

The Basics of Reaction Kinetics for Chemical Reaction Engineering

1.1 | The Scope of Chemical Reaction Engineering

The subject of chemical reaction engineering initiated and evolved primarily to accomplish the task of describing how to choose, size, and determine the optimal operating conditions for a reactor whose purpose is to produce a given set of chemicals in a petrochemical application. However, the principles developed for chemical reactors can be applied to most if not all chemically reacting systems (e.g., atmospheric chemistry, metabolic processes in living organisms, etc.). In this text, the principles of chemical reaction engineering are presented in such rigor to make possible a comprehensive understanding of the subject. Mastery of these concepts will allow for generalizations to reacting systems independent of their origin and will furnish strategies for attacking such problems.

The two questions that must be answered for a chemically reacting system are: (1) what changes are expected to occur and (2) how fast will they occur? The initial task in approaching the description of a chemically reacting system is to understand the answer to the first question by elucidating the thermodynamics of the process. For example, dinitrogen (N_2) and dihydrogen (H_2) are reacted over an iron catalyst to produce ammonia (NH_3):



where ΔH_r is the enthalpy of the reaction (normally referred to as the heat of reaction). This reaction proceeds in an industrial ammonia synthesis reactor such that at the reactor exit approximately 50 percent of the dinitrogen is converted to ammonia. At first glance, one might expect to make dramatic improvements on the production of ammonia if, for example, a new catalyst (a substance that increases

the rate of reaction without being consumed) could be developed. However, a quick inspection of the thermodynamics of this process reveals that significant enhancements in the production of ammonia are not possible unless the temperature and pressure of the reaction are altered. Thus, the constraints placed on a reacting system by thermodynamics should always be identified first.

VIGNETTE 1.1.1

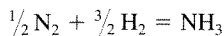
The initial success of a large-scale catalytic technology began in 1913 when the first industrial chemical reactor to synthesize ammonia from dinitrogen and dihydrogen began operation in Germany. Most of the ammonia manufactured today is used to produce nitrogen-rich fertilizers that have an enormous impact on meeting worldwide food demands. According to figures for U.S. agriculture, the 800,000 tons of dinitrogen converted to ammonia in the first Haber reactor (ammonia synthesis over an iron catalyst is called the Haber process after the inventor F. Haber) could grow 700 million additional bushels of corn, enough to nourish 50 million man-years [P. B. Weisz, *CHEMTECH*, **14** (1984) 354]. Because ammonia is a low-priced commodity chemical, the catalyst must be cheap and durable, and its activity must be high so that temperature and pressure can be maintained as low as possible to minimize the size and cost of the huge industrial reactors. The catalyst is essentially iron and the reaction is now well understood. Certain groups of iron atoms on the surface of the catalyst dissociate dinitrogen and dihydrogen into atoms of nitrogen and hydrogen and combine them into ammonia. The catalyst operates at high temperature to increase the rate of the reaction and at high pressure to increase the thermodynamic yield of ammonia (see Example 1.1.1). In a commercial reactor, the catalyst can run for a long time before it is replaced. Thus, the high productivity leads to low cost: the catalyst can give products worth approximately 2000 times its value.

EXAMPLE 1.1.1

In order to obtain a reasonable level of conversion at a commercially acceptable rate, ammonia synthesis reactors operate at pressures of 150 to 300 atm and temperatures of 700 to 750 K. Calculate the equilibrium mole fraction of dinitrogen at 300 atm and 723 K starting from an initial composition of $X_{N_2} = 0.25$, $X_{H_2} = 0.75$ (X_i is the mole fraction of species i). At 300 atm and 723 K, the equilibrium constant, K_a , is 6.6×10^{-3} . (K. Denbigh, *The Principles of Chemical Equilibrium*, Cambridge Press, 1971, p. 153).

■ Answer

(See Appendix A for a brief overview of equilibria involving chemical reactions):



$$K_a = \left[\frac{a_{NH_3}}{a_{N_2}^{1/2} a_{H_2}^{3/2}} \right], \quad \text{where } a = \text{activity}$$

The definition of the activity of species i is:

$$a_i = \bar{f}_i / \bar{f}_i^0, \quad \bar{f}_i^0 = \text{fugacity at the standard state, that is, 1 atm for gases}$$

and thus

$$K_a = \left[\frac{\bar{f}_{\text{NH}_3}}{\bar{f}_{\text{N}_2}^{1/2} \bar{f}_{\text{H}_2}^{3/2}} \right] \left[\frac{(\bar{f}_{\text{N}_2}^0)^{1/2} (\bar{f}_{\text{H}_2}^0)^{3/2}}{(\bar{f}_{\text{NH}_3}^0)} \right] = \left[\frac{\bar{f}_{\text{NH}_3}}{\bar{f}_{\text{N}_2}^{1/2} \bar{f}_{\text{H}_2}^{3/2}} \right] [1 \text{ atm}]$$

Use of the Lewis and Randall rule gives:

$$\bar{f}_i = X_i \bar{\phi}_i P, \quad \bar{\phi}_i = \text{fugacity coefficient of pure component } i \text{ at } T \text{ and } P \text{ of system}$$

then

$$K_a = K_X K_{\bar{\phi}} K_P = \left[\frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}} \right] \left[\frac{\bar{\phi}_{\text{NH}_3}}{\bar{\phi}_{\text{N}_2}^{1/2} \bar{\phi}_{\text{H}_2}^{3/2}} \right] [P^{-1}] [1 \text{ atm}]$$

Upon obtaining each $\bar{\phi}_i$ from correlations or tables of data (available in numerous references that contain thermodynamic information):

$$\left[\frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}} \right] = \left[\frac{(1.14)^{1/2} (1.09)^{3/2}}{(0.91)} \right] (6.6 \times 10^{-3})(300 \text{ atm})(1 \text{ atm})^{-1}$$

$$\left[\frac{X_{\text{NH}_3}}{X_{\text{N}_2}^{1/2} X_{\text{H}_2}^{3/2}} \right] = 2.64$$

If a basis of 100 mol is used (ξ is the number of moles of N_2 reacted):

Species	Initial	At equilibrium
N_2	25	$25 - \xi$
H_2	75	$75 - 3\xi$
NH_3	0	2ξ
total	100	$100 - 2\xi$

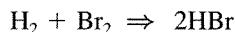
then

$$\frac{2\xi / (100 - 2\xi)}{\left(\frac{25 - \xi}{100 - 2\xi} \right)^{1/2} \left(\frac{75 - 3\xi}{100 - 2\xi} \right)^{3/2}} = \frac{(2\xi)(100 - 2\xi)}{(25 - \xi)^{1/2} (75 - 3\xi)^{3/2}} = 2.64$$

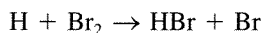
Thus, $\xi = 13.1$ and $X_{\text{N}_2} = (25 - 13.1) / (100 - 26.2) = 0.16$. At 300 atm, the equilibrium mole fraction of ammonia is 0.36 while at 100 atm it falls to approximately 0.16. Thus, the equilibrium amount of ammonia increases with the total pressure of the system at a constant temperature.

The next task in describing a chemically reacting system is the identification of the reactions and their arrangement in a *network*. The kinetic analysis of the network is then necessary for obtaining information on the rates of individual *reactions* and answering the question of how fast the chemical conversions occur. Each reaction of the network is stoichiometrically simple in the sense that it can be described by the single parameter called the *extent of reaction* (see Section 1.2). Here, a stoichiometrically simple reaction will just be called a reaction for short. The expression “simple reaction” should be avoided since a stoichiometrically simple reaction does not occur in a simple manner. In fact, most chemical reactions proceed through complicated sequences of *steps* involving reactive intermediates that do not appear in the stoichiometries of the reactions. The identification of these intermediates and the sequence of steps are the core problems of the kinetic analysis.

If a step of the sequence can be written as it proceeds at the molecular level, it is denoted as an *elementary step* (or an *elementary reaction*), and it represents an irreducible molecular event. Here, elementary steps will be called *steps* for short. The hydrogenation of dibromine is an example of a stoichiometrically simple reaction:



If this reaction would occur by H_2 interacting directly with Br_2 to yield two molecules of HBr , the step would be elementary. However, it does not proceed as written. It is known that the hydrogenation of dibromine takes place in a sequence of two steps involving hydrogen and bromine atoms that do not appear in the stoichiometry of the reaction but exist in the reacting system in very small concentrations as shown below (an initiator is necessary to start the reaction, for example, a photon: $\text{Br}_2 + \text{light} \rightarrow 2\text{Br}$, and the reaction is terminated by $\text{Br} + \text{Br} + \text{TB} \rightarrow \text{Br}_2$ where TB is a third body that is involved in the recombination process—see below for further examples):



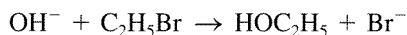
In this text, stoichiometric reactions and elementary steps are distinguished by the notation provided in Table 1.1.1.

Table 1.1.1 | Notation used for stoichiometric reactions and elementary steps.

	Stoichiometric reaction	Elementary step
Irreversible (one-way)	\Rightarrow	\rightarrow
Reversible (two-way)	\rightleftharpoons	\rightleftharpoons
Equilibrated	\rightleftharpoons (circled)	\rightleftharpoons (circled)
Rate-determining		\nrightarrow or \nleftarrow

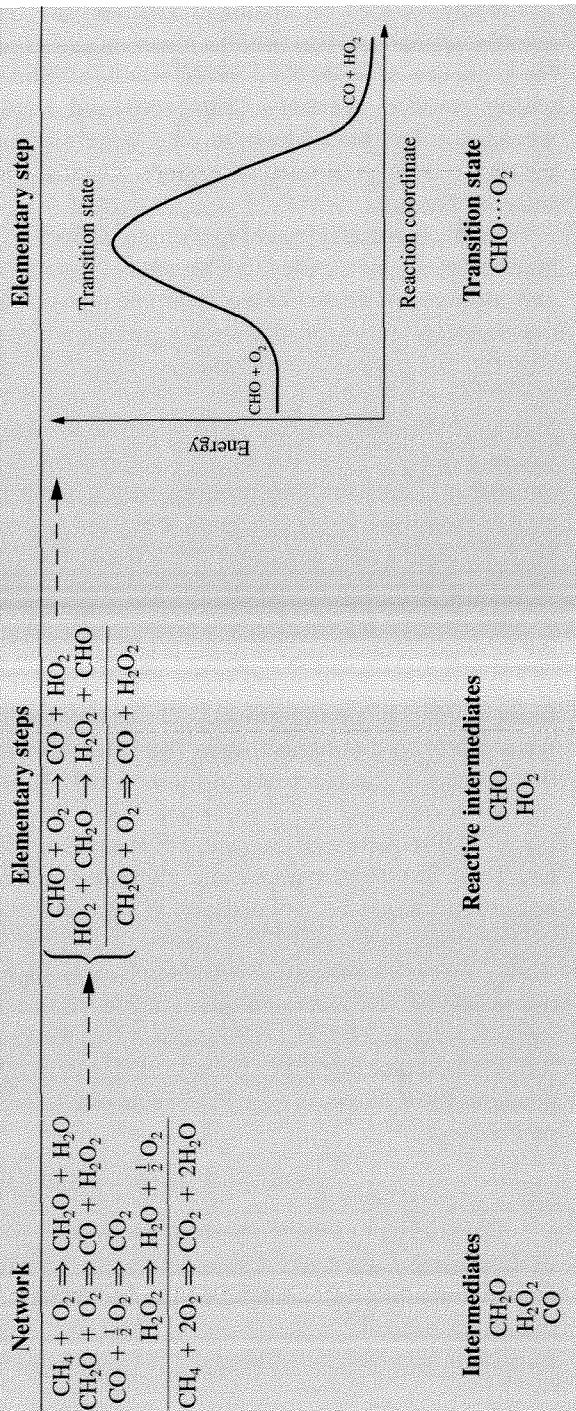
In discussions on chemical kinetics, the terms *mechanism* or *model* frequently appear and are used to mean an assumed reaction network or a plausible sequence of steps for a given reaction. Since the levels of detail in investigating reaction networks, sequences and steps are so different, the words *mechanism* and *model* have to date largely acquired bad connotations because they have been associated with much speculation. Thus, they will be used carefully in this text.

As a chemically reacting system proceeds from reactants to products, a number of species called *intermediates* appear, reach a certain concentration, and ultimately vanish. Three different types of intermediates can be identified that correspond to the distinction among networks, reactions, and steps. The first type of intermediates has reactivity, concentration, and lifetime comparable to those of stable reactants and products. These intermediates are the ones that appear in the reactions of the network. For example, consider the following proposal for how the oxidation of methane at conditions near 700 K and atmospheric pressure may proceed (see Scheme 1.1.1). The reacting system may evolve from two stable reactants, CH₄ and O₂, to two stable products, CO₂ and H₂O, through a network of four reactions. The intermediates are formaldehyde, CH₂O; hydrogen peroxide, H₂O₂; and carbon monoxide, CO. The second type of intermediate appears in the sequence of steps for an individual reaction of the network. These species (e.g., free radicals in the gas phase) are usually present in very small concentrations and have short lifetimes when compared to those of reactants and products. These intermediates will be called *reactive intermediates* to distinguish them from the more stable species that are the ones that appear in the reactions of the network. Referring to Scheme 1.1.1, for the oxidation of CH₂O to give CO and H₂O₂, the reaction may proceed through a postulated sequence of two steps that involve two reactive intermediates, CHO and HO₂. The third type of intermediate is called a *transition state*, which by definition cannot be isolated and is considered a species in transit. Each elementary step proceeds from reactants to products through a transition state. Thus, for each of the two elementary steps in the oxidation of CH₂O, there is a transition state. Although the nature of the transition state for the elementary step involving CHO, O₂, CO, and HO₂ is unknown, other elementary steps have transition states that have been elucidated in greater detail. For example, the configuration shown in Fig. 1.1.1 is reached for an instant in the transition state of the step:



The study of elementary steps focuses on transition states, and the kinetics of these steps represent the foundation of chemical kinetics and the highest level of understanding of chemical reactivity. In fact, the use of lasers that can generate femtosecond pulses has now allowed for the “viewing” of the real-time transition from reactants through the transition-state to products (A. Zewail, *The*

SCHEME 1.1.1 ILLUSTRATION OF THREE TYPES OF INTERMEDIATES



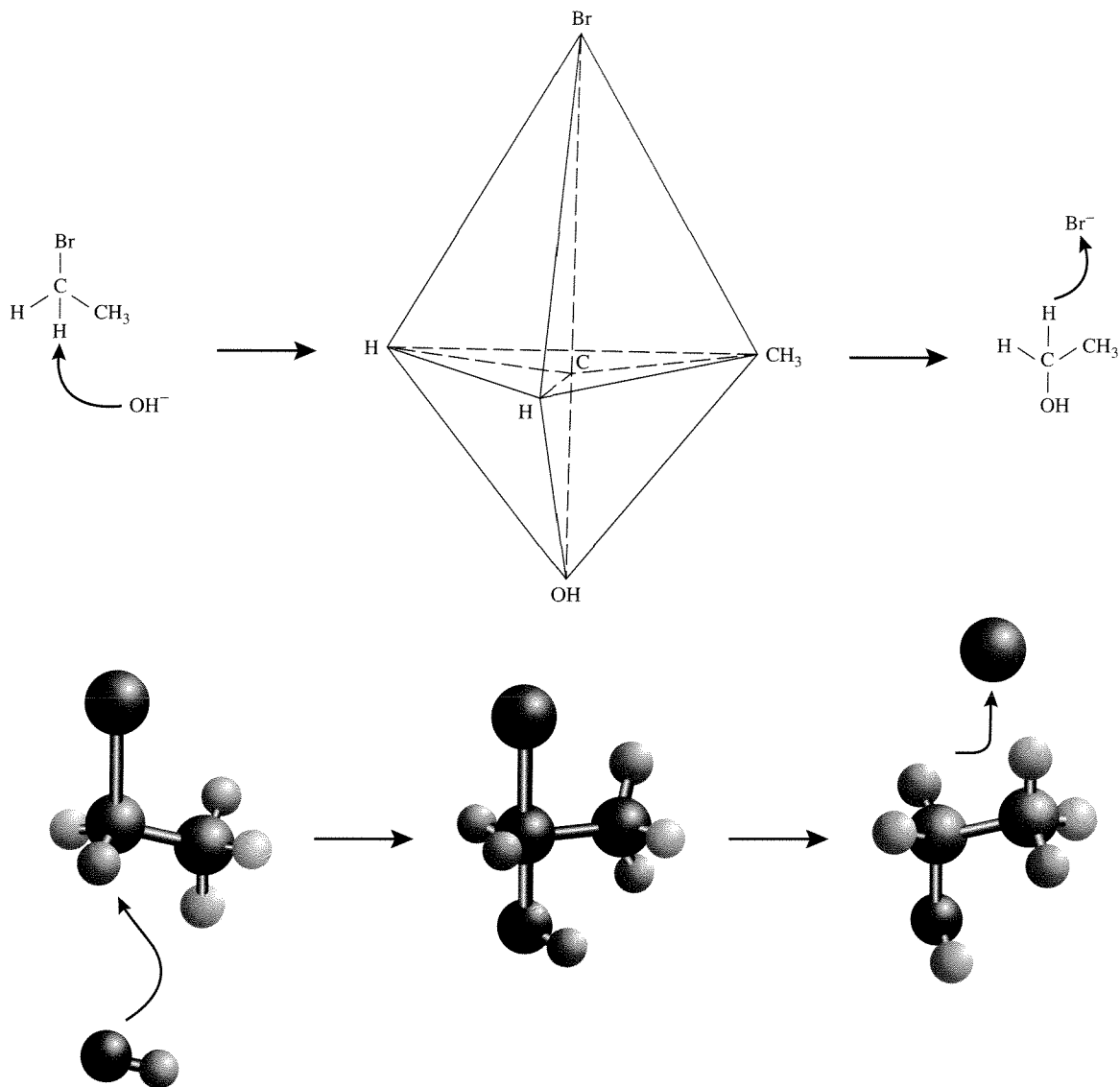
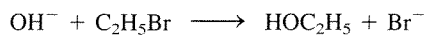


Figure 1.1.1 |

The transition state (trigonal bipyramid) of the elementary step:



The nucleophilic substituent OH^- displaces the leaving group Br^- .

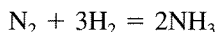
Chemical Bond: Structure and Dynamics, Academic Press, 1992). However, in the vast majority of cases, chemically reacting systems are investigated in much less detail. The level of sophistication that is conducted is normally dictated by the purpose of the work and the state of development of the system.

1.2 | The Extent of Reaction

The changes in a chemically reacting system can frequently, but not always (e.g., complex fermentation reactions), be characterized by a stoichiometric equation. The stoichiometric equation for a simple reaction can be written as:

$$0 = \sum_{i=1}^{NCOMP} \nu_i A_i \quad (1.2.1)$$

where $NCOMP$ is the number of components, A_i , of the system. The stoichiometric coefficients, ν_i , are positive for products, negative for reactants, and zero for inert components that do not participate in the reaction. For example, many gas-phase oxidation reactions use air as the oxidant and the dinitrogen in the air does not participate in the reaction (serves only as a diluent). In the case of ammonia synthesis the stoichiometric relationship is:



Application of Equation (1.2.1) to the ammonia synthesis, stoichiometric relationship gives:

$$0 = 2\text{NH}_3 - \text{N}_2 - 3\text{H}_2$$

For stoichiometric relationships, the coefficients can be ratioed differently, e.g., the relationship:

$$0 = 2\text{NH}_3 - \text{N}_2 - 3\text{H}_2$$

can be written also as:

$$0 = \text{NH}_3 - \frac{1}{2}\text{N}_2 - \frac{3}{2}\text{H}_2$$

since they are just mole balances. However, for an elementary reaction, the stoichiometry is written as the reaction should proceed. Therefore, an elementary reaction such as:



CANNOT be written as:



EXAMPLE 1.2.1

If there are several simultaneous reactions taking place, generalize Equation (1.2.1) to a system of $NRXN$ different reactions. For the methane oxidation network shown in Scheme 1.1.1, write out the relationships from the generalized equation.

■ Answer

If there are $NRXN$ reactions and $NCOMP$ species in the system, the generalized form of Equation (1.2.1) is:

$$0 = \sum_i^{NCOMP} v_{i,j} A_i, \quad j = 1, \dots, NRXN \quad (1.2.2)$$

For the methane oxidation network shown in Scheme 1.1.1:

$$0 = 0\text{CO}_2 + 1\text{H}_2\text{O} - 1\text{O}_2 + 0\text{CO} + 0\text{H}_2\text{O}_2 + 1\text{CH}_2\text{O} - 1\text{CH}_4$$

$$0 = 0\text{CO}_2 + 0\text{H}_2\text{O} - 1\text{O}_2 + 1\text{CO} + 1\text{H}_2\text{O}_2 - 1\text{CH}_2\text{O} + 0\text{CH}_4$$

$$0 = 1\text{CO}_2 + 0\text{H}_2\text{O} - \frac{1}{2}\text{O}_2 - 1\text{CO} + 0\text{H}_2\text{O}_2 + 0\text{CH}_2\text{O} + 0\text{CH}_4$$

$$0 = 0\text{CO}_2 + 1\text{H}_2\text{O} + \frac{1}{2}\text{O}_2 + 0\text{CO} - 1\text{H}_2\text{O}_2 + 0\text{CH}_2\text{O} + 0\text{CH}_4$$

or in matrix form:

$$\begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 0 & 1 & -1 & 0 & 0 & 1 & -1 \\ 0 & 0 & -1 & 1 & 1 & -1 & 0 \\ 1 & 0 & -1/2 & -1 & 0 & 0 & 0 \\ 0 & 1 & 1/2 & 0 & -1 & 0 & 0 \end{bmatrix} \begin{bmatrix} \text{CO}_2 \\ \text{H}_2\text{O} \\ \text{O}_2 \\ \text{CO} \\ \text{H}_2\text{O}_2 \\ \text{CH}_2\text{O} \\ \text{CH}_4 \end{bmatrix}$$

Note that the sum of the coefficients of a column in the matrix is zero if the component is an intermediate.

Consider a closed system, that is, a system that exchanges no mass with its surroundings. Initially, there are n_i^0 moles of component A_i present in the system. If a single reaction takes place that can be described by a relationship defined by Equation (1.2.1), then the number of moles of component A_i at any time t will be given by the equation:

$$n_i(t) = n_i^0 + v_i \Phi(t) \quad (1.2.3)$$

that is an expression of the *Law of Definitive Proportions* (or more simply, a mole balance) and defines the parameter, Φ , called the *extent of reaction*. The extent of reaction is a function of time and is a natural reaction variable.

Equation (1.2.3) can be written as:

$$\Phi(t) = \frac{n_i(t) - n_i^0}{v_i} \quad (1.2.4)$$

Since there is only one Φ for each reaction:

$$\frac{n_i(t) - n_i^0}{v_i} = \frac{n_j(t) - n_j^0}{v_j} \quad (1.2.5)$$

or

$$n_j(t) = n_j^0 + \left(\frac{v_j}{v_i}\right)[n_i(t) - n_i^0] \quad (1.2.6)$$

Thus, if n_i is known or measured as a function of time, then the number of moles of all of the other reacting components can be calculated using Equation (1.2.6).

EXAMPLE 1.2.2

If there are numerous, simultaneous reactions occurring in a closed system, each one has an extent of reaction. Generalize Equation (1.2.3) to a system with $NRXN$ reactions.

■ Answer

$$n_i = n_i^0 + \sum_{j=1}^{NRXN} v_{i,j} \Phi_j \quad (1.2.7)$$

EXAMPLE 1.2.3

Carbon monoxide is oxidized with the stoichiometric amount of air. Because of the high temperature, the equilibrium:



has to be taken into account in addition to:



The total pressure is one atmosphere and the equilibrium constants of reactions (1) and (2) are:

$$K_{X_1} = \frac{(X_{\text{NO}})^2}{(X_{\text{N}_2})(X_{\text{O}_2})}, \quad K_{X_2} = \frac{(X_{\text{CO}_2})}{(X_{\text{CO}})(X_{\text{O}_2})^{\frac{1}{2}}}$$

where $K_{X_1} = 8.26 \times 10^{-3}$, $K_{X_2} = 0.7$, and X_i is the mole fraction of species i (assuming ideal gas behavior). Calculate the equilibrium composition.

■ Answer

Assume a basis of 1 mol of CO with a stoichiometric amount of air (ξ_1 and ξ_2 are the number of moles of N_2 and CO reacted, respectively):

Species	Initial	At equilibrium
N ₂	1.88	1.88 - ξ_1
O ₂	0.5	0.5 - $\frac{1}{2}\xi_2 - \xi_1$
CO	1	1 - ξ_2
CO ₂	0	ξ_2
NO	0	$2\xi_1$
total	3.38	3.38 - $\frac{1}{2}\xi_2$

$$K_{x_1} = \frac{(2\xi_1)^2}{(1.88 - \xi_1)(0.5 - \frac{1}{2}\xi_2 - \xi_1)} = 8.26 \times 10^{-3}$$

$$K_{x_2} = \frac{(\xi_2)(3.38 - \frac{1}{2}\xi_2)^{\frac{1}{2}}}{(1 - \xi_2)(0.5 - \frac{1}{2}\xi_2 - \xi_1)^{\frac{1}{2}}} = 0.7$$

The simultaneous solution of these two equations gives:

$$\xi_1 = 0.037, \quad \xi_2 = 0.190$$

Therefore,

Species	Mole fraction at equilibrium
N ₂	0.561
O ₂	0.112
CO	0.247
CO ₂	0.058
NO	0.022
	1.000

EXAMPLE 1.2.4

Using the results from Example 1.2.3, calculate the two equilibrium extents of reaction.

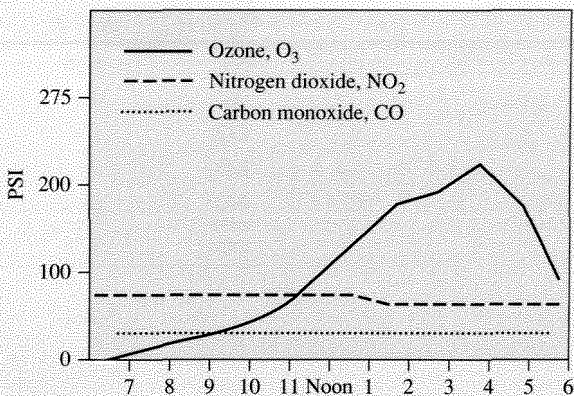
■ **Answer**

$$\Phi_1^{\text{eq}} = \xi_1^{\text{eq}} = 0.037$$

$$\Phi_2^{\text{eq}} = \xi_2^{\text{eq}} = 0.190$$

VIGNETTE 1.2.1

Below is shown the pollution standard index (PSI) for Pasadena, California, in July 1995 from 7 A.M. until 6 P.M.:



On these scales, 100 is the Federal standard and values above this are unhealthy. Notice that the ozone somewhat follows the intensity of the sunlight. That is because ozone is formed by numerous reactions that involve sunlight, for example,



where *TB* represents N₂, O₂ or another third body that absorbs the excess vibrational energy and thereby stabilizes the O₃ formed. One major source of NO₂ is exhaust from vehicles. NO_x formation occurs when N₂ and O₂ are raised to a high temperature (see Example 1.2.3) via the reactions:



and is called thermal NO_x. Additionally, fuels possess nitrogen-containing compounds like porphyrins that when combusted in an engine also give NO_x (called fuel NO_x). Since NO_x and O₃ are health hazards, much effort has been extended to develop catalytic converters for automobiles. The main function of the catalytic converter is to accomplish the following reactions:



Catalytic converters (see Figure 1.2.1) contain metal catalysts (Pd, Pt, Rh) that carry out the above reactions and thus significantly reduce pollution. These catalysts have been in use since 1980 and have dramatically aided the reduction of air pollution in Los Angeles and elsewhere. For example, in the 1970s the PSI in Pasadena showed levels over 400 on really smoggy days. In the 1990s, these levels never occurred. Thus, catalytic converters

significantly contributed to pollution reduction and are one of the major success stories for chemical reaction engineering.

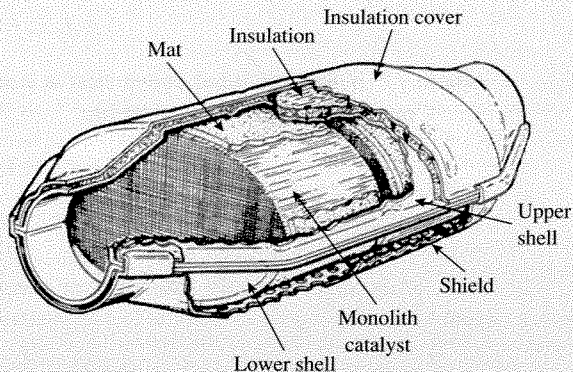


Figure 1.2.1 | Ceramic monolith catalytic converter.
Adapted with permission from K. C. Taylor, *CHEMTECH*,
20 (1990) 551. Copyright 1990 American Chemical Society.

The drawback of Φ is that it is an extensive variable, that is, it is dependent upon the mass of the system. The *fractional conversion*, f , does not suffer from this problem and can be related to Φ . In general, reactants are not initially present in stoichiometric amounts and the reactant in the least amount determines the maximum value for the extent of reaction, Φ_{\max} . This component, called the *limiting component* (subscript ℓ) can be totally consumed when Φ reaches Φ_{\max} . Thus,

$$0 = n_{\ell}^0 + \nu_{\ell}\Phi_{\max} \quad (1.2.8)$$

The fractional conversion is defined as:

$$f(t) = \frac{\Phi(t)}{\Phi_{\max}} \quad (1.2.9)$$

and can be calculated from Equations (1.2.3) and (1.2.8):

$$f_{\ell} = (-\nu_{\ell}) \frac{\Phi}{n_{\ell}^0} = 1 - \frac{n_{\ell}}{n_{\ell}^0} \quad (1.2.10)$$

Equation (1.2.10) can be rearranged to give:

$$n_{\ell} = n_{\ell}^0(1 - f_{\ell}) \quad (1.2.11)$$

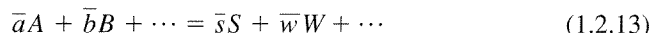
where $0 \leq f_{\ell} \leq 1$. When the thermodynamics of the system limit Φ such that it cannot reach Φ_{\max} (where $n_{\ell} = 0$), Φ will approach its equilibrium value Φ^{eq} ($n_{\ell} \neq 0$ value of n_{ℓ} determined by the equilibrium constant). When a reaction is limited by thermodynamic equilibrium in this fashion, the reaction has historically been called

reversible. Alternatively, the reaction can be denoted as *two-way*. When Φ^{eq} is equal to Φ_{max} for all practical purposes, the reaction has been denoted *irreversible* or *one-way*. Thus, when writing the fractional conversion for the limiting reactant,

$$0 \leq f_{\ell} \leq f_{\ell}^{\text{eq}} \leq 1 \quad (1.2.12)$$

where f_{ℓ}^{eq} is the fractional conversion at equilibrium conditions.

Consider the following reaction:



Expressions for the change in the number of moles of each species can be written in terms of the fractional conversion and they are [assume A is the limiting reactant, lump all inert species together as component I and refer to Equations (1.2.6) and (1.2.11)]:

$$\begin{aligned} n_A &= n_A^0 - n_A^0 f_A \\ n_B &= n_B^0 - \left(\frac{\bar{b}}{\bar{a}}\right) n_A^0 f_A \\ &\vdots \\ n_S &= n_S^0 + \left(\frac{\bar{s}}{\bar{a}}\right) n_A^0 f_A \\ n_W &= n_W^0 + \left(\frac{\bar{w}}{\bar{a}}\right) n_A^0 f_A \\ &\vdots \\ n_I &= n_I^0 \quad (\text{inerts}) \\ n_{\text{TOTAL}} &= n_{\text{TOTAL}}^0 + n_A^0 \left[\frac{\bar{s} + \bar{w} + \cdots - \bar{a} - \bar{b} \cdots}{\bar{a}} \right] f_A \end{aligned}$$

or

$$\frac{n_{\text{TOTAL}}}{n_{\text{TOTAL}}^0} = 1 + \frac{n_A^0}{n_{\text{TOTAL}}^0} \left[\frac{\bar{s} + \bar{w} + \cdots - \bar{a} - \bar{b} \cdots}{\bar{a}} \right] f_A \quad (1.2.14)$$

By defining ε_A as the *molar expansion factor*, Equation (1.2.14) can be written as:

$$n_{\text{TOTAL}} = n_{\text{TOTAL}}^0 (1 + \varepsilon_A f_A) \quad (1.2.15)$$

where

$$\varepsilon_A = \frac{n_A^0}{n_{\text{TOTAL}}^0} \left[\frac{\sum_i v_i}{|v_A|} \right] = X_A^0 \left[\frac{\sum_i v_i}{|v_A|} \right] \quad (1.2.16)$$

Notice that ε_A contains two terms and they involve stoichiometry and the initial mole fraction of the limiting reactant. The parameter ε_A becomes important if the density of the reacting system is changing as the reaction proceeds.

EXAMPLE 1.2.5


Calculate ε_A for the following reactions:

- (i) n-butane = isobutane (isomerization)
- (ii) n-hexane \Rightarrow benzene + dihydrogen (aromatization)
- (iii) reaction (ii) where 50 percent of the feed is dinitrogen.


■ Answer

- (i) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 = \text{CH}_3\text{CH}(\text{CH}_3)_2$, pure n-butane feed

$$\varepsilon_A = \frac{n_{\text{TOTAL}}^0}{n_{\text{TOTAL}}^0} \left[\frac{1 - 1}{|-1|} \right] = 0$$

- (ii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \Rightarrow$  + 4H₂, pure n-hexane feed

$$\varepsilon_A = \frac{n_{\text{TOTAL}}^0}{n_{\text{TOTAL}}^0} \left[\frac{4 + 1 - 1}{|-1|} \right] = 4$$

- (iii) $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \Rightarrow$  + 4H₂, 50 percent of feed is n-hexane

$$\varepsilon_A = \frac{0.5n_{\text{TOTAL}}^0}{n_{\text{TOTAL}}^0} \left[\frac{4 + 1 - 1}{|-1|} \right] = 2$$

EXAMPLE 1.2.6

If the decomposition of N₂O₅ into N₂O₄ and O₂ were to proceed to completion in a closed volume of size V , what would the pressure rise be if the starting composition is 50 percent N₂O₅ and 50 percent N₂?

■ Answer

The ideal gas law is:

$$PV = n_{\text{TOTAL}}R_gT \quad (R_g : \text{universal gas constant})$$

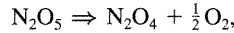
At fixed T and V , the ideal gas law gives:

$$P = P^0 \left(\frac{n_{\text{TOTAL}}}{n_{\text{TOTAL}}^0} \right) = P^0(1 + \varepsilon_A f_A)$$

The reaction proceeds to completion so $f_A = 1$ at the end of the reaction. Thus,

$$\frac{P}{P^0} = 1 + \varepsilon_A, \quad A : \text{N}_2\text{O}_5$$

with



$$\varepsilon_A = \frac{0.5n_{\text{TOTAL}}^0}{n_{\text{TOTAL}}^0} \left[\frac{1 + 0.5 - 1}{|-1|} \right] = 0.25$$

Therefore,

$$\frac{P}{P^0} = 1.25$$

1.3 | The Rate of Reaction

For a homogeneous, closed system at uniform pressure, temperature, and composition in which a single chemical reaction occurs and is represented by the stoichiometric Equation (1.2.1), the extent of reaction as given in Equation (1.2.3) increases with time, t . For this situation, the *reaction rate* is defined in the most general way by:

$$\frac{d\Phi}{dt} \left(\frac{\text{mol}}{\text{time}} \right) \quad (1.3.1)$$

This expression is either positive or equal to zero if the system has reached equilibrium. The reaction rate, like Φ , is an extensive property of the system. A specific rate called the *volumic rate* is obtained by dividing the reaction rate by the volume of the system, V :

$$r = \frac{1}{V} \frac{d\Phi}{dt} \left(\frac{\text{mol}}{\text{time} \cdot \text{volume}} \right) \quad (1.3.2)$$

Differentiation of Equation (1.2.3) gives:

$$dn_i = v_i d\Phi \quad (1.3.3)$$

Substitution of Equation (1.3.3) into Equation (1.3.2) yields:

$$r = \frac{1}{v_i V} \frac{dn_i}{dt} \quad (1.3.4)$$

since v_i is not a function of time. Note that the volumic rate as defined is an extensive variable and that the definition is not dependent on a particular reactant or product. If the volumic rate is defined for an individual species, r_i , then:

$$r_i = v_i r = \frac{1}{V} \frac{dn_i}{dt} \quad (1.3.5)$$

Since v_i is positive for products and negative for reactants and the reaction rate, $d\Phi/dt$, is always positive or zero, the various r_i will have the same sign as the v_i (dn_i/dt has the same sign as r_i since r is always positive). Often the use of molar concentrations, C_i , is desired. Since $C_i = n_i/V$, Equation (1.3.4) can be written as:

$$r = \frac{1}{v_i V} \frac{d}{dt} (C_i V) = \frac{1}{v_i} \frac{dC_i}{dt} + \frac{C_i}{v_i V} \frac{dV}{dt} \quad (1.3.6)$$

Note that only when the volume of the system is constant that the volumic rate can be written as:

$$r = \frac{1}{v_i} \frac{dC_i}{dt}, \text{ constant } V \quad (1.3.7)$$

When it is not possible to write a stoichiometric equation for the reaction, the rate is normally expressed as:

$$r = \frac{(\text{COEF})}{V} \frac{dn_i}{dt}, (\text{COEF}) = \begin{cases} -, & \text{reactant} \\ +, & \text{product} \end{cases} \quad (1.3.8)$$

For example, with certain polymerization reactions for which no unique stoichiometric equation can be written, the rate can be expressed by:

$$r = \frac{-1}{V} \frac{dn}{dt}$$

where n is the number of moles of the monomer.

Thus far, the discussion of reaction rate has been confined to *homogeneous* reactions taking place in a closed system of uniform composition, temperature, and pressure. However, many reactions are *heterogeneous*; they occur at the interface between phases, for example, the interface between two fluid phases (gas-liquid, liquid-liquid), the interface between a fluid and solid phase, and the interface between two solid phases. In order to obtain a convenient, specific rate of reaction it is necessary to normalize the reaction rate by the interfacial surface area available for the reaction. The interfacial area must be of uniform composition, temperature, and pressure. Frequently, the interfacial area is not known and alternative definitions of the specific rate are useful. Some examples of these types of rates are:

$$r = \frac{1}{gm} \frac{d\Phi}{dt} \left(\frac{\text{mol}}{\text{mass} \cdot \text{time}} \right) \quad (\text{specific rate})$$

$$r = \frac{1}{SA} \frac{d\Phi}{dt} \left(\frac{\text{mol}}{\text{area} \cdot \text{time}} \right) \quad (\text{areal rate})$$

where gm and SA are the mass and surface area of a solid phase (catalyst), respectively. Of course, alternative definitions for specific rates of both homogeneous and heterogeneous reactions are conceivable. For example, numerous rates can be defined

for enzymatic reactions, and the choice of the definition of the specific rate is usually adapted to the particular situation.

For heterogeneous reactions involving fluid and solid phases, the areal rate is a good choice. However, the catalysts (solid phase) can have the same surface area but different concentrations of active sites (atomic configuration on the catalyst capable of catalyzing the reaction). Thus, a definition of the rate based on the number of active sites appears to be the best choice. The *turnover frequency* or *rate of turnover* is the number of times the catalytic cycle is completed (or turned-over) per catalytic site (active site) per time for a reaction at a given temperature, pressure, reactant ratio, and extent of reaction. Thus, the turnover frequency is:

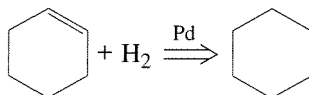
$$r_t = \frac{1}{\bar{S}} \frac{dn}{dt} \quad (1.3.9)$$

where \bar{S} is the number of active sites on the catalyst. The problem of the use of r_t is how to count the number of active sites. With metal catalysts, the number of metal atoms exposed to the reaction environment can be determined via techniques such as chemisorption. However, how many of the surface atoms that are grouped into an active site remains difficult to ascertain. Additionally, different types of active sites probably always exist on a real working catalyst; each has a different reaction rate. Thus, r_t is likely to be an average value of the catalytic activity and a lower bound for the true activity since only a fraction of surface atoms may contribute to the activity. Additionally, r_t is a rate and *not* a rate constant so it is always necessary to specify all conditions of the reaction when reporting values of r_t .

The number of turnovers a catalyst makes before it is no longer useful (e.g., due to an induction period or poisoning) is the best definition of the life of the catalyst. In practice, the turnovers can be very high, $\sim 10^6$ or more. The turnover frequency on the other hand is commonly in the range of $r_t = 1 \text{ s}^{-1}$ to $r_t = 0.01 \text{ s}^{-1}$ for practical applications. Values much smaller than these give rates too slow for practical use while higher values give rates so large that they become influenced by transport phenomena (see Chapter 6).

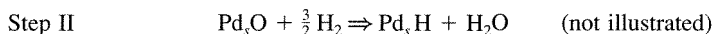
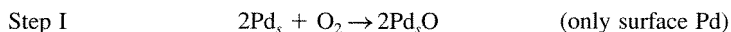
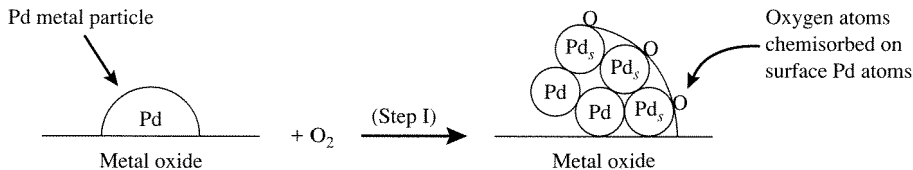
EXAMPLE 1.3.1

Gonzo and Boudart [*J. Catal.*, **52** (1978) 462] studied the hydrogenation of cyclohexene over Pd supported on Al_2O_3 and SiO_2 at 308 K, atmospheric pressure of dihydrogen and 0.24M cyclohexene in cyclohexane in a stirred flask:



The specific rates for 4.88 wt. % Pd on Al_2O_3 and 3.75 wt. % Pd on SiO_2 were 7.66×10^{-4} and $1.26 \times 10^{-3} \text{ mol}/(\text{gcat} \cdot \text{s})$, respectively. Using a technique called *titration*, the percentage of Pd metal atoms on the surface of the Pd metal particles on the Al_2O_3 and SiO_2 was 21 percent and 55 percent, respectively. Since the specific rates for Pd on Al_2O_3 and SiO_2 are different, does the metal oxide really influence the reaction rate?

Titration is a technique that can be used to measure the number of surface metal atoms. The procedure involves first chemisorbing (chemical bonds formed between adsorbing species and surface atoms) molecules onto the metal atoms exposed to the reaction environment. Second, the chemisorbed species are reacted with a second component in order to recover and count the number of atoms chemisorbed. By knowing the stoichiometry of these two steps, the number of surface atoms can be calculated from the amount of the recovered chemisorbed atoms. The technique is illustrated for the problem at hand:



By counting the number of H_2 molecules consumed in Step II, the number of surface Pd atoms (Pd_s) can be ascertained. Thus, the percentage of Pd atoms on the surface can be calculated since the total number of Pd atoms is known from the mass of Pd.

■ Answer

The best way to determine if the reaction rates are really different for these two catalysts is to compare their values of the turnover frequency. Assume that each surface Pd atom is an active site. Thus, to convert a specific rate to a turnover frequency:

$$r_t (s^{-1}) = r \left(\frac{\text{mol}}{\text{gcat} \cdot \text{s}} \right) \cdot \left(\frac{\text{gcat}}{\text{mass metal}} \right) \cdot \left(\frac{\text{molecular weight of metal}}{\text{fraction of surface atoms}} \right)$$

$$r_{t_{\text{Pd}/\text{Al}_2\text{O}_3}} = (7.66 \times 10^{-4}) \cdot \left(\frac{1}{0.0488} \right) (106.4) (0.21)^{-1}$$

$$r_{t_{\text{Pd}/\text{Al}_2\text{O}_3}} = 8.0 s^{-1}$$

Likewise for Pd on SiO_2 ,

$$r_{t_{\text{Pd}/\text{SiO}_2}} = 6.5 s^{-1}$$

Since the turnover frequencies are approximately the same for these two catalysts, the metal oxide support does not appear to influence the reaction rate.

1.4 | General Properties of the Rate Function for a Single Reaction

The rate of reaction is generally a function of temperature and composition, and the development of mathematical models to describe the form of the reaction rate is a central problem of applied chemical kinetics. Once the reaction rate is known,

information can often be derived for rates of individual steps, and reactors can be designed for carrying out the reaction at optimum conditions.

Below are listed general rules on the form of the reaction rate function (M. Boudart, *Kinetics of Chemical Processes*, Butterworth-Heinemann, 1991, pp. 13–16). The rules are of an approximate nature but are sufficiently general that exceptions to them usually reveal something of interest. It must be stressed that the utility of these rules is their applicability to many single reactions.

Rule 1

The rate function, r , at constant temperature generally decreases in a monotonic fashion with the extent of reaction (see Figure 1.4.1).

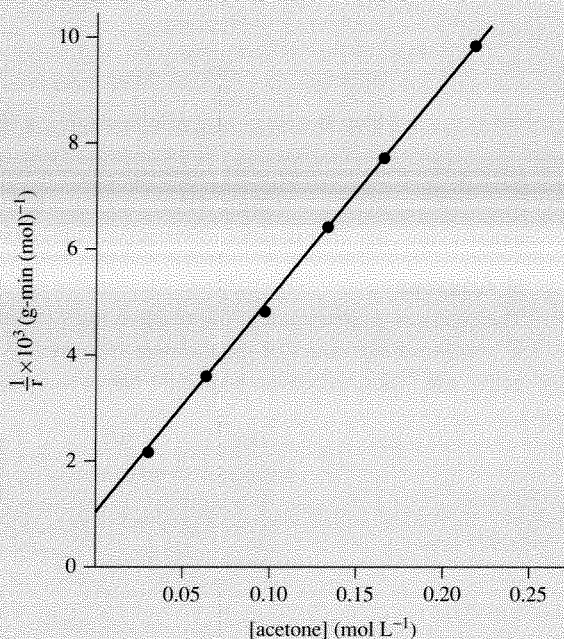
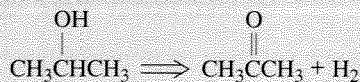


Figure 1.4.1 | The rate function r decreases with concentration of acetone [a measure of the extent of reaction: Equation (1.2.4)]. Adapted from D. E. Mears and M. Boudart, *AIChE J.* **12** (1966) 313, with permission of the American Institute of Chemical Engineers. Copyright © 1966 AIChE. All rights reserved. The rate data are from the following reaction that occurs in the gas-phase with a nickel catalyst:



Rule II

The rate of an irreversible (one-way) reaction can generally be written in the form:

$$r = k(T)\bar{F}(C_i, T) \quad (1.4.1)$$

where $\bar{F}(C_i, T)$ is a function that depends on the composition of the system as expressed by the concentrations C_i .

The coefficient k does not depend on the composition of the system or time. For this reason, k is called the *rate constant*. If \bar{F} is not a function of the temperature,

$$r = k(T)\bar{F}(C_i)$$

then the reaction rate is called *separable* since the temperature and composition dependencies are separated in k and \bar{F} , respectively.

Rule III

The rate constant generally depends on the absolute temperature, T , following the law first proposed by Arrhenius in 1889:

$$k = \bar{A} \exp\left[-\frac{E}{RT}\right] \quad (1.4.2)$$

In Equation (1.4.2), the *pre-exponential factor*, \bar{A} , does not depend appreciably on temperature, and E is called the *activation energy*. Figure 1.4.2 is an example of a typical Arrhenius plot.

Rule IV

Frequently, the function $\bar{F}(C_i)$ in the expression $r = k\bar{F}(C_i)$ can approximately be written as:

$$\bar{F}(C_i) = \prod_i C_i^{\alpha_i}$$

The product \prod is taken over all components of the system. The exponents α_i are small integers or fractions that are positive, negative, or zero and are temperature independent at least over a restricted interval (see Table 1.4.1 for an example).

Consider the general reaction:



If the reaction rate follows Rule IV then it can be written as:

$$r = kC_A^{\alpha_A}C_B^{\alpha_B}$$

The exponent α_i is called the *order of reaction* with respect to the corresponding component of the system and the sum of the exponents is called the *total order of*

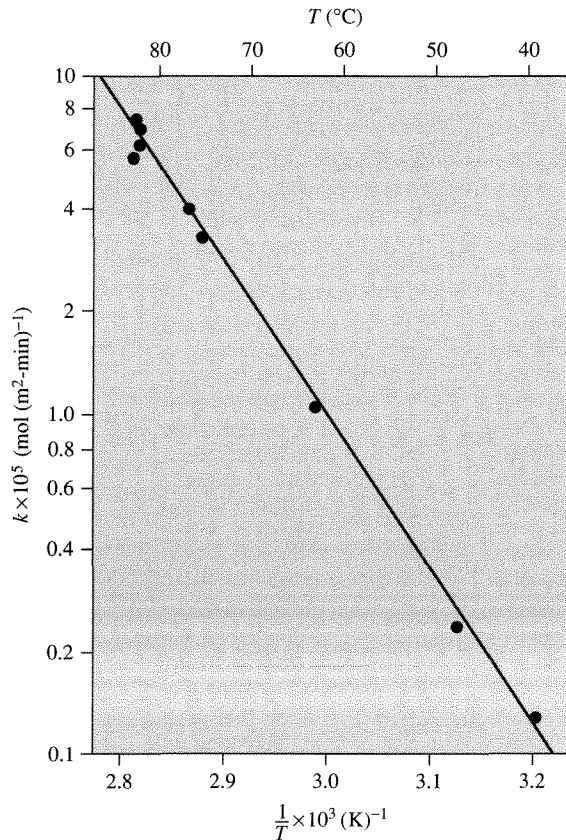


Figure 1.4.2 |

A typical Arrhenius plot, $\ln k$ vs $1/T$. The slope corresponds to $-E/R_g$. Adapted from D. E. Mears and M. Boudart, *AIChE J.* **12** (1966) 313, with permission of the American Institute of Chemical Engineers. Copyright © 1966 AIChE. All rights reserved.

the reaction. In general $\alpha_i \neq |v_i|$ and is rarely larger than two in absolute value. If $\alpha_i = |v_i|$ for reactants and equal to zero for all other components of the system, the expression:

$$\bar{F}(C_i) = \prod_i C_i^{|v_i|} \quad (\text{for reactants only})$$

would be of the form first suggested by Guldberg and Waage (1867) in their Law of Mass Action. Thus, a rate function of the form:

$$r = k \prod_i C_i^{\alpha_i} \quad (1.4.4)$$

Table 1.4.1 | Kinetic parameters for the simultaneous hydroformylation¹ and hydrogenation² of propene over a rhodium zeolite catalyst at $T = 423$ K and 1 atm total pressure [from Rode et al., *J. Catal.*, **96** (1985) 563].

$$\text{Rate} \left(\frac{\text{mol}}{\text{gRh} \cdot \text{hr}} \right) = \bar{A} \exp \left[\frac{-E}{(R_g T)} \right] P_{C_3}^{\alpha_1} P_{H_2}^{\alpha_2} P_{CO}^{\alpha_3}$$

	$(C_3H_8)^1$	$(i-C_4H_8O)^2$	$(n-C_4H_8O)^2$
\bar{A}	4.12×10^6	1.36×10^3	1.86×10^3
E (kcal/mol), (393–423 K)	15.8	11.0	10.8
α_1	1.01	1.00	0.97
α_2	0.35	0.40	0.48
α_3	-0.71	-0.70	-0.72

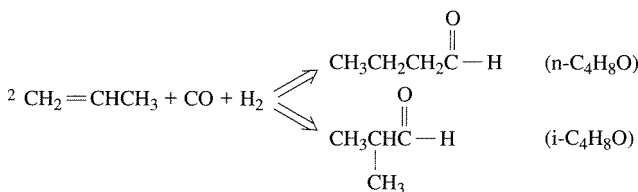
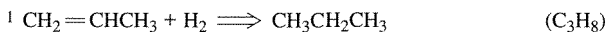


Table 1.4.2¹ | Examples of rate functions of the type: $r = k \prod_i C_i^{\alpha_i}$.

Reaction	Rate function
$\text{CH}_3\text{CHO} \Rightarrow \text{CH}_4 + \text{CO}$	$k(\text{CH}_3\text{CHO})^{1.5}$
$\text{C}_2\text{H}_6 + \text{H}_2 \Rightarrow 2\text{CH}_4$ (catalytic)	$k(\text{C}_2\text{H}_6)^{0.9} (\text{H}_2)^{-0.7}$
$\text{SbH}_3 \Rightarrow \text{Sb} + \frac{3}{2} \text{H}_2$	$k(\text{SbH}_3)^{0.6}$
$\text{N}_2 + 3\text{H}_2 \Rightarrow 2\text{NH}_3$ (catalytic)	$k(\text{N}_2)(\text{H}_2)^{2.25} (\text{NH}_3)^{-1.5}$

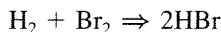
¹From M. Boudart, *Kinetics of Chemical Processes*, Butterworth-Heinemann, 1991, p. 17.

which is normally referred to as “pseudo mass action” or “power law” is really the Guldberg-Waage form only when $\alpha_i = |v_i|$ for reactants and zero for all other components (note that orders may be negative for catalytic reactions, as will be discussed in a later chapter). For the reaction described by Equation (1.4.3), the Guldberg-Waage rate expression is:

$$r = k C_A^{\bar{\alpha}} C_B^{\bar{\beta}}$$

Examples of power law rate expressions are shown in Table 1.4.2.

For elementary steps, $\alpha_i = |v_i|$. Consider again the gas-phase reaction:



If this reaction would occur by H_2 interacting directly with Br_2 to yield two molecules of HBr , the step would be elementary and the rate could be written as:

$$r = k C_{\text{H}_2} C_{\text{Br}_2}$$

However, it is known that this is not how the reaction proceeds (Section 1.1) and the real rate expression is:

$$r = \frac{k_1 C_{\text{H}_2} C_{\text{Br}_2}^{1/2}}{k_2 + \frac{C_{\text{HBr}}}{C_{\text{Br}_2}}}$$

For elementary steps the number of molecules that participate in the reaction is called the molecularity of the reaction (see Table 1.4.3).

Rule V

When a reaction is two-way (or reversible), its rate can generally be expressed as the difference between a rate in the forward direction r_+ and in the reverse direction r_-

$$r = r_+ - r_- \quad (1.4.5)$$

When Rule II applies to the rate functions r_+ and r_- so that:

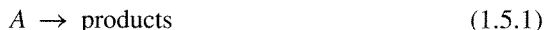
$$\begin{aligned} r_+ &= k_+ \bar{F}_+(C_i) \\ r_- &= k_- \bar{F}_-(C_i) \end{aligned}$$

both rate constants k_+ and k_- are related to the equilibrium constant, K_C . For example, the reaction $A \rightleftharpoons B$ at ideal conditions gives (see Chapter 5 for a more rigorous explanation of the relationships between rates and equilibrium expressions):

$$K_C = \frac{k_+}{k_-} \quad (1.4.6)$$

1.5 | Examples of Reaction Rates

Consider the unimolecular reaction:



Using the Guldberg-Waage form of the reaction rate to describe this reaction gives:

$$r = kC_A \quad (1.5.2)$$

From Equations (1.3.4) and (1.5.2):

$$r = \frac{1}{\nu_i V} \frac{dn_i}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = kC_A$$

or

$$\frac{dn_A}{dt} = -kn_A \quad (\text{variable } V) \quad (1.5.3)$$

$$\frac{df_A}{dt} = k(1 - f_A) \quad [\text{using Equation (1.2.11)}] \quad (1.5.4)$$

Table 1.4.3 | Molecularity and rates of elementary steps.

Molecularity	Number of reactant molecules	General description	Example (1)	Rate constant (1)
Unimolecular	1	$A \rightarrow$ products	$N_2O_5 \rightarrow NO_2 + NO_3$	$1.96 \times 10^{14} \exp[-10660/T], s^{-1}$
Bimolecular	2	$2A \rightarrow$ products $A + B \rightarrow$ products	— $NO + NO_3 \rightarrow 2NO_2$	— $2.0 \times 10^{11}, cm^3/s/molecule (2)$
Trimolecular (rare)	3	$3A \rightarrow$ products $2A + B \rightarrow$ products $A + B + C \rightarrow$ products	— $2NO + O_2 \rightarrow 2NO_2$ $NO + NO_2 + H_2O \rightarrow 2HNO_2$	— $3.3 \times 10^{-39} \exp(530/T), cm^6/s/molecule^2 (2)$ $\leq 4.4 \times 10^{-40}, cm^6/s/molecule^2 (2)$

(1) From J. H. Seinfeld, *Atmospheric Chemistry and Physics of Air Pollution*, Wiley, 1986, p. 175.

(2) Concentrations are in molecules/cm³.

Table 1.5.1 | Examples of reactions that can be described using first-order reaction rates.

Reactions	Examples
Isomerizations	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \rightleftharpoons \text{CH}_3-\overset{\text{CH}_2}{\underset{\text{ }}{\text{C}}}-\text{CH}_3$
Decompositions	$\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_2 + \text{NO}_3$ $\text{CH}_2-\overset{\text{O}}{\underset{\text{ }}{\text{C}}}-\text{CH}_2 \rightleftharpoons \text{CH}_4 + \text{CO}$
Radioactive decay (each decay can be described by a first-order reaction rate)	$^{135}\text{I} \xrightarrow{-\beta} ^{135}\text{Xe} \xrightarrow{-\beta} ^{135}\text{Cs} \xrightarrow{-\beta} ^{135}\text{Ba}(\text{stable})$

$$\frac{dC_A}{dt} = -kC_A \quad (\text{constant } V) \quad (1.5.5)$$

$$\frac{dP_A}{dt} = -kP_A \quad [\text{constant } V: C_i = P_i/(R_g T)] \quad (1.5.6)$$

Thus, for first-order systems, the rate, r , is proportional (via k) to the amount present, n_i , in the system at any particular time. Although at first glance, first-order reaction rates may appear too simple to describe real reactions, such is not the case (see Table 1.5.1). Additionally, first-order processes are many times used to approximate complex systems, for example, lumping groups of hydrocarbons into a generic hypothetical component so that phenomenological behavior can be described.

In this text, concentrations will be written in either of two notations. The notations C_i and $[A_i]$ are equivalent in terms of representing the concentration of species i or A_i , respectively. These notations are used widely and the reader should become comfortable with both.

EXAMPLE 1.5.1

The natural abundance of ^{235}U in uranium is 0.79 atom %. If a sample of uranium is enriched to 3 at. % and then is stored in salt mines under the ground, how long will it take the sample to reach the natural abundance level of ^{235}U (assuming no other processes form ^{235}U ; this is not the case if ^{238}U is present since it can decay to form ^{235}U)? The half-life of ^{235}U is 7.13×10^8 years.

■ Answer

Radioactive decay can be described as a first-order process. Thus, for any first-order decay process, the amount of material present declines in an exponential fashion with time. This is easy to see by integrating Equation (1.5.3) to give:

$$n_i = n_i^0 \exp(-kt), \quad \text{where } n_i^0 \text{ is the amount of } n_i \text{ present at } t = 0.$$

The *half-life*, $t_{\frac{1}{2}}$, is defined as the time necessary to reduce the amount of material in half. For a first-order process $t_{\frac{1}{2}}$ can be obtained as follows:

$$\frac{1}{2} n_i^0 = n_i^0 \exp(-kt_{\frac{1}{2}})$$

or

$$t_{\frac{1}{2}} = \frac{\ln(2)}{k}$$

Given $t_{\frac{1}{2}}$, a value of k can be calculated. Thus, for the radioactive decay of ^{235}U , the first-order rate constant is:

$$k = \frac{\ln(2)}{t_{\frac{1}{2}}} = 9.7 \times 10^{-10} \text{ years}^{-1}$$

To calculate the time required to have 3 at. % ^{235}U decay to 0.79 at. %, the first-order expression:

$$\frac{n_i}{n_i^0} = \exp(-kt) \quad \text{or} \quad t = \frac{\ln\left(\frac{n_i^0}{n_i}\right)}{k}$$

can be used. Thus,

$$t = \frac{\ln\left(\frac{3}{0.79}\right)}{9.7 \times 10^{-10}} = 1.4 \times 10^9 \text{ years}$$

or a very long time.

EXAMPLE 1.5.2

N_2O_5 decomposes into NO_2 and NO_3 with a rate constant of $1.96 \times 10^{14} \exp[-10,660/T] \text{ s}^{-1}$. At $t = 0$, pure N_2O_5 is admitted into a constant temperature and volume reactor with an initial pressure of 2 atm. After 1 min, what is the total pressure of the reactor? $T = 273 \text{ K}$.

■ Answer

Let n be the number of moles of N_2O_5 such that:

$$\frac{dn}{dt} = -kn$$

Since $n = n^0(1 - f)$:

$$\frac{df}{dt} = k(1 - f), f = 0 @ t = 0$$

Integration of this first-order, initial-value problem yields:

$$\ln\left(\frac{1}{1 - f}\right) = kt \quad \text{for } t \geq 0$$

or

$$f = 1 - \exp(-kt) \quad \text{for } t \geq 0$$

At 273 K, $k = 2.16 \times 10^{-3} \text{ s}^{-1}$. After reaction for 1 min:

$$f = 1 - \exp[-(60)(2.16 \times 10^{-3})] = 0.12$$

From the ideal gas law at constant T and V :

$$\frac{P}{P^0} = \frac{n}{n^0} = \frac{n^0(1 + \varepsilon f)}{n^0}$$

For this decomposition reaction:

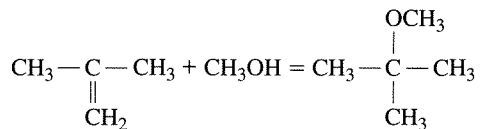
$$\varepsilon_{\text{N}_2\text{O}_5} = 1.0 \left[\frac{2 - 1}{|-1|} \right] = 1$$

Thus,

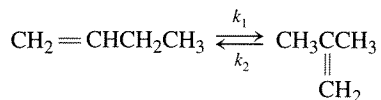
$$P = P^0(1 + f) = 2(1 + 0.12) = 2.24 \text{ atm}$$

EXAMPLE 1.5.3

Often isomerization reactions are highly two-way (reversible). For example, the isomerization of 1-butene to isobutene is an important step in the production of methyl tertiary butyl ether (MTBE), a common oxygenated additive in gasoline used to lower emissions. MTBE is produced by reacting isobutene with methanol:



In order to make isobutene, n-butane (an abundant, cheap C_4 hydrocarbon) can be dehydrogenated to 1-butene then isomerized to isobutene. Derive an expression for the concentration of isobutene formed as a function of time by the isomerization of 1-butene:



■ Answer

Let isobutene be denoted as component I and 1-butene as B . If the system is at constant T and V , then:

$$\frac{dC_B}{dt} = -k_1 C_B + k_2 C_I \quad \text{or} \quad \frac{d[B]}{dt} = -k_1 [B] + k_2 [I]$$

Since $[B] = [B]^0(1 - f_B)$:

$$[I] = [I]^0 + [B]^0 f_B = [B]^0 (\bar{M} + f_B), \quad \bar{M} = [I]^0 / [B]^0 \neq 0$$

Thus,

$$\frac{df_B}{dt} = k_1(1 - f_B) - k_2(\bar{M} + f_B)$$

At equilibrium $\frac{df_B}{dt} = 0$, so:

$$K_C = \frac{k_1}{k_2} = \frac{[I]^{\text{eq}}}{[B]^{\text{eq}}} = \frac{[B]^0(\bar{M} + f_B^{\text{eq}})}{[B]^0(1 - f_B^{\text{eq}})}$$

Insertion of the equilibrium relationship into the rate expression yields:

$$\frac{df_B}{dt} = k_1(1 - f_B) - k_1(1 - f_B^{\text{eq}}) \left[\frac{\bar{M} + f_B}{\bar{M} + f_B^{\text{eq}}} \right]$$

or after rearrangement:

$$\frac{df_B}{dt} = \frac{k_1(\bar{M} + 1)}{(\bar{M} + f_B^{\text{eq}})} (f_B^{\text{eq}} - f_B), \quad f_B = 0 @ t = 0$$

Integration of this equation gives:

$$\ln \left[\frac{1 - \frac{f_B}{f_B^{\text{eq}}}}{1 - \frac{f_B^{\text{eq}}}{f_B^{\text{eq}}}} \right] = \left[\frac{k_1(\bar{M} + 1)}{\bar{M} + f_B^{\text{eq}}} \right] t, \quad \bar{M} \neq 0$$

or

$$f_B = f_B^{\text{eq}} \left\{ 1 - \exp \left[- \left(\frac{k_1(\bar{M} + 1)}{\bar{M} + f_B^{\text{eq}}} \right) t \right] \right\}$$

Using this expression for f_B :

$$[I] = [B]^0(\bar{M} + f_B)$$

Consider the bimolecular reaction:



Using the Guldberg-Waage form of the reaction rate to describe this reaction gives:

$$r = k C_A C_B \quad (1.5.8)$$

From Equations (1.3.4) and (1.5.8):

$$r = \frac{1}{\nu_i V} \frac{dn_i}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = k C_A C_B$$

or

$$V \frac{dn_A}{dt} = -k n_A n_B \quad (\text{variable } V) \quad (1.5.9)$$

$$\frac{dC_A}{dt} = -k C_A C_B \quad (\text{constant } V) \quad (1.5.10)$$

$$\frac{dP_A}{dt} = -\frac{k}{R_g T} P_A P_B \quad [\text{constant } V: C_i = P_i / (R_g T)] \quad (1.5.11)$$

For second-order kinetic processes, the limiting reactant is always the appropriate species to follow (let species denoted as A be the limiting reactant). Equations (1.5.9–1.5.11) cannot be integrated unless C_B is related to C_A . Clearly, this can be done via Equation (1.2.5) or Equation (1.2.6). Thus,

$$n_B = n_B^0 - (n_A^0 - n_A)$$

or if the volume is constant:

$$C_B = C_B^0 - (C_A^0 - C_A) \quad \text{or} \quad P_B = P_B^0 - (P_A^0 - P_A)$$

If $\bar{M} = \frac{n_B^0}{n_A^0} = \frac{C_B^0}{C_A^0} = \frac{P_B^0}{P_A^0}$ then:

$$\left. \begin{aligned} n_B &= n_A + n_A^0(\bar{M} - 1) \quad (\text{variable } V) \\ C_B &= C_A + C_A^0(\bar{M} - 1) \quad (\text{constant } V) \\ P_B &= P_A + P_A^0(\bar{M} - 1) \quad (\text{constant } V) \end{aligned} \right\} \quad (1.5.12)$$

Inserting Equation (1.5.12) into Equations (1.5.9–1.5.11) gives:

$$V \frac{dn_A}{dt} = -k n_A [n_A + n_A^0(\bar{M} - 1)] \quad (\text{variable } V) \quad (1.5.13)$$

$$\frac{dC_A}{dt} = -k C_A [C_A + C_A^0(\bar{M} - 1)] \quad (\text{constant } V) \quad (1.5.14)$$

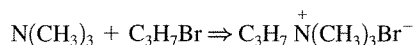
$$\frac{dP_A}{dt} = -\frac{k}{R_g T} P_A [P_A + P_A^0(\bar{M} - 1)] \quad (\text{constant } V) \quad (1.5.15)$$

If V is not constant, then $V = V^0(1 + \varepsilon_A f_A)$ by using Equation (1.2.15) and the ideal gas law. Substitution of this expression into Equation (1.5.13) gives:

$$\frac{df_A}{dt} = \frac{k \left(\frac{n_A^0}{V^0} \right) (1 - f_A) [\bar{M} - f_A]}{(1 + \varepsilon_A f_A)} \quad (1.5.16)$$

EXAMPLE 1.5.4

Equal volumes of 0.2 M trimethylamine and 0.2 M n-propylbromine (both in benzene) were mixed, sealed in glass tubes, and placed into a constant temperature bath at 412 K. After various times, the tubes were removed and quickly cooled to room temperature to stop the reaction:



The quaternization of a tertiary amine gives a quaternary ammonium salt that is not soluble in nonpolar solvents such as benzene. Thus, the salt can easily be filtered from the remaining reactants and the benzene. From the amount of salt collected, the conversion can be calculated and the data are:

Time at 412 K (min)	Conversion (%)
5	4.9
13	11.2
25	20.4
34	25.6
45	31.6
59	36.7
80	45.3
100	50.7
120	55.2

Are these data consistent with a first- or second-order reaction rate?

Answer

The reaction occurs in the liquid phase and the concentrations are dilute. Thus, a good assumption is that the volume of the system is constant. Since $C_A^0 = C_B^0$:

$$\begin{aligned} \text{(first-order)} \quad \ln \left[\frac{1}{1 - f_A} \right] &= kt \\ \text{(second-order)} \quad \frac{f_A}{1 - f_A} &= k C_A^0 t \end{aligned}$$

In order to test the first-order model, the $\ln[1/(1 - f_A)]$ is plotted versus t while for the second-order model, $f_A/(1 - f_A)$ is plotted versus t (see Figures 1.5.1 and 1.5.2). Notice that both models conform to the equation $y = \bar{\alpha}_1 t + \bar{\alpha}_2$. Thus, the data can be fitted via linear

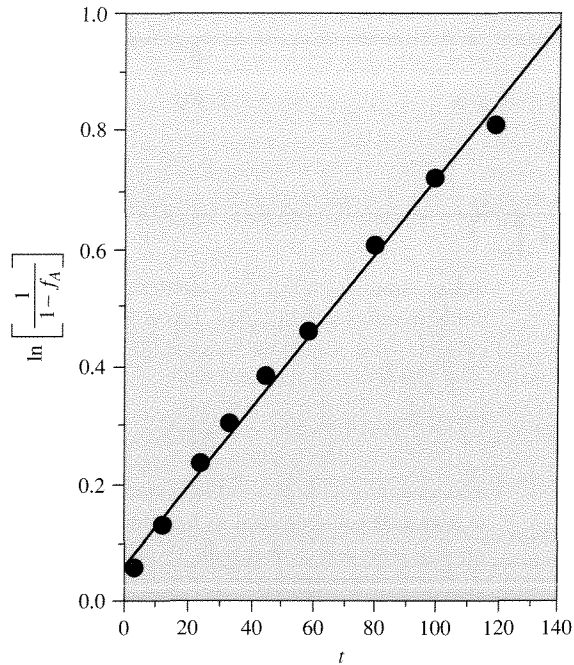


Figure 1.5.1 |
Reaction rate data for first-order kinetic model.

regression to both models (see Appendix B). From visual inspection of Figures 1.5.1 and 1.5.2, the second-order model appears to give a better fit. However, the results from the linear regression are (SE is the standard error):

$$\begin{array}{lll}
 \text{first-order} & \bar{\alpha}_1 = 6.54 \times 10^{-3} & SE(\bar{\alpha}_1) = 2.51 \times 10^{-4} \\
 & \bar{\alpha}_2 = 5.55 \times 10^{-2} & SE(\bar{\alpha}_2) = 1.63 \times 10^{-2} \\
 & \bar{R}_{cc} = 0.995 & \\
 \\
 \text{second-order} & \bar{\alpha}_1 = 1.03 \times 10^{-2} & SE(\bar{\alpha}_1) = 8.81 \times 10^{-5} \\
 & \bar{\alpha}_2 = -5.18 \times 10^{-3} & SE(\bar{\alpha}_2) = 5.74 \times 10^{-3} \\
 & \bar{R}_{cc} = 0.999 &
 \end{array}$$

Both models give high correlation coefficients (\bar{R}_{cc}), and this problem shows how the correlation coefficient may not be useful in determining “goodness of fit.” An appropriate way to determine “goodness of fit” is to see if the models give $\bar{\alpha}_2$ that is not statistically different from zero. This is the reason for manipulating the rate expressions into forms that have zero intercepts (i.e., a known point from which to check statistical significance). If a student \bar{t}^* -test is used to test significance (see Appendix B), then:

$$\bar{t}^* = \frac{|\bar{\alpha}_2 - 0|}{SE(\bar{\alpha}_2)}$$

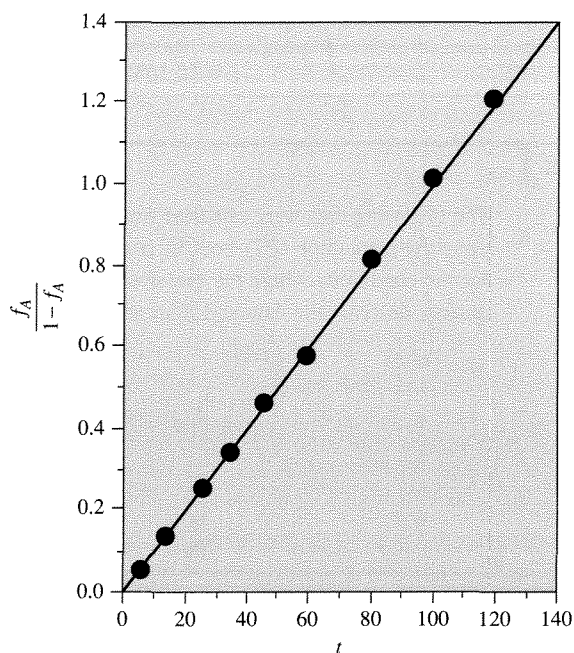


Figure 1.5.2 |
Reaction rate data for second-order kinetic model.

The values of \bar{t}^* for the first- and second-order models are:

$$\bar{t}_1^* = \frac{|5.55 \times 10^{-2} - 0|}{1.63 \times 10^{-2}} = 3.39$$

$$\bar{t}_2^* = \frac{|-5.18 \times 10^{-3} - 0|}{5.74 \times 10^{-3}} = 0.96$$

For 95 percent confidence with 9 data points or 7 degrees of freedom (from table of student \bar{t}^* values):

$$\bar{t}_{\text{exp}}^* = \frac{\text{expected deviation}}{\text{standard error}} = 1.895$$

Since $\bar{t}_1^* > \bar{t}_{\text{exp}}^*$ and $\bar{t}_2^* < \bar{t}_{\text{exp}}^*$, the first-order model is rejected while the second-order model is accepted. Thus,

$$kC_A^0 = 1.030 \times 10^{-2}$$

and

$$k = \frac{1.030 \times 10^{-2}}{0.1 \text{ M}} = 0.1030 \frac{1}{\text{M} \cdot \text{min}}$$

When the standard error is known, it is best to report the value of the correlated parameters:

$$r = [0.1030 \pm 0.0009 \text{ M}^{-1} \text{ min}^{-1}] C_A C_B$$

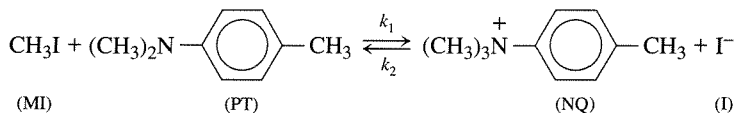
EXAMPLE 1.5.5

The following data were obtained from an initial solution containing methyl iodide (MI) and dimethyl-p-toluidine (PT) both in concentrations of 0.050 mol/L. The equilibrium constant for the conditions where the rate data were collected is 1.43. Do second-order kinetics adequately describe the data and if so what are the rate constants?

Data:

t (min)	Fractional conversion of PT
10	0.18
26	0.34
36	0.40
78	0.52

■ Answer



At constant volume,

$$\begin{aligned}
 \frac{dC_{\text{PT}}}{dt} &= -k_1 C_{\text{PT}} C_{\text{MI}} + k_2 C_{\text{NQ}} C_{\text{I}} \\
 C_{\text{PT}}^0 &= C_{\text{MI}}^0 = 0.05, \quad C_{\text{NQ}}^0 = C_{\text{I}}^0 = 0, \\
 C_{\text{PT}} &= C_{\text{PT}}^0 (1 - f_{\text{PT}}), \quad C_{\text{MI}} = C_{\text{PT}}^0 (1 - f_{\text{PT}}) \\
 C_{\text{NQ}} &= C_{\text{I}} = C_{\text{PT}}^0 f_{\text{PT}}
 \end{aligned}$$

Therefore,

$$\frac{df_{\text{PT}}}{dt} = k_1 C_{\text{PT}}^0 (1 - f_{\text{PT}})^2 - k_2 C_{\text{PT}}^0 f_{\text{PT}}^2$$

At equilibrium,

$$K_C = \frac{k_1}{k_2} = \frac{(f_{\text{PT}}^{\text{eq}})^2}{(1 - f_{\text{PT}}^{\text{eq}})^2}$$

Substitution of the equilibrium expression into the rate expression gives:

$$\frac{df_{\text{PT}}}{dt} = k_1 C_{\text{PT}}^0 (1 - f_{\text{PT}})^2 \left[\left(\frac{1 - f_{\text{PT}}}{1 - f_{\text{PT}}^{\text{eq}}} \right)^2 - \left(\frac{f_{\text{PT}}}{f_{\text{PT}}^{\text{eq}}} \right)^2 \right]$$

Upon integration with $f_{PT} = 0$ at $t = 0$:

$$\ln \left[\frac{f_{PT}^{eq} - (2f_{PT}^{eq} - 1)f_{PT}}{(f_{PT}^{eq} - f_{PT})} \right] = 2k_1 \left[\frac{1}{f_{PT}^{eq}} - 1 \right] C_{PT}^0 t$$

Note that this equation is again in a form that gives a zero intercept. Thus, a plot and linear least squares analysis of:

$$\ln \left[\frac{f_{PT}^{eq} - (2f_{PT}^{eq} - 1)f_{PT}}{(f_{PT}^{eq} - f_{PT})} \right] \text{ versus } t$$

will show if the model can adequately describe the data. To do this, f_{PT}^{eq} is calculated from K_C and it is $f_{PT}^{eq} = 0.545$. Next, from the linear least squares analysis, the model does fit the data and the slope is 0.0415. Thus,

$$0.0415 = 2k_1 \left[\frac{1}{f_{PT}^{eq}} - 1 \right] C_{PT}^0$$

giving $k_1 = 0.50$ L/mol/min. From K_C and k_1 , $k_2 = 0.35$ L/mol/min.

Consider the trimolecular reaction:



Using the Guldberg-Waage form of the reaction rate to describe this reaction gives:

$$r = kC_A C_B C_C \quad (1.5.18)$$

From Equations (1.3.4) and (1.5.18):

$$r = \frac{1}{\nu_i V} \frac{dn_i}{dt} = \frac{-1}{V} \frac{dn_A}{dt} = kC_A C_B C_C$$

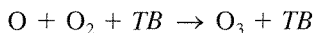
$$V^2 \frac{dn_A}{dt} = -k n_A n_B n_C \quad (\text{variable } V) \quad (1.5.19)$$

$$\frac{dC_A}{dt} = -k C_A C_B C_C \quad (\text{constant } V) \quad (1.5.20)$$

$$\frac{dP_A}{dt} = -\frac{k}{(R_g T)^2} P_A P_B P_C \quad (\text{constant } V) \quad (1.5.21)$$

Trimolecular reactions are very rare. If viewed from the statistics of collisions, the probability of three objects colliding with sufficient energy and in the correct configuration for reaction to occur is very small. Additionally, only a small amount of these collisions would successfully lead to reaction (see Chapter 2, for a detailed discussion). Note the magnitudes of the reaction rates for unimolecular and

bimolecular reactions as compared to trimolecular reactions (see Table 1.4.3). However, trimolecular reactions do occur, for example:



where the third body TB is critical to the success of the reaction since it is necessary for it to absorb energy to complete the reaction (see Vignette 1.2.1).

In order to integrate Equation (1.5.20), C_B and C_C must be related to C_A and this can be done by the use of Equation (1.2.5). Therefore, analysis of a trimolecular process is a straightforward extension of bimolecular processes. If trimolecular processes are rare and give slow rates, then the question arises as to how reactions like hydroformylations (Table 1.4.1) can be accomplished on a commercial scale (Vignette 1.5.1). The hydroformylation reaction is for example (see Table 1.4.1):

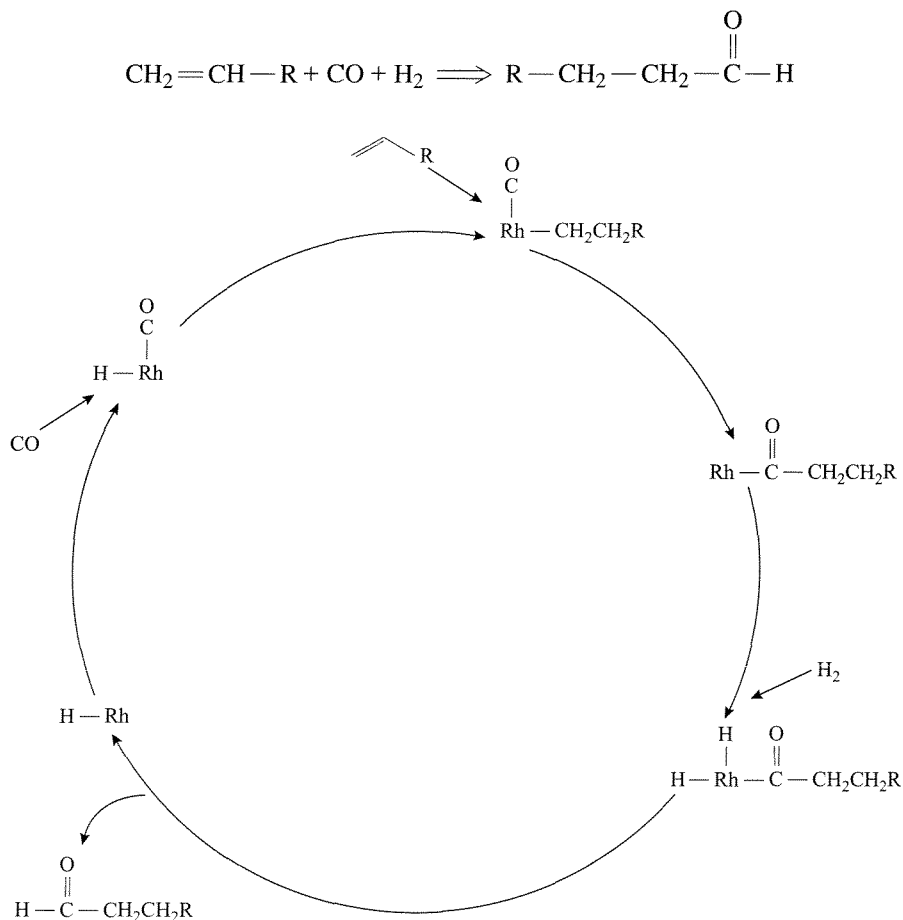
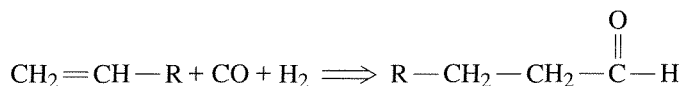


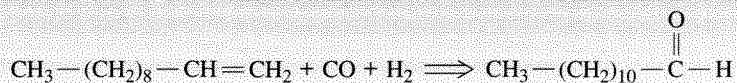
Figure 1.5.3 |

Simplified version of the hydroformylation mechanism. Note that other ligands on the Rh are not shown for ease in illustrating what happens with reactants and products.

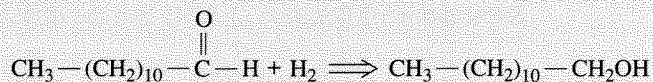
This reaction involves three reactants and the reason that it proceeds so efficiently is that a catalyst is used. Referring to Figure 1.5.3, note that the rhodium catalyst coordinates and combines the three reactants in a closed cycle, thus breaking the “statistical odds” of having all three reactants collide together simultaneously. Without a catalyst the reaction proceeds only at nonsignificant rates. This is generally true of reactions where catalysts are used. More about catalysts and their functions will be described later in this text.

VIGNETTE 1.5.1

Ingredients in soap (e.g., a shampoo) contain compounds like sodium lauryl sulfate. Sodium lauryl sulfate is $\text{CH}_3(\text{CH}_2)_{10}-\text{CH}_2-\text{OSO}_3\text{Na}^+$ and is a good detergent because “oily” substances interact with the hydrocarbon chain and the sodium sulfate portion of the molecule makes them water-soluble. Thus, when molecules like sodium lauryl sulfate contact “oily” clothes, dishes, hair, etc., they are able to “solubilize” the “oily” fraction and remove it when combined with water. Sodium lauryl sulfate is manufactured from lauryl alcohol (1-dodecanol) by sulfonation and neutralization with NaOH. Lauryl alcohol is produced by the hydroformylation of 1-undecene:



after which the aldehyde is hydrogenated to the alcohol:



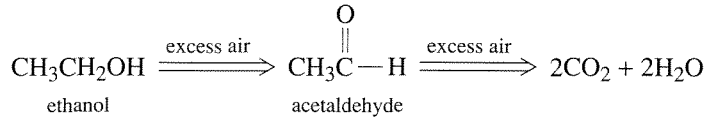
Thus, large-scale hydroformylation reactors are used worldwide to ultimately produce detergent-grade surfactants.

When conducting a reaction to give a desired product, it is common that other reactions proceed simultaneously. Thus, more than a single reaction must be considered (i.e., a reaction network), and the issue of selectivity becomes important. In order to illustrate the challenges presented by reaction networks, small reaction networks are examined next. Generalizations of these concepts to larger networks are only a matter of patience.

Consider the reaction network of two irreversible (one-way), first-order reactions in series:



This network can represent a wide variety of important classes of reactions. For example, oxidation reactions occurring in excess oxidant adhere to this reaction network, where B represents the partial oxidation product and C denotes the complete oxidation product CO_2 :



For this situation the desired product is typically B , and the difficulty arises in how to obtain the maximum concentration of B given a particular k_1 and k_2 . Using the Guldberg-Waage form of the reaction rates to describe the network in Equation (1.5.22) gives for constant volume:

$$\left. \begin{aligned}
 \frac{dC_A}{dt} &= -k_1 C_A \\
 \frac{dC_B}{dt} &= k_1 C_A - k_2 C_B \\
 \frac{dC_C}{dt} &= k_2 C_B
 \end{aligned} \right\} \quad (1.5.23)$$

with

$$C_A^0 + C_B^0 + C_C^0 = C^0 = C_A + C_B + C_C$$

Integration of the differential equation for C_A with $C_A = C_A^0$ at $t = 0$ yields:

$$C_A = C_A^0 \exp[-k_1 t] \quad (1.5.24)$$

Substitution of Equation (1.5.24) into the differential equation for C_B gives:

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_A^0 \exp[-k_1 t]$$

This equation is in the proper form for solution by the integrating factor method, that is:

$$\begin{aligned}
 \frac{dy}{dt} + p(t)y &= g(t), \quad I = \exp\left[\int p(t)dt\right] \\
 \int d(Iy) &= \int Ig(t)dt
 \end{aligned}$$

Now, for the equation concerning C_B , $p(t) = k_2$ so that:

$$\int d(C_B \exp[k_2 t]) = \int k_1 C_A^0 \exp[(k_2 - k_1)t] dt$$

Integration of the above equation gives:

$$C_B \exp[k_2 t] = \left[\frac{k_1 C_A^0}{k_2 - k_1} \right] \exp[(k_2 - k_1)t] + \gamma$$

or

$$C_B = \left[\frac{k_1 C_A^0}{k_2 - k_1} \right] \exp(-k_1 t) + \gamma \exp(-k_2 t)$$

where γ is the integration constant. Since $C_B = C_B^0$ at $t = 0$, γ can be written as a function of C_A^0 , C_B^0 , k_1 and k_2 . Upon evaluation of γ , the following expression is found for $C_B(t)$:

$$C_B = \frac{k_1 C_A^0}{k_2 - k_1} [\exp(-k_1 t) - \exp(-k_2 t)] + C_B^0 \exp(-k_2 t) \quad (1.5.25)$$

By knowing $C_B(t)$ and $C_A(t)$, $C_C(t)$ is easily obtained from the equation for the conservation of mass:

$$C_C = C^0 - C_A - C_B \quad (1.5.26)$$

For $C_B^0 = C_C^0 = 0$ and $k_1 = k_2$, the normalized concentrations of C_A , C_B , and C_C are plotted in Figure 1.5.4.

Notice that the concentration of species B initially increases, reaches a maximum, and then declines. Often it is important to ascertain the maximum amount of species B and at what time of reaction the maximum occurs. To find these quantities, notice that at C_B^{\max} , $dC_B/dt = 0$. Thus, if the derivative of Equation (1.5.25) is set equal to zero then t_{\max} can be found as:

$$t_{\max} = \frac{1}{(k_2 - k_1)} \ln \left[\left(\frac{k_2}{k_1} \right) \left(1 + \frac{C_B^0}{C_A^0} - \left(\frac{k_2}{k_1} \right) \frac{C_B^0}{C_A^0} \right) \right] \quad (1.5.27)$$

Using the expression for t_{\max} (Equation (1.5.27)) in Equation (1.5.25) yields C_B^{\max} .

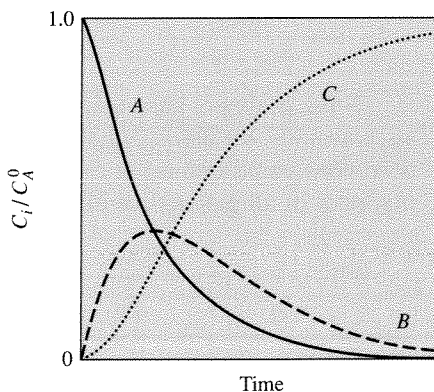


Figure 1.5.4 |

Normalized concentration of species i as a function of time for $k_1 = k_2$.

EXAMPLE 1.5.6

For $C_B^0 = C_C^0 = 0$, find the maximum concentration of C_B for $k_1 = 2k_2$.

■ Answer

From Equation (1.5.27) with $C_B^0 = 0$, t_{\max} is:

$$t_{\max} = \frac{1}{(k_2 - k_1)} \ln \left[\left(\frac{k_2}{k_1} \right) \right]$$

Substitution of t_{\max} into Equation (1.5.25) with $C_B^0 = 0$ gives:

$$C_B^{\max}/C_A^0 = \frac{k_1}{(k_2 - k_1)} \left[\exp \left[\frac{-k_1}{(k_2 - k_1)} \ln \left(\frac{k_2}{k_1} \right) \right] - \exp \left[\frac{-k_2}{(k_2 - k_1)} \ln \left(\frac{k_2}{k_1} \right) \right] \right]$$

or

$$C_B^{\max}/C_A^0 = \frac{k_1}{(k_2 - k_1)} \left[\left(\frac{k_1}{k_2} \right)^{\left(\frac{k_1}{k_2 - k_1} \right)} - \left(\frac{k_1}{k_2} \right)^{\left(\frac{k_2}{k_2 - k_1} \right)} \right]$$

This equation can be simplified as follows:

$$C_B^{\max}/C_A^0 = \frac{k_1}{(k_2 - k_1)} \left[\left(\frac{k_1}{k_2} \right)^{\left(\frac{k_2}{k_2 - k_1} \right)} \right] \left[\left(\frac{k_1}{k_2} \right)^{\left(\frac{k_1 - k_2}{k_2 - k_1} \right)} - 1 \right]$$

or

$$C_B^{\max}/C_A^0 = \frac{k_1}{(k_2 - k_1)} \left[\left(\frac{k_1}{k_2} \right)^{\left(\frac{k_2}{k_2 - k_1} \right)} \right] \left[\left(\frac{k_1}{k_2} \right)^{-1} - 1 \right] = \left(\frac{k_1}{k_2} \right)^{\left(\frac{k_2}{k_2 - k_1} \right)}$$

With $k_1 = 2k_2$,

$$C_B^{\max} = 0.5C_A^0$$

When dealing with multiple reactions that lead to various products, issues of selectivity and yield arise. The *instantaneous selectivity*, s_i , is a function of the local conditions and is defined as the production rate of species i divided by the production rates of all products of interest:

$$s_i = \frac{r_i}{\sum r_j}, \quad j = 1, \dots, \text{all products of interest} \quad (1.5.28)$$

where r_i is the rate of production of the species i . An *overall selectivity*, S_i , can be defined as:

$$S_i = \frac{\text{total amount of species } i}{\text{total amount of products of interest}} \quad (1.5.29)$$

The yield, Y_i , is denoted as below:

$$Y_i = \frac{\text{total amount of product } i \text{ formed}}{\text{initial amount of reactant fed}} \quad (1.5.30)$$

where the initial amount of reactant fed is for the limiting component. For the network given by Equation (1.5.22):

$$S_B = \frac{\text{amount of } B \text{ formed}}{\text{amount of } B \text{ and } C \text{ formed}} = \frac{\text{amount of } B \text{ formed}}{\text{amount of } A \text{ reacted}}$$

or

$$S_B = \frac{C_B}{C_A^0 - C_A} \quad (1.5.31)$$

and

$$Y_B = \frac{\text{amount of } B \text{ formed}}{\text{initial amount of } A \text{ fed}} = \frac{C_B}{C_A^0} \quad (1.5.32)$$

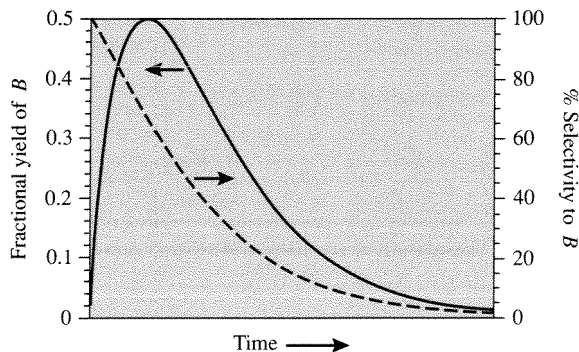
The selectivity and yield should, of course, correctly account for the stoichiometry of the reaction in all cases.

EXAMPLE 1.5.7

Plot the percent selectivity and the yield of B [Equation (1.5.31) multiplied by 100 percent and Equation (1.5.32), respectively] as a function of time. Does the time required to reach C_B^{\max} give the maximum percent selectivity to B and/or the maximum fractional yield of B ? Let $k_1 = 2k_2$, $C_B^0 = C_C^0 = 0$.

■ Answer

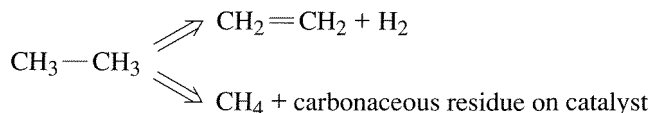
From the plot shown below the answer is obvious. For practical purposes, what is important is the maximum yield.



Consider the reaction network of two irreversible (one-way), first-order reactions in parallel:



Again, like the series network shown in Equation (1.5.22), the parallel network of Equation (1.5.33) can represent a variety of important reactions. For example, dehydrogenation of alkanes can adhere to this reaction network where the desired product DP is the alkene and the undesired side-product SP is a hydrogenolysis ($C-C$ bond-breaking reaction) product:



Using the Guldberg-Waage form of the reaction rates to describe the network in Equation (1.5.33) gives for constant volume:

$$\left. \begin{array}{l}
 \frac{dC_A}{dt} = -(k_1 + k_2)C_A \\
 \frac{dC_{DP}}{dt} = k_1C_A \\
 \frac{dC_{SP}}{dt} = k_2C_A
 \end{array} \right\} \quad (1.5.34)$$

with

$$C_A^0 + C_{DP}^0 + C_{SP}^0 = C^0 = C_A + C_{DP} + C_{SP}$$

Integration of the differential equation for C_A with $C_A = C_A^0$ at $t = 0$ gives:

$$C_A = C_A^0 \exp[-(k_1 + k_2)t] \quad (1.5.35)$$

Substitution of Equation (1.5.35) into the differential equation for C_{DP} yields:

$$\frac{dC_{DP}}{dt} = k_1 C_A^0 \exp[-(k_1 + k_2)t]$$

The solution to this differential equation with $C_{DP} = C_{DP}^0$ at $t = 0$ is:

$$C_{DP} = C_{DP}^0 + \frac{k_1 C_A^0}{(k_1 + k_2)} [1 - \exp[-(k_1 + k_2)t]] \quad (1.5.36)$$

Likewise, the equation for C_{SP} can be obtained and it is:

$$C_{SP} = C_{SP}^0 + \frac{k_2 C_A^0}{(k_1 + k_2)} [1 - \exp[-(k_1 + k_2)t]] \quad (1.5.37)$$

The percent selectivity and yield of DP for this reaction network are:

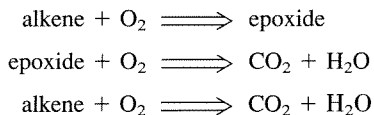
$$s_{DP} \times 100\% = \frac{dC_{DP}}{-dC_A} \times 100\% = \frac{k_1 C_A}{k_1 C_A + k_2 C_A} \times 100\% = \frac{k_1}{k_1 + k_2} \times 100\% \quad (1.5.38)$$

and

$$Y = \frac{C_{DP}}{C_A^0} \quad (1.5.39)$$

EXAMPLE 1.5.8

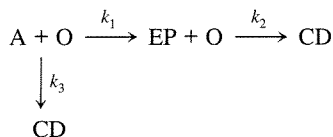
The following reactions are observed when an olefin is epoxidized with dioxygen:



Derive the rate expression for this mixed-parallel series-reaction network and the expression for the percent selectivity to the epoxide.

■ Answer

The reaction network is assumed to be:



where A: alkene, O: dioxygen, EP: epoxide, and CD: carbon dioxide. The rate expressions for this network are:

$$\frac{dC_A}{dt} = -k_1 C_A C_O - k_3 C_A C_O$$

$$\frac{dC_{EP}}{dt} = k_1 C_A C_O - k_2 C_{EP} C_O$$

$$\frac{dC_{CD}}{dt} = k_2 C_{EP} C_O + k_3 C_A C_O$$

The percent selectivity to EP is:

$$s_{EP} = \frac{r_{EP}}{r_{EP} + r_{CD}} \times 100\% = \frac{k_1 C_A C_O - k_2 C_{EP} C_O}{k_1 C_A C_O + k_3 C_A C_O} \times 100\%$$

EXAMPLE 1.5.9

In Example 1.5.6, the expression for the maximum concentration in a series reaction network was illustrated. Example 1.5.8 showed how to determine the selectivity in a mixed-parallel series-reaction network. Calculate the maximum epoxide selectivity attained from the reaction network illustrated in Example 1.5.8 assuming an excess of dioxygen.

■ Answer

If there is an excess of dioxygen then C_O can be held constant. Therefore,

$$s_{EP} = \frac{k_1 C_A C_O - k_2 C_{EP} C_O}{k_1 C_A C_O + k_3 C_A C_O} = \frac{k_1 C_A - k_2 C_{EP}}{(k_1 + k_3) C_A}$$

From this expression it is clear that the selectivity for any C_A will decline as $k_2 C_{EP}$ increases. Thus, the maximum selectivity will be:

$$s_{EP}^{\max} = \frac{k_1 C_A}{(k_1 + k_3) C_A} = \frac{k_1}{k_1 + k_3}$$

and that this would occur at $t = 0$, as was illustrated in Example 1.5.7. Here, the maximum selectivity is not 100 percent at $t = 0$ but rather the fraction $k_1/(k_2 + k_3)$ due to the parallel portion of the network.

EXAMPLE 1.5.10

Find the maximum yield of the epoxide using the conditions listed for Example 1.5.9.

■ Answer

The maximum yield, C_{EP}^{\max}/C_A^0 will occur at C_{EP}^{\max} . If $\tilde{k}_1 = k_1 C_O$, $\tilde{k}_2 = k_2 C_O$, $\tilde{k}_3 = k_3 C_O$, $y = C_{EP}/C_A^0$ and $x = C_{EP}/C_A^0$, the rate expressions for this network can be written as:

$$\frac{dy}{dt} = -\tilde{k}_1 y - \tilde{k}_3 y = -(\tilde{k}_1 + \tilde{k}_3) y$$

$$\frac{dx}{dt} = \tilde{k}_1 y - \tilde{k}_2 x$$

Note the analogy to Equation (1.5.23). Solving the differential equation for y and substituting this expression into the equation for x gives:

$$\frac{dx}{dt} + \tilde{k}_2 x = \tilde{k}_1 \exp[-(\tilde{k}_1 + \tilde{k}_3)t]$$

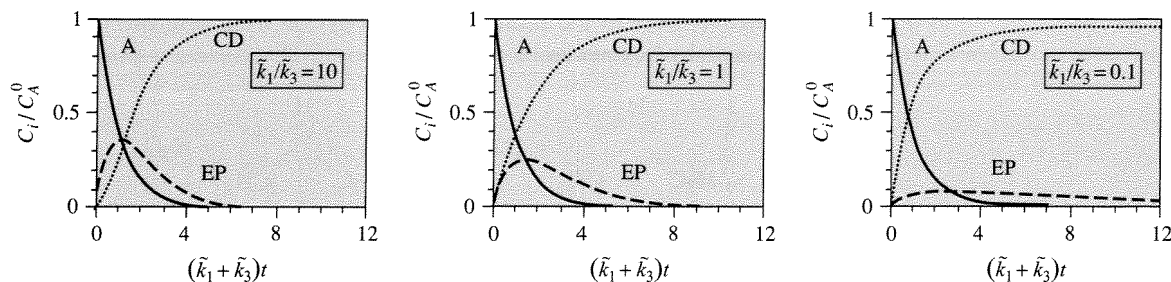


Figure 1.5.5 |

Normalized concentration of species i as a function of time for $\tilde{k}_1 = \tilde{k}_2$.

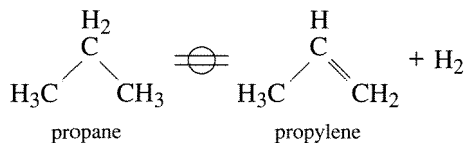
Solution of this differential equation by methods employed for the solution of Equation (1.5.23) gives:

$$x = \frac{\tilde{k}_1}{\tilde{k}_2 - (\tilde{k}_1 + \tilde{k}_3)} [\exp[-(\tilde{k}_1 + \tilde{k}_3)t] - \exp(-\tilde{k}_2 t)]$$

If $\tilde{k}_3 = 0$, then the expression is analogous to Equation (1.5.25). In Figure 1.5.5, the normalized concentration profiles for various ratios of \tilde{k}_1/\tilde{k}_3 are plotted. The maximum yields of epoxide are located at the x^{\max} for each ratio of \tilde{k}_1/\tilde{k}_3 . Note how increased reaction rate to deep oxidation of alkane decreases the yield to the epoxide.

Exercises for Chapter 1

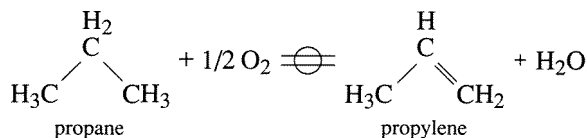
- Propylene can be produced from the dehydrogenation of propane over a catalyst. The reaction is:



At atmospheric pressure, what is the fraction of propane converted to propylene at 400, 500, and 600°C if equilibrium is reached at each temperature? Assume ideal behavior.

Temperature (°C)	400	500	600
K_a	0.000521	0.0104	0.104

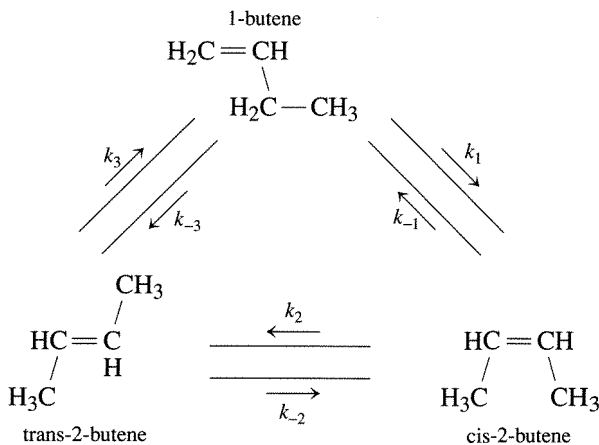
2. An alternative route to the production of propylene from propane would be through oxydehydrogenation:



At atmospheric pressure, what is the fraction of propane converted to propylene at 400, 500, and 600°C if equilibrium is reached at each temperature? Compare the results to those from Exercise 1. What do you think is the major impediment to this route of olefin formation versus dehydrogenation? Assume ideal behavior.

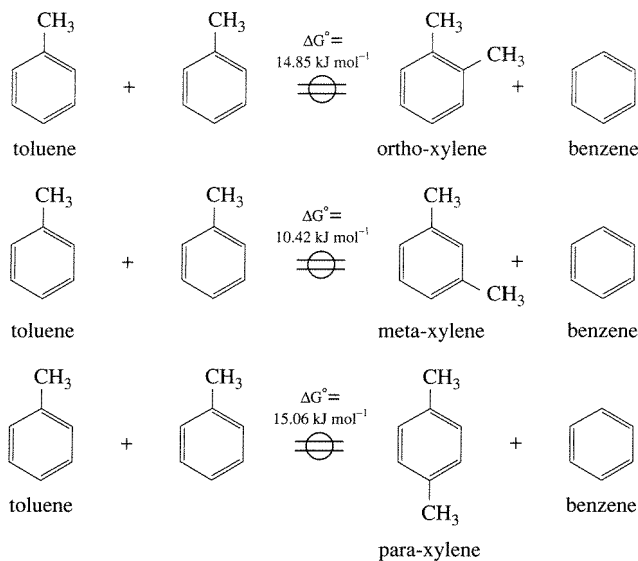
Temperature (°C)	400	500	600
K_a	1.16×10^{26}	5.34×10^{23}	8.31×10^{21}

3. The following reaction network represents the isomerization of 1-butene to cis- and trans-2-butene:



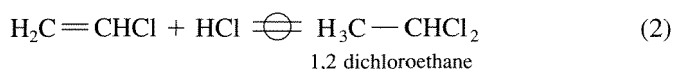
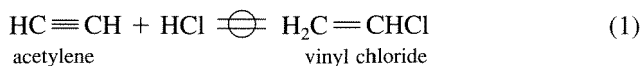
The equilibrium constants (K_a 's) for steps 1 and 2 at 400 K are 4.30 and 2.15, respectively. Consider the fugacity coefficients to be unity.

- Calculate the equilibrium constant of reaction 3.
 - Assuming pure 1-butene is initially present at atmospheric pressure, calculate the equilibrium conversion of 1-butene and the equilibrium composition of the butene mixture at 400 K. (Hint: only two of the three reactions are independent.)
4. Xylene can be produced from toluene as written schematically:



The values of ΔG° were determined at 700 K. What is the equilibrium composition (including all xylene isomers) at 700 K and 1.0 atm pressure? Propose a method to manufacture para-xylene without producing significant amounts of either ortho- or meta-xylene.

5. Vinyl chloride can be synthesized by reaction of acetylene with hydrochloric acid over a mercuric chloride catalyst at 500 K and 5.0 atm total pressure. An undesirable side reaction is the subsequent reaction of vinyl chloride with HCl. These reactions are illustrated below.



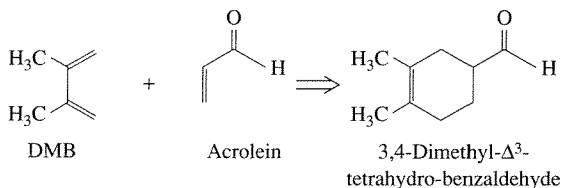
The equilibrium constants at 500 K are 6.6×10^3 and 0.88 for reaction 1 and 2, respectively. Assume ideal behavior.

- (a) Find the equilibrium composition at 5.0 atm and 500 K for the case when acetylene and HCl are present initially as an equimolar mixture. What is the equilibrium conversion of acetylene?
- (b) Redo part (a) with a large excess of inert gas. Assume the inert gas constitutes 90 vol. % of the initial gas mixture.
6. Acetone is produced from 2-propanol in the presence of dioxygen and the photocatalyst TiO_2 when the reactor is irradiated with ultraviolet light. For a

reaction carried out at room temperature in 1.0 mol of liquid 2-propanol containing 0.125 g of catalyst, the following product concentrations were measured as a function of irradiation time (J. D. Lee, M.S. Thesis, Univ. of Virginia, 1993.) Calculate the first-order rate constant.

Reaction time (min)	20	40	60	80	100	120	140	160	180
Acetone produced ($g_{\text{acetone}}/g_{2\text{-propanol}} \times 10^4$)	1.9	3.9	5.0	6.2	8.2	10	11.5	13.2	14.0

7. The Diels-Alder reaction of 2,3-dimethyl-1,3-butadiene (DMB) and acrolein produces 3,4-dimethyl- Δ^3 -tetrahydro-benzaldehyde.



This overall second-order reaction was performed in methanol solvent with equimolar amounts of DMB and acrolein (C. R. Clontz, Jr., M.S. Thesis, Univ. of Virginia, 1997.) Use the data shown below to evaluate the rate constant at each temperature.

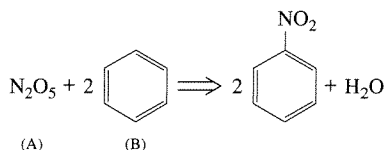
Temperature (K)	Reaction time (hours)	[DMB] (mol L^{-1})
323	0	0.097
323	20	0.079
323	40	0.069
323	45	0.068
298	0	0.098
298	74	0.081
298	98	0.078
298	125	0.074
298	170	0.066
278	0	0.093
278	75	0.091
278	110	0.090
278	176	0.088
278	230	0.087

8. Some effluent streams, especially those from textile manufacturing facilities using dyeing processes, can be highly colored even though they are considered to be fairly nontoxic. Due to the stability of modern dyes, conventional

biological treatment methods are ineffective for decolorizing such streams. Davis et al. studied the photocatalytic decomposition of wastewater dyes as a possible option for decolorization [R. J. Davis, J. L. Gainer, G. O'Neal, and I.-W. Wu, *Water Environ. Res.* **66** (1994) 50]. The effluent from a municipal water treatment facility whose influent contained a high proportion of dyeing wastewater was mixed with TiO_2 photocatalyst (0.40 wt. %), sparged with air, and irradiated with UV light. The deep purple color of the original wastewater lightened with reaction time. Since the absolute concentration of dye was not known, the progress of the reaction was monitored colorimetrically by measuring the relative absorbance of the solution at various wavelengths. From the relative absorbance data collected at 438 nm (shown below), calculate the apparent order of the decolorization reaction and the rate constant. The relative absorbance is the absorbance at any time t divided by the value at $t = 0$.

Reaction time (min)	30	60	90	120	150	180	210
Relative absorbance	0.79	0.67	0.50	0.39	0.30	0.23	0.17

9. The following reaction is investigated in a constant density batch reactor:

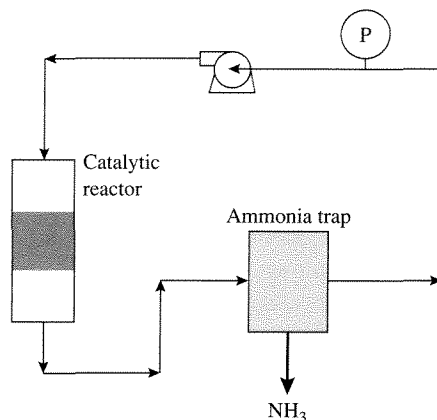


The reaction rate is:

$$\frac{dC_A}{dt} = -kC_A C_B^2$$

The reactor is initially charged with C_A^0 and C_B^0 and $C_B^0/C_A^0 = 3.0$. Find the value of k if $C_A^0 = 0.01$ mol/L and after 10 min of reaction the conversion of N_2O_5 is 50 percent.

10. As discussed in Vignette 1.1.1, ammonia is synthesized from dinitrogen and dihydrogen in the presence of a metal catalyst. Fishel et al. used a constant volume reactor system that circulated the reactants over a heated ruthenium metal catalyst and then immediately condensed the product ammonia in a cryogenic trap [C. T. Fishel, R. J. Davis, and J. M. Garces, *J. Catal.* **163** (1996) 148]. A schematic diagram of the system is:



From the data presented in the following tables, determine the rates of ammonia synthesis (moles NH_3 produced per min per gcat) at 350°C over a supported ruthenium catalyst (0.20 g) and the orders of reaction with respect to dinitrogen and dihydrogen. Pressures are referenced to 298 K and the total volume of the system is 0.315 L. Assume that no ammonia is present in the gas phase.

$\text{N}_2:\text{H}_2:\text{He} = 3:1:0$

Pressure (torr)	766.2	731.9	711.9	686.2	661.5
Time (min)	0	18	30	42	54

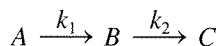
$\text{N}_2:\text{H}_2:\text{He} = 1:1:2$

Pressure (torr)	753.4	737.5	726.6	709.5	700.3
Time (min)	0	15	30	45	60

$\text{N}_2:\text{H}_2:\text{He} = 1:3:0$

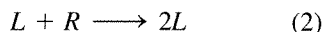
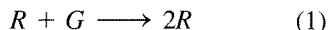
Pressure (torr)	707.1	700.2	693.2	683.5	675.5
Time (min)	0	15	30	45	55

11. In Example 1.5.6, the series reaction:



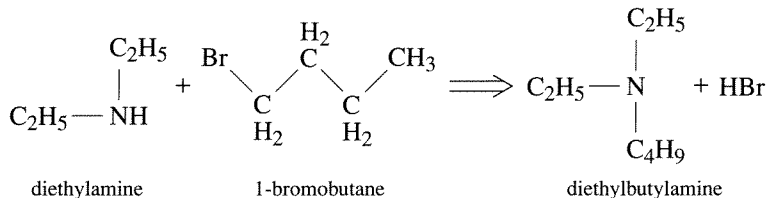
was analyzed to determine the time (t_{\max}) and the concentration (C_B^{\max}) associated with the maximum concentration of the intermediate B when $k_1 = 2k_2$. What are t_{\max} and C_B^{\max} when $k_1 = k_2$?

12. The Lotka-Volterra model is often used to characterize predator-prey interactions. For example, if R is the population of rabbits (which reproduce autocatalytically), G is the amount of grass available for rabbit food (assumed to be constant), L is the population of lynxes that feeds on the rabbits, and D represents dead lynxes, the following equations represent the dynamic behavior of the populations of rabbits and lynxes:



Each step is irreversible since, for example, rabbits cannot turn back into grass.

- (a) Write down the differential equations that describe how the populations of rabbits (R) and lynxes (L) change with time.
- (b) Assuming G and all of the rate constants are unity, solve the equations for the evolution of the animal populations with time. Let the initial values of R and L be 20 and 1, respectively. Plot your results and discuss how the two populations are related.
13. Diethylamine (DEA) reacts with 1-bromobutane (BB) to form diethylbutylamine (DEBA) according to:



From the data given below (provided by N. Leininger, Univ. of Virginia), find the effect of solvent on the second-order rate constant.

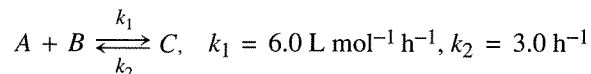
Time (min)	[DEBA] (mol L ⁻¹)
0	0.000
35	0.002
115	0.006
222	0.012
455	0.023

Solvent = 1,4-butanediol
 T = 22°C
 [DEA]⁰ = [BB]⁰ = 0.50 mol L⁻¹

Time (min)	[DEBA] (mol L ⁻¹)
0	0.000
31	0.004
58	0.007
108	0.013
190	0.026

Solvent = acetonitrile
 T = 22°C
 [DEA]⁰ = 1.0 mol L⁻¹
 [BB]⁰ = 0.10 mol L⁻¹

14. A first-order homogeneous reaction of A going to $3B$ is carried out in a constant pressure batch reactor. It is found that starting with pure A the volume after 12 min is increased by 70 percent at a pressure of 1.8 atm. If the same reaction is to be carried out in a constant volume reactor and the initial pressure is 1.8 atm, calculate the time required to bring the pressure to 2.5 atm.
15. Consider the reversible, elementary, gas phase reaction shown below that occurs at 300 K in a constant volume reactor of 1.0 L.



For an initial charge to the reactor of 1.0 mol of A , 2.0 mol of B , and no C , find the equilibrium conversion of A and the final pressure of the system. Plot the composition in the reactor as a function of time.

16. As an extension of Exercise 15, consider the reversible, elementary, gas phase reaction of A and B to form C occurring at 300 K in a variable volume (constant pressure) reactor with an *initial* volume of 1.0 L. For a reactant charge to the reactor of 1.0 mol of A , 2.0 mol of B , and no C , find the equilibrium conversion of A . Plot the composition in the reactor and the reactor volume as a function of time.
17. As an extension of Exercise 16, consider the effect of adding an inert gas, I , to the reacting mixture. For a reactant charge to the reactor of 1.0 mol of A , 2.0 mol of B , no C , and 3.0 mol of I , find the equilibrium conversion of A . Plot the composition in the reactor and the reactor volume as a function of time.