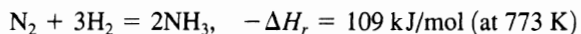


The Basics of Reaction Kinetics for Chemical Reaction Engineering

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

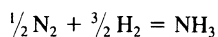
The initial success of a large-scale catalytic technology began in 1913 when the first industrial chemical reactor to synthesize ammonia from dinitrogen and dihydrogen began operation in Germany. Most of the ammonia manufactured today is used to produce nitrogen-rich fertilizers that have an enormous 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):

N_2	25	$25 - \xi$
H_2	75	$75 - 3\xi$
NH_3	0	2ξ
total	100	$100 - 2\xi$

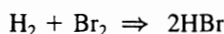
then

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

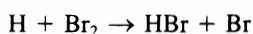
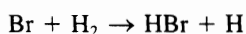
Thus, $\xi = 13.1$ and $X_{\text{N}_2} = (25 - 13.1) / (100 - 26.2) = 0.16$. At 300 atm, the equilibrium mole fraction of ammonia is 0.36 while at 100 atm it falls to approximately 0.16. Thus, the equilibrium amount of ammonia increases with the total pressure of the system at a constant temperature.

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):



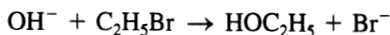
In this text, stoichiometric reactions and elementary steps are distinguished by the notation provided in Table 1.1.1.

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	\rightleftharpoons
Rate-determining		\nrightarrow or \nleftarrow

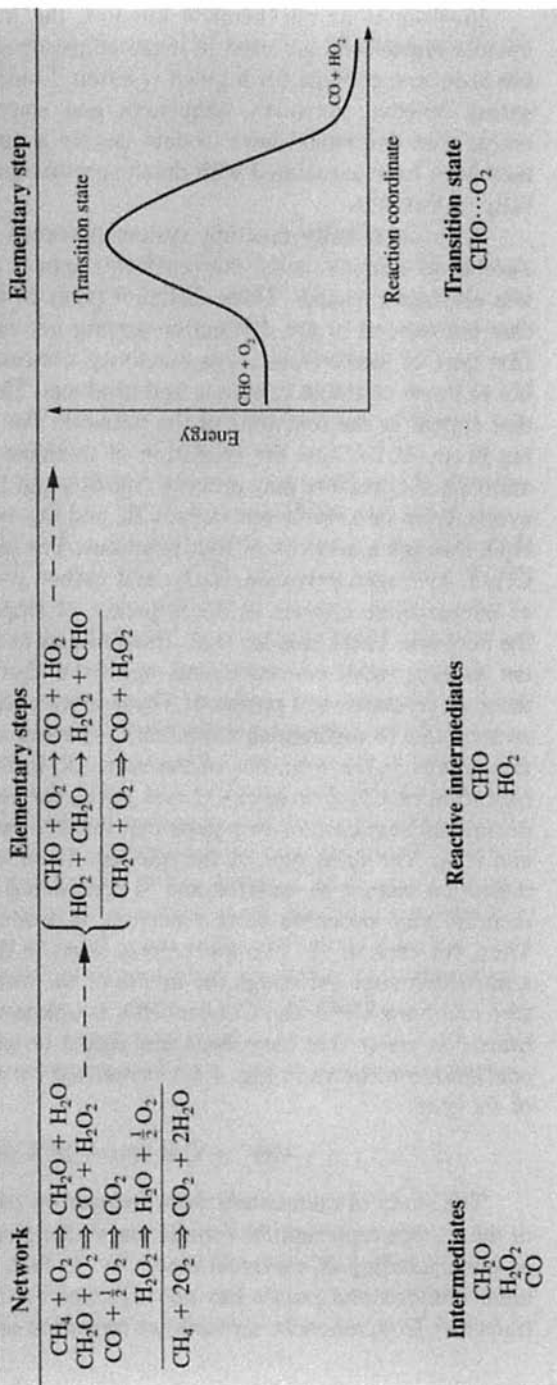
In discussions on chemical kinetics, the terms *mechanism* or *model* frequently appear and are used to mean an assumed reaction network or a plausible sequence of steps for a given reaction. Since the levels of detail in investigating reaction networks, sequences and steps are so different, the words *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



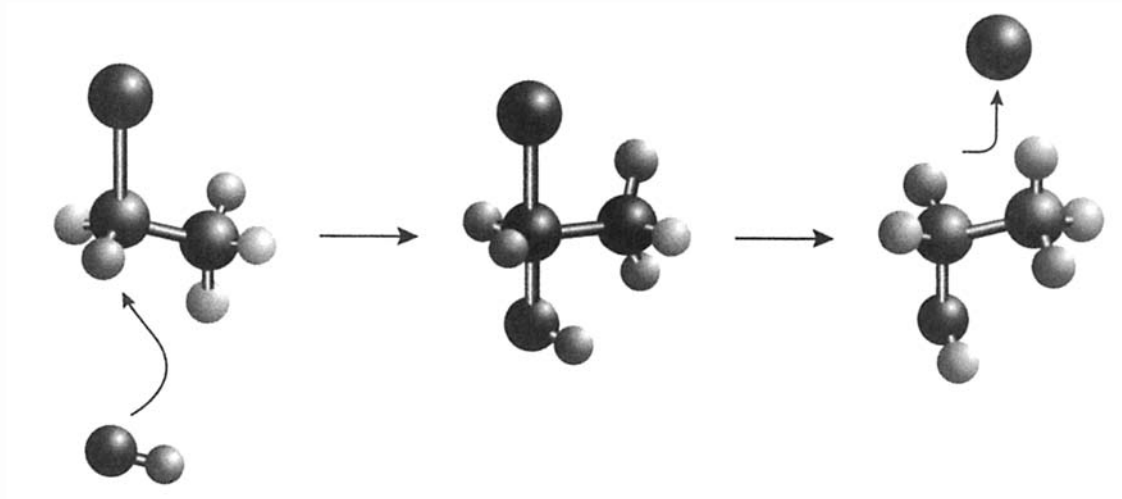
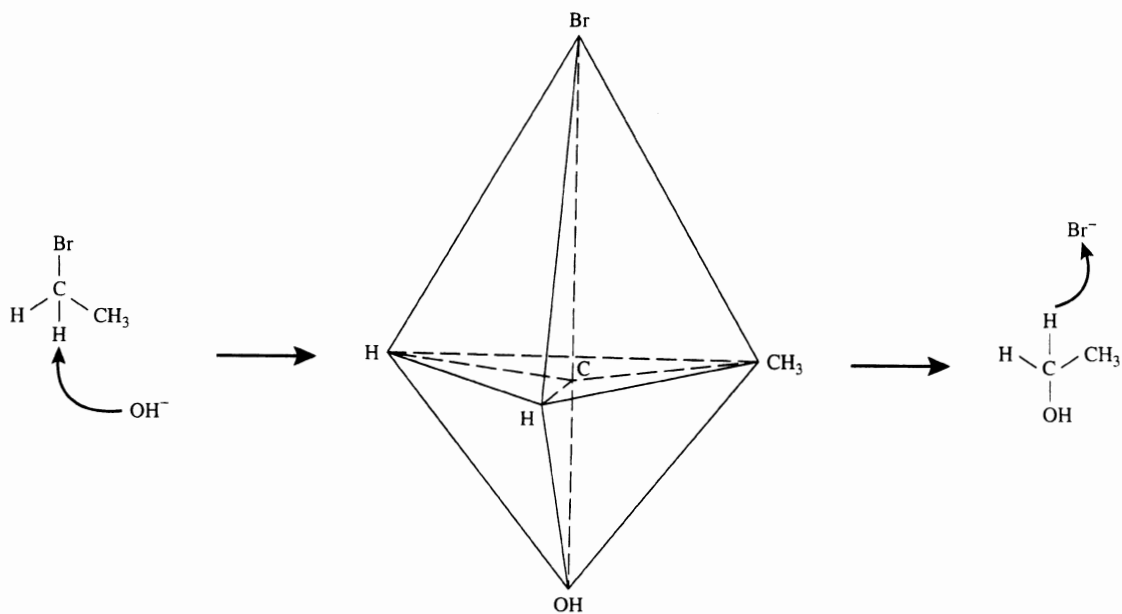


Figure 1.1.1 |

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



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

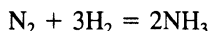
Chemical Bond: Structure and Dynamics, Academic Press, 1992). However, in the vast majority of cases, chemically reacting systems are investigated in much less detail. The level of sophistication that is conducted is normally dictated by the purpose of the work and the state of development of the system.

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:

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

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:

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

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:

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

Since there is only one Φ for each reaction:

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

or

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

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**

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

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:

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

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	<u>0.022</u>
	1.000

EXAMPLE 1.2.4

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

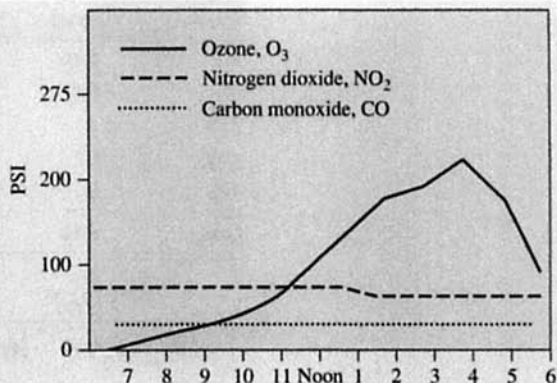
■ **Answer**

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

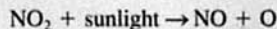
$$\Phi_2^{\text{eq}} = \xi_2^{\text{eq}} = 0.190$$

VIGNETTE 1.2.1

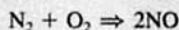
Below is shown the pollution standard index (PSI) for Pasadena, California, in July 1995 from 7 A.M. until 6 P.M.:



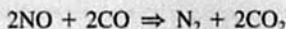
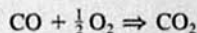
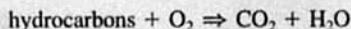
On these scales, 100 is the Federal standard and values above this are unhealthy. Notice that the ozone somewhat follows the intensity of the sunlight. That is because ozone is formed by numerous reactions that involve sunlight, for example,



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.

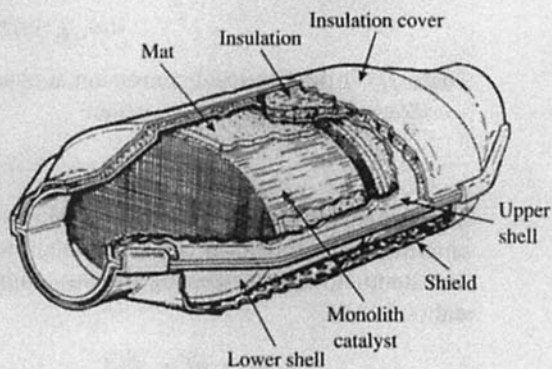


Figure 1.2.1 | Ceramic monolith catalytic converter.
Adapted with permission from K. C. Taylor, *CHEMTECH*,
20 (1990) 551. Copyright 1990 American Chemical Society.

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:

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

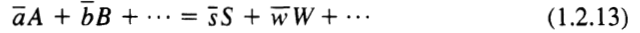
where $0 \leq f_{\ell} \leq 1$. When the thermodynamics of the system limit Φ such that it cannot reach Φ_{\max} (where $n_{\ell} = 0$), Φ will approach its equilibrium value Φ^{eq} ($n_{\ell} \neq 0$ value of n_{ℓ} determined by the equilibrium constant). When a reaction is limited by thermodynamic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

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

or

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

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:

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

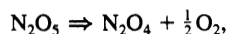
At fixed T and V, the ideal gas law gives:

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

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:

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

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 :

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

Differentiation of Equation (1.2.3) gives:

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

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

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

since ν_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:

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

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:

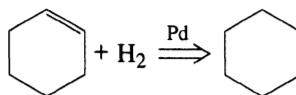
$$r_t = \frac{1}{\bar{S}} \frac{dn}{dt} \quad (1.3.9)$$

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).

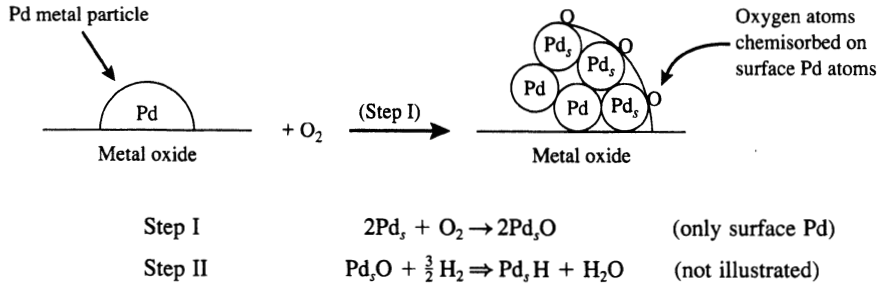
EXAMPLE 1.3.1

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 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 H₂ 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:

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

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

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

Likewise for Pd on SiO₂,

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

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).

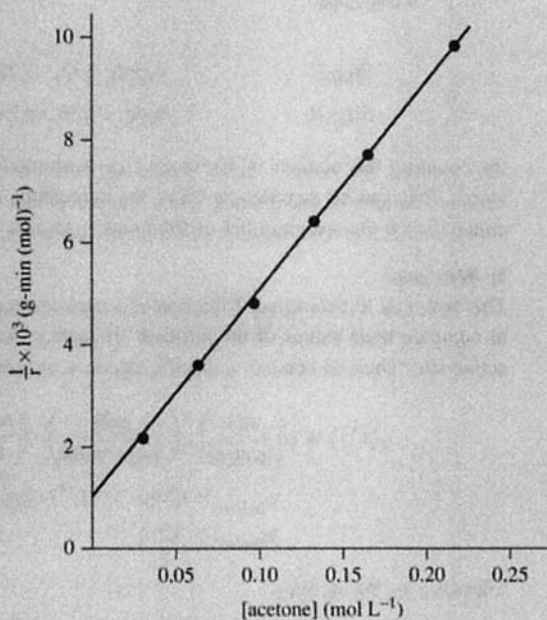
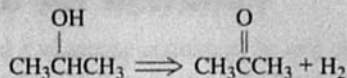


Figure 1.4.1 | The rate function r decreases with concentration of acetone [a measure of the extent of reaction: Equation (1.2.4)]. Adapted from D. E. Mears and M. Boudart, *AIChE J.* 12 (1966) 313, with permission of the American Institute of Chemical Engineers. Copyright © 1966 AIChE. All rights reserved.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

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

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 Π 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

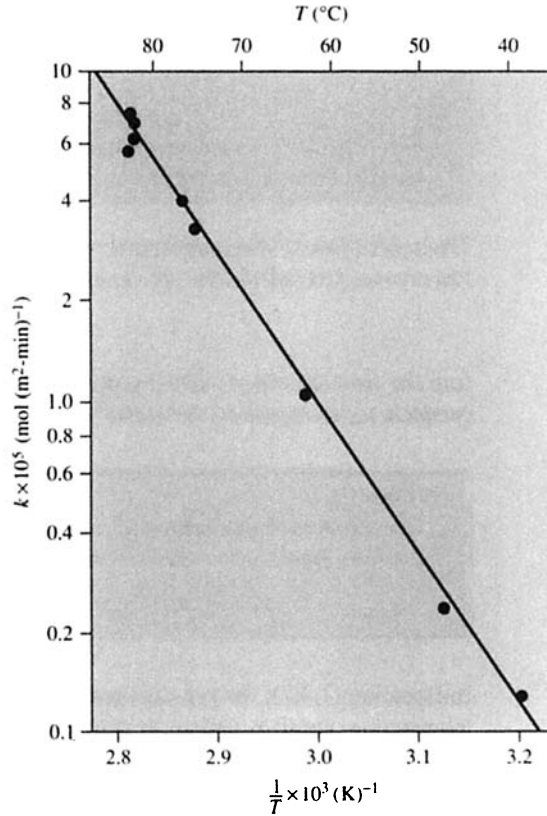


Figure 1.4.2 |

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:

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

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):

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

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 → products	$\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$	$1.96 \times 10^{14} \exp[-10660/T], \text{s}^{-1}$
Bimolecular	2	2A → products A + B → products	$\text{NO} + \text{NO}_3 \rightarrow 2\text{NO}_2$	$2.0 \times 10^{11}, \text{cm}^3/\text{s}/\text{molecule} \text{ (2)}$
Trimolecular (rare)	3	3A → products 2A + B → products A + B + C → products	$2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$ $\text{NO} + \text{NO}_2 + \text{H}_2\text{O} \rightarrow 2\text{HNO}_2$	$3.3 \times 10^{-39} \exp(530/T), \text{cm}^6/\text{s}/\text{molecule}^2 \text{ (2)}$ $\leq 4.4 \times 10^{-40}, \text{cm}^6/\text{s}/\text{molecule}^2 \text{ (2)}$

(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	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2 \rightleftharpoons \text{CH}_3-\underset{\text{CH}_2}{\underset{\parallel}{\text{C}}}-\text{CH}_3$
Decompositions	$\text{N}_2\text{O}_5 \rightleftharpoons \text{NO}_2 + \text{NO}_3$ $\text{CH}_2-\underset{\text{O}}{\underset{\diagdown}{\text{C}}}-\text{CH}_2 \rightleftharpoons \text{CH}_4 + \text{CO}$
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 :

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

For this decomposition reaction:

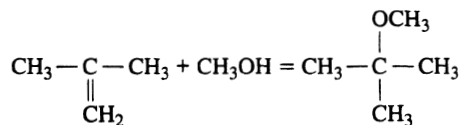
$$\epsilon_{\text{N}_2\text{O}} = 1.0 \left[\frac{2 - 1}{|-1|} \right] = 1$$

Thus,

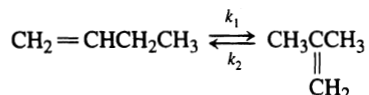
$$P = P^0(1 + f) = 2(1 + 0.12) = 2.24 \text{ atm}$$

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:

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