}$$

Consequently, we see the need to define the rate constant, k, wrt a particular species.

Finally, we need to check to see if the rate law given by Equation (3-14) is thermodynamically consistent at equilibrium. Applying Equation (3-10) (and Appendix C) to the diphenyl reaction and substituting the appropriate species concentration and exponents, thermodynamics tells us that

$$K_C = \frac{C_{De}C_{H_2e}}{C_{Be}^2} \tag{3-17}$$

At equilibrium, the rate law must reduce to an equation consistent wth thermodynamic equilibrium.

Now let's look at the rate law. At equilibrium, $-r_B \equiv 0$, and the rate law given by Equation (3-14) becomes

$$-r_B \equiv 0 = k_B\left[C_{Be}^2 - \frac{C_{De}C_{H_2e}}{K_C}\right]$$

Rearranging, we obtain, as expected, the equilibrium expression

$$K_C = \frac{C_{De}C_{H_2e}}{C_{Be}^2}$$

which is identical to Equation (3-17) obtained from thermodynamics.

From Appendix C, Equation (C-9), we know that when there is no change in the total number of moles and the heat capacity term, $\Delta C_P = 0$ the temperature dependence of the concentration equilibrium constant is

Endothermic

K_c [graph] T

$$K_C(T) = K_C(T_1)\exp\left[\frac{\Delta H_{Rx}}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right] \tag{C-9}$$

Exothermic

K_c [graph] T

Therefore, if we know the equilibrium constant at one temperature, T_1 [i.e., $K_C(T_1)$], and the heat of reaction, ΔH_{Rx}, we can calculate the equilibrium constant at any other temperature T. For endothermic reactions, the equilibrium constant, K_C, increases with increasing temperature; for exothermic reactions, K_C decreases with increasing temperature. A further discussion of the equilibrium constant and its thermodynamic relationship is given in Appendix C.

3.3   The Reaction Rate Constant

The reaction rate constant k is not truly a constant; it is merely independent of the concentrations of the species involved in the reaction. The quantity k is referred to as either the **specific reaction rate** or **the rate constant**. It is almost always strongly dependent on temperature. It depends on whether or not a catalyst is present, and in gas-phase reactions, it may be a function of total pressure. In liquid systems it can also be a function of other parameters, such as ionic strength and choice of solvent. These other variables normally exhibit much less effect on the specific reaction rate than temperature does with the exception of supercritical solvents, such as super critical water.
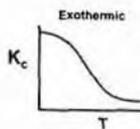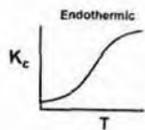
Consequently. for the purposes of the material presented here, it will b assumed that k_A depends only on temperature. This assumption is valid in mo: laboratory and industrial reactions and seems to work quite well.

It was the great Swedish chemist Arrhenius who first suggested that th temperature dependence of the specific reaction rate, k_A, could be correlated b an equation of the type

Arrhenius equation

$$k_A(T) = Ae^{-E/RT}$$

(3-18

where A = preexponential factor or frequency factor
          E = activation energy, J/mol or cal/mol
          R = gas constant = 8.314 J/mol · K = 1.987 cal/mol · K
 T = absolute temperature, K
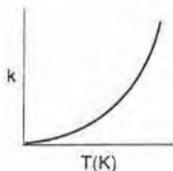
Equation (3-18), known as the *Arrhenius equation*, has been verified empiri cally to give the temperature behavior of most reaction rate constants withi experimental accuracy over fairly large temperature ranges. The Arrheniu equation is derived in the Professional Reference Shelf 3.A: *Collision Theor* on the CD-ROM.

Why is there an activation energy? If the reactants are free radicals tha essentially react immediately on collision. there usually isn't an activatio energy. However, for most atoms and molecules undergoing reaction, there i an activation energy. A couple of the reasons are that in order to react,

1. The molecules need energy to distort or stretch their bonds so that the break them and thus form new bonds.
2. The steric and electron repulsion forces must be overcome as th reacting molecules come close together.

The activation energy can be thought of as a barrier to energy transfe (from the kinetic energy to the potential energy) between reacting molecule that must be overcome. One way to view the barrier to a reaction is throug the use of the *reaction coordinates*. These coordinates denote the potentia energy of the system as a function of the progress along the reaction path a we go from reactants to an intermediate to products. For the reaction

$$A + BC \rightleftharpoons A - B - C \longrightarrow AB + C$$
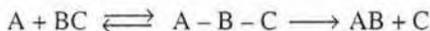
the reaction coordinate is shown in Figure 3-1.

Figure 3-1(a) shows the potential energy of the three atom (or molecule system. A. B. and C. as well as the reaction progress as we go from reactan species A and BC to products AB and C. Initially A and BC are far apart an the system energy is just the bond energy BC. At the end of the reaction, th products AB and C are far apart, and the system energy is the bond energy AB As we move along the reaction coordinate (x-axis) to the right in Figure 3-1(a) the reactants A and BC approach each other, the BC bond begins to break, an the energy of the reaction pair increases until the top of the barrier is reached At the top, the *transition state* is reached where the intermolecular distance between AB and between BC are equal (i.e., A–B–C). As a result, the potentia energy of the initial three atoms (molecules) is high. As the reaction proceed
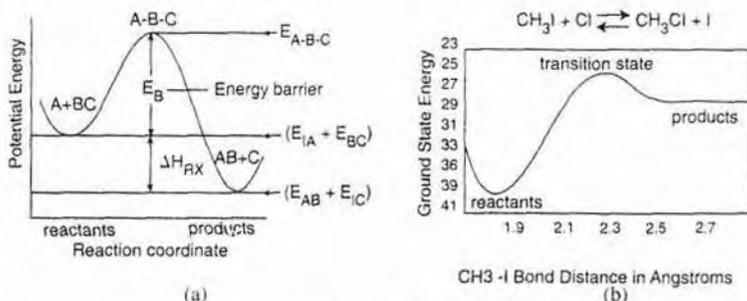
Figure 3-1   Progress along reaction path. (a) Symbolic reaction; (b) Calculated from computational software on the CD-ROM Chapter 3 Web Module.

further, the distance between A and B decreases, and the AB bond begins to form. As we proceed further, the distance between AB and C increases and the energy of the reacting pair decreases to that of the AB bond energy. The calculations to arrive at Figure 3-1(b) are discussed in the CD-ROM web module, and transition state theory is discussed in the CD-ROM Professional Reference Shelf R3.2 Transition State Theory.

We see that for the reaction to occur, the reactants must overcome an energy barrier, E_B, shown in Figure 3-1. The energy barrier, E_B, is related to the activation energy, E. The energy barrier height, E_B, can be calculated from differences in the energies of formation of the transition state molecule and the energy of formation of the reactants, that is,

$$E_B = E^\circ_{fA-B-C} - (E^\circ_{fA} + E^\circ_{fB-C})$$ (3-19)

The energy of formation of the reactants can be found in the literature while the energy of formation of transition state can be calculated using a number of software programs such as CACHE, Spartan, or Cerius[2]. The activation energy, E_A, is often approximated by the barrier height, which is a good approximation in the absence as quantum mechanical tunneling.

Now that we have the general idea for a reaction coordinate let's consider another real reaction system:

$$H \cdot + C_2H_6 \rightarrow H_2 + C_2H_5 \cdot$$
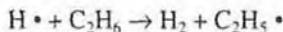
The energy-reaction coordinate diagram for the reaction between a hydrogen atom and an ethane molecule is shown in Figure 3.2 where the bond distortions, breaking, and forming are identified.

One can also view the activation energy in terms of collision theory (Professional Reference Shelf R3.1). By increasing the temperature, we increase the kinetic energy of the reactant molecules. This kinetic energy can in turn be transferred through molecular collisions to internal energy to increase the stretching and bending of the bonds, causing them to reach an activated state, vulnerable to bond breaking and reaction (cf. Figures 3-1 and 3-2).
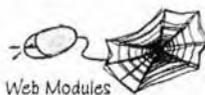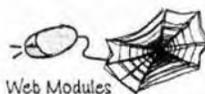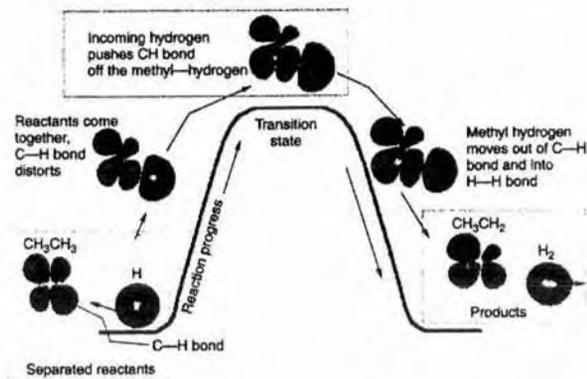
Figure 3-2 A diagram of the orbital distortions during the reaction
$$H \cdot + CH_3CH_3 \rightarrow H_2 + CH_2CH_3 \cdot$$
The diagram shows only the interaction with the energy state of ethane (the C–H bond).
Other molecular orbitals of the ethane also distort. [Courtesy of R. Masel, *Chemical Kinetics*
(McGraw Hill, 2002), p. 594.]

The energy of the individual molecules falls within a distribution of ener-
gies where some molecules have more energy than others. One such distribu-
tion is shown in Figure 3-3 where $f(E,T)$ is the energy distribution function for
the kinetic energies of the reacting molecules. It is interpreted most easily by
recognizing $(f \cdot dE)$ as the fraction of molecules that have an energy between
E and $(E + dE)$. The activation energy has been equated with a minimum
energy that must be possessed by reacting molecules before the reaction will
occur. The fraction of the reacting molecules that have an energy E_A or greater
is shown by the shaded areas in Figure 3-3. The molecules in the shaded area
have sufficient kinetic energy to cause the bond to break and reaction to occur.
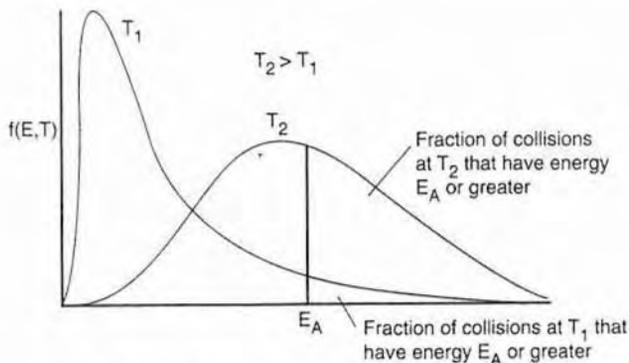One observes that, as the temperature increases, more molecules have sufficient

**Figure 3-3** Energy distribution of reacting molecules.

energy to react as noted by an increase in the shaded area, and the rate of reaction, $-r_A$, increases.

Postulation of the Arrhenius equation, Equation (3-18), remains the greatest single step in chemical kinetics, and retains its usefulness today, nearly a century later. The activation energy, E, is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of Equation (3-18) we obtain

Calculation of the activation energy

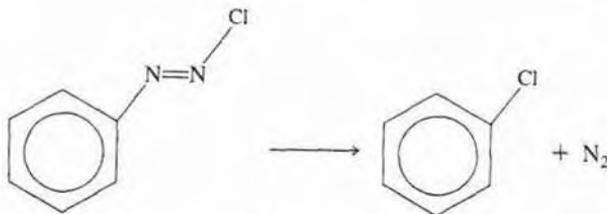$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{3-20}$$

and see that the activation energy can be found from a plot of $\ln k_A$ as a function of $(1/T)$.
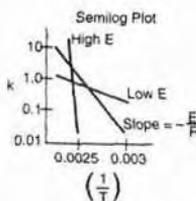
Example 3–1   Determination of the Activation Energy

Calculate the activation energy for the decomposition of benzene diazonium chloride to give chlorobenzene and nitrogen:

using the information in Table E3-1.1 for this first-order reaction.

TABLE E3–1.1 DATA

k (s^{-1})	0.00043	0.00103	0.00180	0.00355	0.00717
T (K)	313.0	319.0	323.0	328.0	333.0

Solution

We start by recalling Equation (3-20)

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \tag{3-20}$$

Summary Notes

Tutorials

We can use the data in Table E3-1.1 to determine the activation energy, E, and frequency factor, A, in two different ways. One way is to make a semilog plot of k vs. $(1/T)$ and determine E from the slope. Another way is to use Excel or Polymath to regress the data. The data in Table E3-1.1 was entered in Excel and is shown in Figure E3-1.1 which was then used to obtain Figure E3-1.2.

A step-by-step tutorial to construct both an Excel and a Polymath spread sheet is given in the Chapter 3 Summary Notes on the CD-ROM.
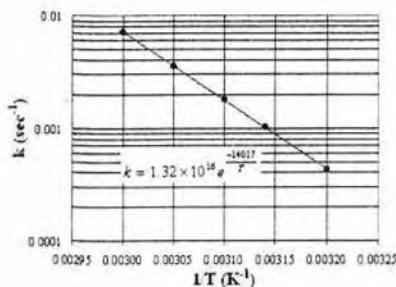
Figure E3-1.1   Excel spreadsheet.
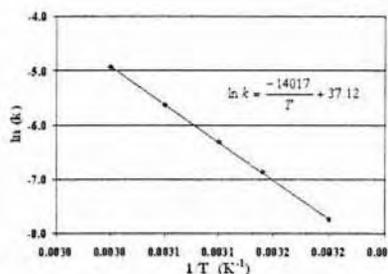
$$k = k_1 \exp\left[\frac{E}{R}\left(\frac{1}{T_1} - \frac{1}{T}\right)\right]$$

Figure E3-1.2   (a) Excel semilog plot; (b) Excel normal plot.

(a) *Graphical Solution*

Figure E3-1.2(a) shows the semilog plots from which we can calculate the activatio
energy. From CD-ROM Appendix D, we show how to rearrange Equation (3-20) i
the form

$$\log \frac{k_2}{k_1} = \frac{-E}{2.3R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{E3-1.1}$$

Rearranging

$$E = -\frac{(2.3)(R)\log(k_2/k_1)}{1/T_2 - 1/T_1} \tag{E3-1.2}$$

To use the decade method, choose $1/T_1$ and $1/T_2$ so that $k_2 = 0.1k_1$. Ther
$\log(k_1/k_2) = 1$.

When $k_1 = 0.005$: $\dfrac{1}{T_1} = 0.003025$ and   when $k_2 = 0.0005$: $\dfrac{1}{T_2} = 0.00319$

Therefore, $E = \dfrac{2.303R}{1/T_2 - 1/T_1} = \dfrac{(2.303)(8.314 \text{ J/mol} \cdot \text{K})}{(0.00319 - 0.003025)/\text{K}}$

$= 116 \dfrac{\text{kJ}}{\text{mol}}$ or 28.7 kcal/mol

(b) *Excel Analysis*

The equation for the best fit of the data

$$\ln k = \frac{14,017}{T} + 37.12 \qquad\qquad (E3\text{-}1.3)$$

is also shown in Figure E3-1.2(b). From the slope of the line given in Figure 3-1.2(b)

$$-\frac{E}{R} = -14,017 \text{ K}$$

$$E = (14,017 \text{ K})R = (14,017 \text{ K})\left(8.314 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}\right)$$

$$\boxed{E = 116.5 \frac{\text{kJ}}{\text{mol}}}$$

From Figure E3-1.2(b) and Equation (E3-1.3), we see

$$\ln A = 37.12$$

taking the antilog

$$A = 1.32 \times 10^{16} \text{ s}^{-1}$$

$$k = 1.32 \times 10^{16} \ exp\left[-\frac{14,017 \text{ K}}{T}\right] \qquad\qquad (E3\text{-}1.4)$$

The rate does not always double for a temperature increase of 10°C.

There is a rule of thumb that states that the rate of reaction doubles for every 10°C increase in temperature. However, this is true only for a specific combination of activation energy and temperature. For example, if the activation energy is 53.6 kJ/mol, the rate will double only if the temperature is raised from 300 K to 310 K. If the activation energy is 147 kJ/mol, the rule will be valid only if the temperature is raised from 500 K to 510 K. (See Problem P3-7 for the derivation of this relationship.)

The larger the activation energy, the more temperature-sensitive is the rate of reaction. While there are no typical values of the frequency factor and activation energy for a first-order gas-phase reaction, if one were forced to make a guess, values of A and E might be 10^{13} s^{-1} and 200 kJ/mol. However, for families of reactions (e.g., halogenation), a number of correlations can be used to estimate the activation energy. One such correlation is the Polanyi-Semenov equation, which relates activation energy to the heat of reaction (see Professional Reference Shelf 3.1). Another correlation relates activation energy to

Reference Shelf

differences in bond strengths between products and reactants.[3] While activation energy cannot be currently predicted a priori, significant research efforts are under way to calculate activation energies from first principles.[4] (Also see Appendix J.)

One final comment on the Arrhenius equation, Equation (3-18). It can be put in a most useful form by finding the specific reaction rate at a temperature T_0, that is,

$$k(T_0) = Ae^{-E/RT_0}$$

and at a temperature T

$$k(T) = Ae^{-E/RT}$$

A most useful form of $k(T)$ — and taking the ratio to obtain

$$k(T) = k(T_0)e^{\frac{E}{R}\left(\frac{1}{T_0} - \frac{1}{T}\right)} \tag{3-21}$$

This equation says that if we know the specific reaction rate $k_0(T_0)$ at a temperature, T_0, and we know the activation energy, E, we can find the specific reaction rate $k(T)$ at any other temperature, T, for that reaction.

3.4 Present Status of Our Approach to Reactor Sizing and Design

Where are we? — In Chapter 2, we showed how it was possible to size CSTRs, PFRs, and PBRs using the design equations in Table 3-2 (page 99) *if* the rate of disappearance of A is known as a function of conversion, X:

$$-r_A = g(X)$$

In general, information in the form $-r_A = g(X)$ is not available. However, we have seen in Section 3.2 that the rate of disappearance of A, $-r_A$, is normally expressed in terms of the concentration of the reacting species. This functionality,

$-r_A = f(C_j)$

$$-r_A = [k_A(T)][\text{fn}(C_A, C_B, \dots)] \tag{3-2}$$

$+$

$C_j = h_j(X)$ — is called a *rate law*. In Part 2, Sections 3.5 and 3.6, we show how the concentration of the reacting species may be written in terms of the conversion X,

$\downarrow$

$-r_A = g(X)$

$$C_j = h_j(X) \tag{3-22}$$

and then we can design isothermal reactors

[3] M. Boudart, *Kinetics of Chemical Processes* (Upper Saddle River, N.J.: Prentice Hall, 1968), p. 168. J. W. Moore and R. G. Pearson, *Kinetics and Mechanisms*, 3rd ed. (New York: Wiley, 1981), p. 199. S. W. Benson, *Thermochemical Kinetics*, 2nd ed. (New York: Wiley, 1976).

[4] S. M. Senkan, *Detailed Chemical Kinetic Modeling: Chemical Reaction Engineering of the Future*, Advances in Chemical Engineering, Vol. 18 (San Diego: Academic Press, 1992), pp. 95–96.