Chapter 1

Reactions and Reaction Rates

LEARNING OBJECTIVES

After completing this chapter, you should be able to

1. use stoichiometric notation to express chemical reactions and thermodynamic quantities;
2. use the extent of reaction concept to check the consistency of experimental data, and to calculate unknown quantities;
3. formulate a definition of reaction rate based on where the reaction occurs.

1.1 INTRODUCTION

1.1.1 The Role of Chemical Reactions

Chemical reactions are an essential technological element in a huge range of industries, for example, fuels, chemicals, metals, pharmaceuticals, foods, textiles, electronics, trucks and automobiles, and electric power generation. Chemical reactions can be used to convert less-valuable raw materials into higher value products, e.g., the manufacture of sulfuric acid from sulfur, air, and water. Chemical reactions can be used to convert one form of energy to another, e.g., the oxidation of hydrogen in a fuel cell to produce electric power. A complex series of reactions is responsible for the clotting of blood, and the “setting” of concrete is a hydration reaction between water and some of the other inorganic constituents of concrete mix. Chemical reactions are also important in many pollution control processes, ranging from treatment of wastewater to reduce its oxygen demand to removal of nitrogen oxides from the flue gas of power plants.

Our civilization currently faces many serious technical challenges. The concentration of carbon dioxide in the earth’s atmosphere is increasing rather rapidly. Reserves of crude oil and natural gas appear to be stagnant at best, whereas consumption of these fossil fuels is increasing globally. Previously unknown or unrecognized diseases are appearing regularly. Nonbiodegradable waste, such as plastic soda bottles, is accumulating in landfills. Obviously, this list of challenges is not comprehensive, and the items on it will vary from person to person and from country to country. Nevertheless, it is difficult to imagine that challenges such as these can be addressed without harnessing some known chemical reactions, plus some reactions that have yet to be developed.

1 For the sake of brevity, the phrase “chemical reaction” is used in the broadest possible sense throughout this book. The phrase is intended to include biological and biochemical reactions, as well as organic and inorganic reactions.
The successful, practical implementation of a chemical reaction is not a trivial exercise. The creative application of material from a number of technical areas is almost always required. Operating conditions must be chosen so that the reaction proceeds at an acceptable rate and to an acceptable extent. The maximum extent to which a reaction can proceed is determined by stoichiometry and by the branch of thermodynamics known as chemical equilibrium. This book begins with a short discussion of the principles of stoichiometry that are most applicable to chemical reactions. A working knowledge of chemical equilibrium is presumed, based on prior chemistry and/or chemical engineering coursework. However, the book contains problems and examples that will help to reinforce this material.

1.1.2 Chemical Kinetics

The rate at which a reaction proceeds is governed by the principles of chemical kinetics, which is one of the major topics of this book. Chemical kinetics allows us to understand how reaction rates depend on variables such as concentration, temperature, and pressure. Kinetics provides a basis for manipulating these variables to increase the rate of a desired reaction, and minimize the rates of undesired reactions. We will study kinetics first from a rather empirical standpoint, and later from a more fundamental point of view, one that creates a link with the details of the reaction chemistry. Catalysis is an extremely important tool within the domain of chemical kinetics. For example, catalysts are required to ensure that blood clots form fast enough to fight serious blood loss. Approximately 90% of the chemical processes that are carried out industrially involve the use of some kind of catalyst in order to increase the rate(s) of the desired reaction(s). Unfortunately, the behavior of heterogeneous catalysts can be significantly and negatively influenced by the rates of heat and mass transfer to and from the “sites” in the catalyst where the reaction occurs. We will approach the interactions between catalytic kinetics and heat and mass transport conceptually and qualitatively at first, and then take them head-on later in the book.

1.1.3 Chemical Reactors

Chemical reactions are carried out in chemical reactors. Some reactors are easily recognizable, for example, a vessel in the middle of a chemical plant or the furnace that burns natural gas or heating oil to heat our house. Others are less recognizable—a river, the ozone layer, or a heap of compost. The development of a reactor (or a system of reactors) to carry out a particular reaction (or system of reactions) can require imagination and creativity. Today, catalysts are used in every modern refinery to “crack” heavy petroleum fractions into lighter liquids that are suitable for the production of high-octane gasoline. The innovation that brought “catalytic cracking” into such widespread use was the development of very large fluidized-bed reactors that allowed the cracking catalyst to be withdrawn continuously for regeneration. It is very likely that new reactor concepts will have to be developed for the optimal implementation of new reactions, especially reactions arising from the emerging realm of biotechnology.

The design and analysis of chemical reactors is built upon a sound understanding of chemical kinetics, but it also requires the use of information from other areas. For example, the behavior of a reactor depends on the nature of mixing and fluid flow. Moreover, since reactions are either endothermic or exothermic, thermodynamics comes into play once again, as energy balances are a critical determinant of reactor behavior. As part of the energy balance, heat transfer can be an important element of reactor design and analysis.
This book will help to tie all of these topics together, and bring them to bear on the study of Chemical Reactions and Chemical Reactors. Let’s begin by taking a fresh look at stoichiometry, from the standpoint of how we can use it to describe the behavior of a chemical reaction, and systems of chemical reactions.

1.2 STOICHIOMETRIC NOTATION

Let’s consider the chemical reaction

\[ \text{Cl}_2 + \text{C}_3\text{H}_6 + 2\text{NaOH} \rightarrow \text{C}_3\text{H}_6\text{O} + 2\text{NaCl} + \text{H}_2\text{O} \]  

(1-A)

The molecule \( \text{C}_3\text{H}_6\text{O} \) is propylene oxide, an important raw material in the manufacture of unsaturated polyesters, such as those used for boat bodies, and in the manufacture of polyurethanes, such as the foam in automobile seats. Reaction (1-A) describes the stoichiometry of the “chlorohydrin” process for propylene oxide manufacture. This process is used for about one-half of the worldwide production of propylene oxide.

The balanced stoichiometric equation for any chemical reaction can be written using a generalized form of stoichiometric notation

\[
\sum_i v_i A_i = 0
\]  

(1-1)

In this equation, \( A_i \) represents a chemical species. For instance, in Reaction (1-A), we might choose

\[
A_1 = \text{Cl}_2; \ A_2 = \text{C}_3\text{H}_6; \ A_3 = \text{NaOH}; \ A_4 = \text{C}_3\text{H}_6\text{O}; \ A_5 = \text{NaCl}; \ A_6 = \text{H}_2\text{O}
\]

The stoichiometric coefficient for chemical species “\( i \)” is denoted \( v_i \). Equation (1-1) involves a convention for writing the stoichiometric coefficients. The coefficients of the products of a reaction are positive, and the coefficients of the reactants are negative. Thus, for Reaction (1-A):

\[
\begin{align*}
    v_1 &= v_{\text{Cl}_2} = -1; \quad v_2 = v_{\text{C}_3\text{H}_6} = -1; \quad v_3 = v_{\text{NaOH}} = -2; \\
    v_4 &= v_{\text{C}_3\text{H}_6\text{O}} = +1; \quad v_5 = v_{\text{NaCl}} = +2; \quad v_6 = v_{\text{H}_2\text{O}} = +1
\end{align*}
\]

The sum of the stoichiometric coefficients, \( \Delta v = \sum v_i \), shows whether the total number of moles increases, decreases, or remains constant as the reaction proceeds. If \( \Delta v > 0 \), the number of moles increases; if \( \Delta v < 0 \), the number of moles decreases; if \( \Delta v = 0 \), there is no change in the total number of moles. For Reaction (1-A), \( \Delta v = 0 \). As we shall see in Chapter 4, a change in the number of moles on reaction can have an important influence on the design and analysis of reactions that take place in the gas phase.

You may have used this stoichiometric notation in earlier courses, such as thermodynamics. For example, the standard Gibbs free energy change of a reaction (\( \Delta G^0_R \)) and the standard enthalpy change of a reaction (\( \Delta H^0_R \)) can be written as

\[
\Delta G^0_R = \sum_i v_i \Delta G^0_{i,j}
\]

(1-2)

and

\[
\Delta H^0_R = \sum_i v_i \Delta H^0_{i,j}
\]

(1-3)

In these equations, \( \Delta G^0_{i,j} \) and \( \Delta H^0_{i,j} \) are the standard Gibbs free energy of formation and standard enthalpy of formation of species \( i \), respectively. For many reactions, values of \( \Delta G^0_R \) and \( \Delta H^0_R \) can be calculated from tabulated values of \( \Delta G^0_{i,j} \) and \( \Delta H^0_{i,j} \) for the reactants and products.
1.3 EXTENT OF REACTION AND THE LAW OF DEFINITE PROPORTIONS

Consider a closed system in which one chemical reaction takes place. Let

\[ N_i = \text{number of moles of species } i \text{ present at time } t \]
\[ N_{i0} = \text{number of moles of species } i \text{ present at } t = 0 \]
\[ \Delta N_i = N_i - N_{i0} \]

Alternately, consider an open system at steady state, in which one reaction takes place. For this case, let

\[ N_i = \text{number of moles of species } i \text{ that leave the system in the time interval } \Delta t \]
\[ N_{i0} = \text{number of moles of species } i \text{ that enter the system in the same time interval } \Delta t \]
\[ \Delta N_i = N_i - N_{i0} \]

In both of these cases, the reaction is the only thing that causes \( N_i \) to differ from \( N_{i0} \), i.e., the reaction is the only thing that causes \( \Delta N_i \) to be nonzero.

The “extent of reaction,” \( \xi \) is defined as

\[ \xi = \frac{\Delta N_i}{v_i} \]  

(1-4)

The “extent of reaction” is a measure of how far the reaction has progressed. Since reactants disappear as the reaction proceeds, \( \Delta N_i \) for every reactant is less than 0. Conversely, products are formed, so that \( \Delta N_i \) for every product is greater than 0. Therefore, the sign convention for stoichiometric coefficients ensures that the value of \( \xi \) is always positive, as long as we have identified the reactants and products correctly.

When the extent of reaction is defined by Eqn. (1-4), \( \xi \) has units of moles.

The maximum value of \( \xi \) for any reaction results when the limiting reactant has been consumed completely, i.e.,

\[ \xi_{\text{max}} = \frac{-N_{i0}}{v_i} \]

where the subscript “l” denotes the limiting reactant. In fact, the extent of reaction provides a way to make sure that the limiting reactant has been identified correctly. For each reactant, calculate \( \xi_{i0} = \frac{N_{i0}}{v_i} \). This is the value of \( \xi_{\text{max}} \) that would result if reactant “i” was consumed completely. The species with the lowest value of \( \xi_{i0} \) is the limiting reactant. This is the reactant that will disappear first if the reaction goes to completion.

If the reaction is reversible, equilibrium will be reached before the limiting reactant is consumed completely. In this case, the highest achievable value of \( \xi \) will be less than \( \xi_{\text{max}} \).

The balanced stoichiometric equation for a reaction tells us that the various chemical species are formed or consumed in fixed proportions. This idea is expressed mathematically by the Law of Definite Proportions. For a single reaction,

\[ \frac{\Delta N_1}{v_1} = \frac{\Delta N_2}{v_2} = \frac{\Delta N_3}{v_3} = \cdots = \frac{\Delta N_i}{v_i} = \cdots = \xi \]  

(1-5)

According to Eqn. (1-5), the value of \( \xi \) does not depend on the species used for the calculation. A reaction that obeys the Law of Definite Proportions is referred to as a
If the syntheses of propylene oxide (Reaction (1-A)) were stoichiometrically simple, we could write

\[
\Delta N_{\text{H}_2\text{O}}/1 = \Delta N_{\text{NaCl}}/2 = \Delta N_{\text{C}_3\text{H}_6\text{O}}/1 = \Delta N_{\text{C}_3\text{H}_6}/-1 = \Delta N_{\text{NaOH}}/-2 = \Delta N_{\text{Cl}_2}/-1
\]

The extent of reaction concept can be applied to open systems at steady state in a second way, by considering the rates at which various species are fed to and withdrawn from the system, instead of considering the number of moles fed and withdrawn in a specified interval of time. Let

\[ F_i = \text{molar rate at which species } i \text{ flows out of the system (moles } i\text{/time}) \]
\[ F_{i0} = \text{molar rate at which species } i \text{ flows into the system (moles } i\text{/time}) \]
\[ \Delta F_{i0} = F_i - F_{i0} \]

The extent of reaction now can be defined as

\[
\xi = \frac{\Delta F_i}{v_i} \quad (1-6)
\]

When the extent of reaction is based on molar flow rates \( F_i \), rather than on moles \( N_i \), \( \xi \) has units of moles/time rather than moles. For this case, the Law of Definite Proportions is written as

\[
\frac{\Delta F_1}{v_1} = \frac{\Delta F_2}{v_2} = \frac{\Delta F_3}{v_3} = \cdots = \frac{\Delta F_i}{v_i} = \cdots = \xi \quad (1-7)
\]

At first glance, the Law of Definite Proportions and the definition of a stoichiometrically simple reaction might seem trivial. However, Eqns. (1-5) and (1-7) can provide a “reality check” when dealing with an actual system. Consider Example 1-1.

**EXAMPLE 1-1**

*Hydrogenolysis of Thiophene (\( \text{C}_4\text{H}_4\text{S} \))*

The thiophene hydrogenolysis reaction

\[
\text{C}_4\text{H}_4\text{S} + 4\text{H}_2 \rightarrow \text{C}_4\text{H}_{10} + \text{H}_2\text{S} \quad (1-B)
\]

takes place at about 1 atm total pressure and about 250 °C over a solid catalyst containing cobalt and molybdenum. This reaction sometimes is used as a model for the reactions that occur when sulfur is removed from various petroleum fractions (e.g., naphtha, kerosene, and diesel fuel) by reaction with hydrogen over a catalyst.

Suppose that the following data had been obtained in a continuous flow reactor, operating at steady state. The reactor is part of a pilot plant for testing new catalysts. Use these data to determine whether the system is behaving as though one, stoichiometrically simple reaction, i.e., Reaction (1-B), was taking place.

<table>
<thead>
<tr>
<th>Species</th>
<th>Gram moles fed during third shift, 8 h</th>
<th>Gram moles in effluent during third shift, 8 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_4\text{H}_4\text{S} )</td>
<td>75.3</td>
<td>5.3</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>410.9</td>
<td>145.9</td>
</tr>
<tr>
<td>( \text{C}<em>4\text{H}</em>{10} )</td>
<td>20.1</td>
<td>75.1</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>25.7</td>
<td>95.7</td>
</tr>
</tbody>
</table>
**APPROACH**

There are enough data in the preceding table to calculate \( \xi \) for each species. If the pilot-plant data are consistent with the hypothesis that one stoichiometrically simple reaction (Reaction (1-B)) took place, then by the Law of Definite Proportions (Eqn. (1-5)), the value of \( \xi \) should be the same for all four species.

**SOLUTION**

The data for thiophene in the preceding table give the following value of the extent of reaction:

\[
\xi = (5.3 - 75.3)/-1 = 70.
\]

The complete calculations are shown in the following table.

<table>
<thead>
<tr>
<th>Species</th>
<th>( \Delta N_i )</th>
<th>( v_i )</th>
<th>( \xi )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{C}_4\text{H}_4\text{S} )</td>
<td>-70.0</td>
<td>-1</td>
<td>70.0</td>
</tr>
<tr>
<td>( \text{H}_2 )</td>
<td>145.9 - 410.9 = -265.0</td>
<td>-4</td>
<td>66.25</td>
</tr>
<tr>
<td>( \text{C}<em>4\text{H}</em>{10} )</td>
<td>75.1 - 20.1 = 55.0</td>
<td>+1</td>
<td>55.0</td>
</tr>
<tr>
<td>( \text{H}_2\text{S} )</td>
<td>95.7 - 25.7 = 70.0</td>
<td>+1</td>
<td>70.0</td>
</tr>
</tbody>
</table>

The calculated extents of reaction show that the actual system did not behave as though only one stoichiometrically simple reaction took place. Clearly, our preconceived notion concerning Reaction (1-B) is not consistent with the facts.

What’s going on in Example 1-1? The data provide some clues. The calculations show that the amount of hydrogen sulfide (H\(_2\)S) formed and the amount of thiophene consumed are in the exact proportion predicted by the stoichiometry of Reaction (1-B). However, less hydrogen is consumed than predicted by the balanced stoichiometric equation, given the consumption of thiophene. Moreover, less butane (\( \text{C}_4\text{H}_{10} \)) is produced.

As an aside, if we checked the elemental balances for C, H, and S, they would show that all sulfur atoms were accounted for (in = out), but that more hydrogen and carbon atoms entered than left.

It seems likely that the analytical system in the pilot plant failed to detect at least one hydrocarbon species. Moreover, the undetected species must have a lower H/C ratio than butane, since \( \xi_{\text{C}_4\text{H}_{10}} < \xi_{\text{H}_2} \). If the behavior of the actual system cannot be described by one stoichiometrically simple reaction, perhaps more than one reaction is taking place. Can we postulate a system of reactions that is consistent with the data, which might help to identify the missing compound(s)?

### 1.3.1 Stoichiometric Notation—Multiple Reactions

If more than one reaction is taking place, then a given chemical species, say \( A_i \), may participate in more than one reaction. This species will, in general, have a different stoichiometric coefficient in each reaction. It may be a product of one reaction and a reactant in another.

If the index “\( k \)” is used to denote one specific reaction in a system of “\( R \)” reactions, the generalized stoichiometric notation for a reaction becomes

\[
\sum_i v_{ki} A_i = 0, \quad k = 1, 2, \ldots, R
\]

(1-8)

Here, \( R \) is the total number of independent reactions that take place and \( v_{ki} \) is the stoichiometric coefficient of species \( i \) in reaction \( k \).
Each of the $R$ reactions may contribute to $\Delta N_i$, which is the change in the number of moles of species $i$. If the extent of reaction “$k$” is denoted by $\xi_k$, then the total change in the number of moles of species $i$ is

$$\Delta N_i = N_i - N_{i0} = \sum_{k=1}^{R} v_k \xi_k$$  \hspace{1cm} (1-9)$$

The term $v_k \xi_k$ is the change in the number of moles of “$i$” that is caused by reaction “$k$.” The total change in moles of species $i$, $\Delta N_i$, is obtained by summing such terms over all of reactions that take place.

When the extent of reaction is defined in terms of molar flow rates, the equivalent of Eqn. (1-9) is

$$\Delta F_i = F_i - F_{i0} = \sum_{k=1}^{R} v_k \xi_k$$ \hspace{1cm} (1-10)$$

**EXAMPLE 1-2**

**Thiophene Hydrogenolysis—Multiple Reactions?**

Suppose that the two reactions shown below were taking place in the thiophene hydrogenolysis pilot plant of Example 1-1.

\[
\begin{align*}
\text{(1-C)} & \quad \text{C}_4\text{H}_4\text{S} + 3\text{H}_2 \rightarrow \text{C}_4\text{H}_8 + \text{H}_2\text{S} \\
\text{(1-D)} & \quad \text{C}_4\text{H}_8 + \text{H}_2 \rightarrow \text{C}_4\text{H}_{10}
\end{align*}
\]

Are the pilot-plant data stoichiometrically consistent with these reactions?

**APPROACH**

If Reactions (1-C) and (1-D) are sufficient to account for the behavior of the actual system, then all of the equations for $\Delta N_i$, one equation for each species, must be satisfied by a single value of $\xi_C$, the extent of Reaction (1-C), plus a single value of $\xi_D$, the extent of Reaction (1-D). There are five chemical species in Reactions (1-C) and (1-D). However, the table in Example 1-1 lacks data for butene ($\text{C}_4\text{H}_8$), so only four equations for $\Delta N_i$ can be formulated with values for $\Delta N_i$. Two of these equations will be used to calculate values of $\xi_C$ and $\xi_D$. The two remaining equations will be used to check the values of $\xi_C$ and $\xi_D$ that we calculated.

**SOLUTION**

Let $v_{C,i}$ be the stoichiometric coefficient of species “$i$” in Reaction (1-C) and let $v_{D,i}$ be the stoichiometric coefficient of species “$i$” in Reaction (1-D). For thiophene (T), from Eqn. (1-9),

$$\Delta N_T = v_{CT} \xi_C + v_{DT} \xi_D = -70$$

Since $v_{CT} = -1$ and $v_{DT} = 0$, $\xi_C = 70$.

For H$_2$ (H),

$$\Delta N_H = v_{CH} \xi_C + v_{DH} \xi_D = -265$$

Since $v_{CH} = -3$ and $v_{DH} = -1$,

$(-3)(70) + (-1) \xi_D = -265; \quad \xi_D = 55$

These values of $\xi_C$ and $\xi_D$ now must satisfy the remaining two equations for $\Delta N$. For H$_2$S (S),

$$\Delta N_s = v_{CS} \xi_C + v_{DS} \xi_D = 70$$

$$(+1)(70) + (0)(55) = 70 \quad \text{Check!}$$

For butane (B),

$$\Delta N_B = v_{CB} \xi_C + v_{DB} \xi_D = 55$$
These calculations show that the data, as they exist, are consistent with the hypothesis that Reactions (1-C) and (1-D) are the only ones that take place.

This analysis does not prove that these two reactions are taking place. There are other explanations that might account for the experimental data. First, the data may be inaccurate. Perhaps only one reaction takes place, but the number of moles of both \( \text{H}_2 \) and \( \text{C}_4\text{H}_{10} \) was measured incorrectly. Perhaps more than two reactions take place. Clearly, additional data are required. The analysis of pilot-plant operations must be improved so that all the three species balances (carbon, hydrogen, and sulfur) can be closed within reasonable tolerances.

**EXERCISE 1-1**

What specific actions would you recommend to the team that is operating the pilot plant?

**EXAMPLE 1-3**

**Thiophene Hydrogenolysis—Calculation of Butene**

**APPROACH**

Let the subscript “E” be used to denote butene. Equation (1-9) can be written for butene, as follows:

\[
\Delta N_E = \nu_{CE} \xi_C + \nu_{DE} \xi_D
\]

Since all of the quantities on the right-hand side of this equation are known, the value of \( \Delta N_E \) can be calculated directly. The quantity of butene formed during the third shift is \( \Delta N_E \). If there was no butene in the feed to the reactor, \( \Delta N_E \) also is the total amount of butene that would be collected from the effluent during the third shift.

**SOLUTION**

From Example 1-2, \( \xi_C = 70 \) and \( \xi_D = 55 \). From Reactions (1-C) and (1-D), \( \nu_{CE} = +1 \) and \( \nu_{DE} = -1 \). Therefore,

\[
\Delta N_E = ( +1)(70) + ( -1)(55) = 15
\]

If there was no butene in the feed to the reactor, we would expect to find 15 moles in the effluent that was collected during the third shift.

**1.4 DEFINITIONS OF REACTION RATE**

**1.4.1 Species-Dependent Definition**

In order to be useful in reactor design and analysis, the reaction rate must be an *intensive* variable, i.e., one that does not depend on the size of the system. Also, it is very convenient to define the reaction rate so that it refers explicitly to one of the chemical species that participates in the reaction. The reference species usually is shown as part of the symbol for the reaction rate, and the reference species should be specified in the units of the reaction rate.
Consider a system in which one stoichiometrically simple reaction is taking place. Let’s define a reaction rate $r_i$ as

$$r_i = \frac{\text{rate of formation of product } \text{"}i\text{" (moles \text{"}i\text{" formed/time)}}}{\text{unit (something)}}$$  \hspace{1cm} (1-11)

The subscript “$i$” refers to the species whose rate of formation is $r_i$. The denominator of the right-hand side of Eqn. (1-11) is what makes $r_i$ an intensive variable. We will return to this denominator momentarily.

Several things are obvious about this definition of $r_i$. First, if “$i$” actually is being formed, $r_i$ will be positive. However, we may want “$i$” to be a reactant, which is being consumed (disappearing). In this case, the value of $r_i$ would be negative. An alternative, mathematically equivalent, definition can be used when “$i$” is a reactant:

$$-r_i = \frac{\text{rate of disappearance of reactant } \text{"}i\text{" (moles \text{"}i\text{" consumed/time)}}}{\text{unit (something)}}$$  \hspace{1cm} (1-12)

If “$i$” actually is being consumed, then $-r_i$ will be positive, i.e., the rate of disappearance will be positive.

In order to properly and usefully define “unit (something),” we need to know where the reaction actually takes place. Let’s consider a few of the most important cases.

### 1.4.1.1 Single Fluid Phase

A chemical reaction may take place homogeneously throughout a single fluid phase. The reaction might result, for example, from collisions between molecules of the fluid or it might result from the spontaneous decomposition of a molecule of the fluid. In such cases, the overall rate at which “$i$” is generated or consumed, i.e., the number of molecules of “$i$” converted per unit time in the whole system, will be proportional to the volume of the fluid. Fluid volume is the appropriate variable for expressing the rate of a homogeneous reaction as an intensive variable. Thus,

**Reaction rate—homogeneous reaction**

$$-r_i = \frac{\text{rate of disappearance of reactant } \text{"}i\text{" (moles \text{"}i\text{" consumed/time)}}}{\text{unit volume of fluid}}$$  \hspace{1cm} (1-13)

In this case, $r_i$ and $-r_i$ have the dimensions of moles $i$/time-volume.

### 1.4.1.2 Multiple Phases

Multiphase reactors are much more prevalent in industrial practice than single-phase reactors. The behavior of multiphase systems can be very complex. It is not always straightforward to determine whether the reaction takes place in one phase, more than one phase, or at the interface between phases. However, there is one very important case where the locus of reaction is well understood.

**Heterogeneous Catalysis**  Approximately 90% of the reactions that are practiced commercially in fields such as petroleum refining, chemicals and pharmaceuticals manufacture, and pollution abatement involve solid, heterogeneous catalysts. The reaction takes place on
the surface of the catalyst, not in the surrounding fluid phase(s). The overall reaction rate depends on the amount of catalyst present, and so the amount of catalyst must be used to make \( r_i \) and \(-r_i\) intensive.

The amount of catalyst may be expressed in several valid ways, e.g., weight, volume, and surface area. The choice between these measures of catalyst quantity is one of convenience. However, weight is frequently used in engineering applications. For this choice,

\[
\text{Reaction rate—heterogeneous catalytic reaction}
\]

\[
\frac{\text{rate of formation of product } \text{"i"}}{\text{unit weight of catalyst}} = \frac{\text{moles } \text{"i"} \text{ formed}}{\text{time}} \quad (1-14)
\]

In fundamental catalyst research, an attempt usually is made to relate the reaction rate to the number of atoms of the catalytic component that are in contact with the fluid. For example, if the decomposition of hydrogen peroxide (\( \text{H}_2\text{O}_2 \)) is catalyzed by palladium metal, the rate of disappearance of \( \text{H}_2\text{O}_2 \) might be defined as,

\[
\frac{\text{rate of disappearance of } \text{H}_2\text{O}_2}{\text{atoms of Pd in contact with fluid containing } \text{H}_2\text{O}_2} = \frac{\text{molecules reacted}}{\text{time}} \quad (1-15)
\]

Expressed in this manner, \(-r_{\text{H}_2\text{O}_2}\) has units of inverse time and is called a “turnover frequency.” Physically, it is the number of molecular reaction events (i.e., \( \text{H}_2\text{O}_2 \) decompositions) that occur on a single atom of the catalytic component per unit of time.

Unfortunately, except in special cases, the symbol that is used to denote reaction rate is not constructed to tell the user what basis was used to make the rate intensive. This task usually is left to the units of the reaction rate.

Other Cases In some cases, a reaction takes place in one of the phases in a multiphase reactor but not in the others. Obviously, it is critical to know the phase in which the reaction occurs. If the definition of the reaction rate is based on the total reactor volume, serious trouble will result when the ratio of the phases changes. The ratio of the phases generally will depend on variables such as the reactor dimensions, the intensity of mechanical agitation, and the feed rates and compositions of the various fluids. Therefore, difficulty is inevitable, especially on scaleup, if the reaction rate is misdefined.

In a few industrial processes, the reaction occurs at the interface between two phases. The interfacial area then is the appropriate parameter to use in making the reaction rate intensive. The synthesis of poly(bisphenol A carbonate) (polycarbonate) from bisphenol A and phosgene is an example of a reaction that occurs at the interface between two fluid phases.

On occasion, a reaction takes place in more than one phase of a multiphase reactor. An example is the so-called “catalytic combustion.” If the temperature is high enough, a hydrocarbon fuel such as propane can be oxidized catalytically, on the surface of a heterogeneous catalyst, at the same time that a homogeneous oxidation reaction takes place in the gas phase. This situation calls for two separate definitions of the reaction rate, one for the gas phase and the other for the heterogeneous catalyst.

1.4.1.3 Relationship Between Reaction Rates of Various Species (Single Reaction)

For a stoichiometrically simple reaction, that obeys the Law of Definite Proportions, the reaction rates of the various reactants and products are related through stoichiometry,
i.e.,
\[ \frac{r_1}{v_1} = \frac{r_2}{v_2} = \frac{r_3}{v_3} = \cdots = \frac{r_i}{v_i} = \cdots \]  
(1-16)

For example, in the ammonia synthesis reaction
\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]  
(1-E)

\[ \frac{r_{\text{N}_2}}{(-1)} = \frac{r_{\text{H}_2}}{(-3)} = \frac{r_{\text{NH}_3}}{(2)} \]

In words, the molar rate of ammonia formation is twice the molar rate of nitrogen disappearance, and two-thirds the molar rate of hydrogen disappearance.

### 1.4.1.4 Multiple Reactions

If more than one reaction takes place, the rate of each reaction must be known in order to calculate the total rate of formation or consumption of a species. Thus,

\[ r_i = \sum_{k=1}^{R} r_{ki} \]  
(1-17)

where \( R \) is the number of independent reactions that take place, and “\( k \)” again denotes a specific reaction. In words, the total rate of formation of species \( i \) is the sum of the rates at which “\( i \)” is formed in each of the reactions taking place.

### 1.4.2 Species-Independent Definition

The species-dependent definition of the reaction rate is used in a majority of published articles in the chemical engineering literature. The major disadvantage of this definition is that the reaction rates of the various species in one chemical reaction are different if their stoichiometric coefficients are different. The relationship of one rate to another is given by Eqn. (1-16). This disadvantage has led to the occasional use of an alternative, species-independent definition of reaction rate.

In the species-independent definition, the reaction rate is referenced to the reaction itself, rather than to a species. Consider the stoichiometrically simple reaction

\[ \sum_i v_i a_i = 0 \]

Equation (1-16) provides relationships between the various \( r_i \) for this reaction. However, we can define the rate of this reaction as \( r \equiv \frac{r_i}{v_i} \), so that Eqn. (1-16) becomes

\[ r = \frac{r_1}{v_1} = \frac{r_2}{v_2} = \frac{r_3}{v_3} = \cdots = \frac{r_i}{v_i} = \cdots \]  
(1-18)

With this definition, a species does not have to be specified in order to define the reaction rate. However, we do have to specify the exact way in which the balanced stoichiometric equation is written. For example, the value of \( r \) is not the same for

\[ \text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \]  
(1-E)

as it is for

\[ \frac{1}{2}\text{N}_2 + \frac{3}{2}\text{H}_2 \rightleftharpoons \text{NH}_3 \]  
(1-F)

because the stoichiometric coefficients are not the same in these two stoichiometric equations.

**EXERCISE 1-2**

If \( r = 0.45 \) for Reaction (1-E) at a given set of conditions, what is the value of \( r \) for Reaction (1-F)?
Obviously, when using the species-independent definition of reaction rate, great care must be taken to write the balanced stoichiometric equation(s) at the beginning of the analysis, and to use the same stoichiometric equation(s) throughout the analysis.

The species-dependent definition of reaction rate will be used throughout the remainder of this text.

### SUMMARY OF IMPORTANT CONCEPTS

- **Sign convention for stoichiometric coefficients**
  - Products positive; reactants negative

- **Extent of reaction**
  - Single reaction
    - Closed system $\xi = \Delta N_i/v_i$
    - Open system at steady state $\xi = \Delta F_i/v_i$
  - Multiple reactions
    - Closed system $\Delta N_i = \sum_{k=1}^{R} v_{ik} \xi_k$

- **Applications**
  - Checking consistency of data
    - Multiple reactions? Which ones?
  - Calculating unknown quantities
  - Defining the reaction rate
  - Where does the reaction occur?

### PROBLEMS

**Problem 1-1 (Level 1)** A group of researchers is studying the kinetics of the reaction of hydrogen with thiophene ($\text{C}_4\text{H}_4\text{S}$). They have postulated that only one stoichiometrically simple reaction takes place, as shown below.

$$\text{C}_4\text{H}_4\text{S} + 4\text{H}_2 \rightarrow \text{H}_2\text{S} + \text{C}_4\text{H}_{10}$$

In one experiment, the feed to a continuous reactor operating at steady state was

- $\text{C}_4\text{H}_4\text{S} \rightarrow 0.65$ g-mol/min
- $\text{H}_2 \rightarrow 13.53$ g-mol/min
- $\text{H}_2\text{S} \rightarrow 0.59$ g-mol/min
- $\text{C}_4\text{H}_{10} \rightarrow 0.20$ g-mol/min

The effluent rates were

- $\text{C}_4\text{H}_4\text{S} \rightarrow 0.29$ g-mol/min
- $\text{H}_2 \rightarrow 12.27$ g-mol/min
- $\text{H}_2\text{S} \rightarrow 0.56$ g-mol/min
- $\text{C}_4\text{H}_{10} \rightarrow 0.38$ g-mol/min

Are the experimental data consistent with the assumption that only one stoichiometrically simple reaction (i.e., the above reaction) takes place?

**Problem 1-2 (Level 2)** A continuous reactor operating at steady state is being used to study the formation of methanol ($\text{CH}_3\text{OH}$) from mixtures of $\text{H}_2$ and CO according to the reaction

$$\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$$

Some data from one particular run are shown below.

<table>
<thead>
<tr>
<th>Species</th>
<th>Rate in (g·mol/min)</th>
<th>Rate out (g·mol/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>100</td>
<td>83</td>
</tr>
<tr>
<td>$\text{H}_2$</td>
<td>72</td>
<td>38</td>
</tr>
<tr>
<td>$\text{CO}_2$</td>
<td>9</td>
<td>9</td>
</tr>
<tr>
<td>$\text{CH}_4$</td>
<td>19</td>
<td>19</td>
</tr>
<tr>
<td>$\text{CH}_3\text{OH}$</td>
<td>2</td>
<td>13</td>
</tr>
</tbody>
</table>

Does the system behave as though only one stoichiometrically simple reaction, i.e., the above reaction, takes place? If not, develop a hypothesis that quantitatively accounts for any discrepancy in the data. How could your hypothesis be tested?

**Problem 1-3 (Level 1)** The following e-mail is in your in-box at 8 AM on Monday:

To: U. R. Loehmann
From: I. M. DeBoosse
Subject: Quinoline Hydrogenation

U.R.,

I hope that you can help with the following:

When quinoline ($\text{C}_9\text{H}_7\text{N}$) is hydrogenated at about 350 °C over various heterogeneous catalysts, the three reactions shown below take place to varying extents. In one experiment in a batch reactor (closed system), the initial charge to the reactor was 100 mol of quinoline and 500 mol of hydrogen ($\text{H}_2$). After 10 h, the reactor contents were analyzed, with the following results:

- Quinoline ($\text{C}_9\text{H}_7\text{N}$)—40 mol
- Hydrogen ($\text{H}_2$)—290 mol
- Decahydroquinoline ($\text{C}_{15}\text{H}_{15}\text{N}$)—20 mol

When quinoline ($\text{C}_9\text{H}_7\text{N}$) is hydrogenated at about 350 °C over various heterogeneous catalysts...
If the reactions shown below are the only ones that take place, how many moles of tetrahydroquinoline (C9H11N) and butylbenzylamine (C9H13N) should have been present after 10 h?  

[chemical diagrams]

**Problem 1-4 (Level 2)** The following memo is in your in-box at 8 AM on Monday:

To: U. R. Loehmann
From: I. M. DeBosse
Subject: Methanation

U.R.,

Hope you can help with the following:

The methanation of carbon monoxide

\[ \text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O} \]

is an important step in the manufacture of ammonia, and in the manufacture of synthetic natural gas (SNG) from coal or heavy hydrocarbons. The reaction is very exothermic. Especially in the manufacture of SNG, a large quantity of heat must be removed from the methanation reactor in order to avoid catalyst deactivation and to maintain a favorable equilibrium.

A small research company, F. A. Stone, Inc., has offered to license us a novel methanation process. The reaction takes place in a slurry bubble-column reactor. Small particles of the catalyst are suspended in a hydrocarbon liquid (a mixture of heavy paraffins with an average formula of C18H36). A gas containing carbon monoxide (CO) and hydrogen (H2) is sparged (bubbled) continuously through the slurry. The gas leaving the top of the reactor contains unreacted CO and H2, as well as the products, CH4 and H2O. The heat of reaction is removed by water flowing through tubes in the reactor.

Please review the following pilot-plant data provided by F. A. Stone to be sure that the process is performing “as advertised.” These data are from one particular continuous, steady-state run. F. A. Stone will not release additional data until we have made a downpayment on the license fee.

Please write me a short memo (not more than one page) containing the results of your calculations and explaining what you did. Attach your calculations to the memo in case someone wants to review the details.

Thanks, I. M.

**Problem 1-5 (Level 2)** Carbon monoxide (CO) and hydrogen (H2) are fed to a continuous catalytic reactor operating at steady state. There are no other components in the feed. The outlet stream contains unconverted CO and H2, along with the products methanol (CH3OH), ethanol (C2H5OH), isopropanol (C3H7OH), and carbon dioxide (CO2). These are the only species in the product stream.

The reactions occurring are

\[ \text{CO} + 2\text{H}_2 \rightarrow \text{CH}_3\text{OH} \]
\[ 3\text{CO} + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CO}_2 \]
\[ 5\text{CO} + 4\text{H}_2 \rightarrow \text{C}_3\text{H}_7\text{OH} + 2\text{CO}_2 \]

The feed rates of CO and H2 to the reactor are 100 mol/h (each). The rates in the stream that leaves the reactor (in mol/h.)
are H₂-30; CO-30; C₂H₅OH-5. What is the mole fraction of each species in the product stream?

**Problem 1-6 (Level 1)** The hydrogenation of aniline at about 50°C, over a Ru/carbon catalyst, is believed to involve the reactions:

\[
\begin{align*}
\text{Aniline (A)} + 3\text{H}_2 &\rightarrow \text{Cyclohexylamine (CHA)} \\
\text{Aniline (A)} + \text{H}_2 &\rightarrow \text{Cyclohexane (CH)} + \text{NH}_3 \\
2 \text{Aniline (A)} &\rightarrow \text{Dicyclohexylamine (DCHA)} + \text{NH}_3
\end{align*}
\]

In one particular experiment, aniline was hydrogenated in a closed vessel at 50°C and 50 bar of H₂ pressure for 3 h. The following data were obtained:

<table>
<thead>
<tr>
<th>Species</th>
<th>Moles after 3 h/mol of aniline charged</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.476</td>
</tr>
<tr>
<td>CHA</td>
<td>0.346</td>
</tr>
<tr>
<td>CH</td>
<td>0.080</td>
</tr>
<tr>
<td>DCHA</td>
<td>0.049</td>
</tr>
</tbody>
</table>

The amounts of ammonia formed and H₂ consumed were not measured.

1. Is the experimental data consistent with the assumption that these three reactions are the only ones that occur?
2. Estimate the amount of NH₃ formed (mol/mol A charged).
3. Estimate the amount of H₂ consumed (mol/mol A charged).

**Problem 1-7 (Level 2)** The gas-phase reactions

Isobutanol \(\rightarrow\) Isobutene \(\rightarrow\) Hydrogenation

\[
\begin{align*}
\text{Isobutanol (B)} &\rightarrow \text{Isobutene (IB)} + \text{H}_2 \\
\text{(CH}_3\text{)}_2\text{CHCH}_2\text{OH} &\rightarrow (\text{CH}_3\text{)}_2\text{C} = \text{CH}_2 + \text{H}_2 \\
2 \text{ Methanol} &\rightarrow \text{Dimethyl ether (DME)} + \text{H}_2 \\
2\text{CH}_3\text{OH} &\rightarrow \text{CH}_3\text{OCH}_3 + \text{H}_2
\end{align*}
\]

Isobutanol + Methanol

\(\rightarrow\) Methylisobutyl ether (MIBE) + H₂O

\[
\text{(CH}_3\text{)}_2\text{CHCH}_2\text{OH} + \text{CH}_3\text{OH} \rightarrow (\text{CH}_3\text{)}_2\text{CHCH}_2\text{OCH}_3 + \text{H}_2
\]

2 Isobutanol \(\rightarrow\) Disobutyl ether (DIBE) + H₂O

\[
2(\text{CH}_3\text{)}_2\text{CHCH}_2\text{OH} \rightarrow (\text{CH}_3\text{)}_2\text{CHCH}_2\text{OCH}_3\text{CH(CH}_3\text{)}_2 + \text{H}_2
\]

1. What is the fractional conversion of isobutanol?
2. What is the fractional conversion of methanol?
3. What is the mole fraction of water leaving the reactor?

**Problem 1-8 (K2-1) (Level 1)** Consider the reaction

\[
\text{C}_2\text{H}_3\text{Cl}_3 + 3\text{H}_2 \rightarrow \text{C}_2\text{H}_6 + 3\text{HCl}
\]

\(\text{trichloroethane} \rightarrow \text{ethane}\)

If the rate of formation of HCl \((r_{\text{HCl}})\) is \(5 \times 10^{-6} \text{ g mol/g cat-min}\),

1. What is the rate of disappearance of trichloroethane?
2. What is the rate of formation of ethane?

**Problem 1-9 (Level 1)** Look carefully at Reaction (1-A). Refer to the literature as necessary. Prepare brief written answers to the following questions:

1. Is a process based on this reaction a good example of “green chemistry”?
2. What can be done with the NaCl that is produced?
3. Since Cl atoms do not appear in the final product (C₃H₆O), what role does chlorine play in this reaction?

**Problem 1-10 (Level 1)** Calculate the standard enthalpy change on reaction, \(\Delta H^0_R\), for Reaction (1-E) at 25°C. Calculate the standard Gibbs free energy change on reaction, \(\Delta G^0_R\), for Reaction (1-E) at 25°C. What are the units of \(\Delta H^0_R\) and \(\Delta G^0_R\)?

**Problem 1-11 (Level 2)** Styrene, the monomeric building block for the polymer polystyrene, is made by the catalytic dehydrogenation of ethyl benzene. Ethyl benzene, in turn, is made by the alkylation of benzene with ethylene, as shown by Reaction (A) below. A common side reaction is that addition of another alkyl group to ethyl benzene to form diethyl benzene. This reaction is shown as Reaction (B). The second alkyl group may be in the ortho, meta, or para position.
Initially, 100 mol of benzene and 100 mol of ethylene are charged to a reactor. No material flows into or out of the reactor after this initial charge. After a very long time, the contents of the reactor are analyzed, with the following results:

<table>
<thead>
<tr>
<th>Species</th>
<th>Benzene</th>
<th>Ethylene</th>
<th>Ethyl benzene</th>
<th>Diethyl benzene</th>
</tr>
</thead>
<tbody>
<tr>
<td>Number of moles</td>
<td>35</td>
<td>2</td>
<td>39</td>
<td>19</td>
</tr>
</tbody>
</table>

1. Show that the behavior of the reactor is not consistent with the hypothesis that Reactions (A) and (B) are the only ones that take place.

2. Develop an alternative hypothesis that is consistent with all of the data, and demonstrate this consistency.

**Problem 1-12 (Level 2)** The overall reaction for the catalytic hydrodechlorination of 1,1,1-trichloroethane (111-TCA) is

\[
C_2H_3Cl_3 + 3H_2 \rightarrow C_2H_6 + 3HCl
\]

On certain catalysts, this overall reaction appears to take place via the following sequence of simpler reactions:

1. \( C_2H_3Cl_3 + H_2 \rightarrow C_2H_4Cl_2 + HCl \)
2. \( C_2H_4Cl_2 + H_2 \rightarrow C_2H_5Cl + HCl \)
3. \( C_2H_5Cl + H_2 \rightarrow C_2H_6 + HCl \)

A mixture of 111-TCA, H\(_2\), and N\(_2\) was fed to a continuous catalytic reactor operating at 523 K and 1 atm. total pressure at a rate of 1200 L(STP)/h. The feed contained 10 mol % H\(_2\) and 1 mol % 111-TCA, and the reactor operated at steady-state.

It was not possible to accurately measure the outlet concentrations of H\(_2\) and HCl. The flow rates of C\(_2\)H\(_3\)Cl\(_3\), C\(_2\)H\(_4\)Cl\(_2\), C\(_2\)H\(_5\)Cl, and C\(_2\)H\(_6\) out of the reactor were 0.074 mol/h, 0.111 mol/h, 0.050 mol/h, and 0.301 mol/h, respectively.

1. Are these data consistent with the hypothesis that the overall reaction takes place via Reactions (1), (2) and (3) (and only Reactions (1), (2) and (3))? Justify your answer.
2. What is the molar flow rate of H\(_2\) leaving the reactor?
3. What is the molar flow rate of HCl leaving the reactor?