Chapter 7   Chemical Kinetics

Framework of the Chapter

Following the transport rates in the last chapter, this chapter is devoted to the other one, the chemical reaction rates on the macroscopic level. The focal point is to establish the reaction-rate equations which reflect how the reaction rates vary with the concentrations of reactants and products and the temperature. They are the general principles on the macroscopic level. The characteristic properties (parameters) of reactions inherent in the equations should be incorporated in applications. Before the main content, first we distinguish the elementary reactions from the most commonly observed complex reactions, they are connected by reaction mechanisms (7.1). The whole chapter is then divided into three parts as follows:

I. Fundamental Principles of Chemical Kinetics

(1) **Definitions of Reaction Rates**. Various definitions and corresponding formulae of reaction rates and their mutual relations are introduced (7.2).

(2) **Rate Equations of Elementary Reactions and Complex Reactions**. The rate equations are mainly in power-function form and contain several characteristic parameters such as the molecularity of reaction, the reaction rate constant, the reaction order, and the reaction rate coefficient (7.3). The features of the zeroth order, the first order, the second order and other order rate equations, and their integrated forms, as well as corresponding calculations and applications are illustrated by examples. (7.4).

(3) **Opposite Reactions, Consecutive Reactions and Parallel Reactions**.

They represent possible forms of combination of different reactions occurring simultaneously in the system. The features and the applications of rate equations and their integrated forms for the first order opposite reactions (7.5), the first order consecutive reactions (7.6) and the first order parallel reactions (7.7) are presented only which form the basis for studying higher order reactions.

(4) **Effect of Temperature on Reaction Rates**. The temperature effect is embodied in the Arrhenius equation. The establishment of the equation and the meanings of characteristic parameters in the equation such as the Arrhenius activation energy and the pre-exponential factor are discussed (7.8).

II. Characteristic Parameters in Chemical Kinetics

The experimental and semi-empirical methods are presented in this part for obtaining characteristic parameters. Theoretical methods involve the statistical theories of elementary reactions such as the collision theory, the transition state theory and the molecular dynamics, which are on the transition level from microscopic to macroscopic and will be discussed in Chapter 14.

(1) **Experimental Methods in Chemical Kinetics**. Experimental methods in general (7.9) and those for rapid reactions (7.11) are briefly introduced.

(2) **Data Processing in Chemical Kinetics**. The integration methods and the differential methods for obtaining characteristic parameters in kinetics from experimental data are illustrated by examples (7.10).

(3) **Semi-empirical Methods**. A brief introduction is presented (7.12).

III. Reaction Mechanisms   This part is a continuation of the part I.

(1) **Relations between Reaction Mechanisms and Rate Equations**. The pre-equilibrium approximation and the steady-state approximation for obtaining the reaction-rate equations of complex reactions from the reaction mechanisms are discussed (7.13).

(2) **Unimolecular Reactions**. They could not be simply classified as elementary reactions. A little on their peculiarities is introduced (7.14).

(3) **Principle of Microscopic Reversibility and Principle of Detailed Equilibrium**. They are restrictions that must be followed when obtaining rate equations from reaction mechanisms (7.15).

7.1   Introduction

Chemical Kinetics   Chemical kinetics studies the effects of various factors on reaction rates. Briefly, there are three kinds of factors: The first concerns concentrations of reactants, products, catalysts, and other substances. The second is the temperature and pressure of the system. The third is the external fields such as light, electric field and magnetic field.

Elementary Reactions   When the products are formed from reactants by only one single step, and no intermediates can be detected by macroscopic experimental methods, the reaction is called an elementary reaction. If the quantum states of the reactant molecules and product molecules are further assigned and clearly shown, it is called a **state-state**

reaction. An elementary reaction is a summation of various corresponding state-state reactions.

Complex Reactions   A reaction composed of two or more elementary reactions is called a complex reaction. The overwhelming majority of reactions observed in nature or in laboratory are complex reactions. Many reactions even seem very simple, for instance, formation of H_2O from H_2 and O_2, synthesis of NH_3 from N_2 and H_2, are complex reactions with very complex mechanisms.

Reaction Mechanisms   The pattern or sequence of elementary reactions in composing a complex reaction is called the reaction mechanism of this complex reaction. If the reaction mechanism is known, in principle, we can predict the rate of a complex reaction by the rates of the corresponding elementary reactions. However, the determinations of reaction mechanisms are extremely uneasy. Generally, they need kinetic experiments and other experiments such as separation and detection of intermediates, as well as theoretical analysis to make a synthetic judgment. At present, most reaction mechanisms are only reasonable hypotheses.

Macroscopic Chemical Kinetics   The task of the macroscopic chemical kinetics is to establish reaction-rate equations on the macroscopic level. It is the main content of this chapter. The rate equations have various types connecting the rates of elementary reactions and complex reactions with the concentrations, the temperature and the pressure. Some general principles have been induced. On the other hand, there are several parameters in rate equations such as the rate constant or coefficient, the reaction order, the activation energy and the pre-exponential factor. They are characteristic properties of the reaction or substances. Basically, we have three methods, experimental, semi-empirical and theoretical methods for obtaining these characteristic properties, the latter belongs to the microscopic chemical kinetics. Combining the general principles with the reaction characteristics, we can solve practical problems of reaction rates.

Microscopic Chemical Kinetics   The microscopic chemical kinetics starts with the microscopic characteristic properties of substances such as molecular sizes, geometric configurations, and translational, rotational,

vibrational, electronic movements to study the state-state reactions. The rates of the elementary reactions are obtained by statistical average. Three main theories have been established, namely: the collision theory, the transition state theory and the molecular dynamics. They elucidate the microscopic essentials of the rate equations and can be used to predict the macroscopic characteristic properties in kinetics from the microscopic characteristic properties of substances. Refer to Chap. 14 of Part IV Statistics.

Practical Significance of Chemical Kinetics Studies   In laboratories and factories, chemical reactions are usually carried out in various types of reactors. Reaction rates directly determine the yields or output reached in a period of time for reactors with various sizes. Combining with the studies of transport phenomena, **chemical reaction engineering** was evolved after 1950s which provides theoretical foundations for the design, operation and control of reactors of the production processes in the large-scale chemical industry. Reactions in bio fields are carried out in organs and cells which are virtually a kind of reactors. Reaction rates influence the transformation and absorption of nutritious substances, and the growth and metabolism of organisms. For the atmosphere and the earth's crust, reactions proceed in a space of much larger scale. Reaction rates play a vital part on many important events concerning ecological environment and resources such as depletion of the ozone layer, formation of sour rains, degradation of wastes, and creation of minerals.

**How to Write Reaction Formulae or Stoichiometric Equations** Finally, we mention some commonly accepted rules in chemical stoichiometry. If only the balance of the equation is concerned, we use equal sign, the general chemical equation can be written as

$$0 = \sum_{B} \nu_{B} B$$

where B represents reactants or products, ν_B is the corresponding stoichiometric number. For example, the formation of HI from H_2 and I_2,

$$0 = 2HI - H_2 - I_2 \qquad or \qquad H_2 + I_2 = 2HI$$

If we stress that the reaction is in equilibrium, we use two half-arrows,

$$H_2 + I_2 \rightleftharpoons 2HI$$
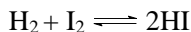
If we want to point out that the reaction happens in a single direction, we use a single arrow. If we are interested in both the forward and the reverse reactions, we use two arrows representing the two directions, respectively,

$$H_2 + I_2 \to 2HI , \qquad H_2 + I_2 \rightleftarrows 2HI$$

For an elementary equation, we use a single full arrow,

$$I + H_2 \longrightarrow HI + H$$
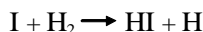
I. Fundamental Principles of Chemical Kinetics

7.2   Rates of Chemical Reactions

Reaction Rate, **Time and Space**   Chemical reaction always proceeds in a certain time interval and in a space with a definite size. A long or short time spent measures the slowness or fastness of the reaction. The size of the space determines the scope of the reaction. Generally, the reaction rate is defined as: The variation of the amount of a reactant or a product in a unit time and in a unit space. Because the variation in a unit time is usually called the rate of change, therefore, the definition can also be expressed as: The rate of change of the amount of a reactant or a product in a unit space. For batch reactors, several specific formulae of the definition are presented as follows: (For continuous reactors, the definition formulae have different forms, referring to Eqs.(8-38, 8-40) of the next chapter.)

Reaction Rate v For a reaction $0 = \sum_B \nu_B B$, according to Eq.(1-48), the differential of the reaction extent ξ is

$$d\xi = dn_B / \nu_B \qquad (7\text{-}1)$$

The reaction rate v is then defined specifically as: The rate of change of the reaction extent ξ in a unit volume,

$$v \overset{\text{def}}{=\!=} \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{\nu_B V}\frac{dn_B}{dt} \qquad (7\text{-}2)$$

The unit of v is $mol\cdot m^{-3}\cdot s^{-1}$, in which dm^3 and min or h can also be used for the units of volume and time. v is always positive irrespective of B selected.

Because $n_B = c_B V$, $dn_B = V dc_B + c_B dV$, Eq.(7-2) can be rewritten as

$$v = \frac{1}{\nu_B} \frac{dc_B}{dt} + \frac{c_B}{\nu_B V} \frac{dV}{dt} \tag{7-3}$$

If keeping the volume of the reaction system unchanged, for instance a gas phase reactor with a definite volume, Eq.(7-3) can be further simplified as

$$v = \frac{1}{\nu_B} \frac{dc_B}{dt} \quad \text{(constant } V\text{)} \tag{7-4}$$

Rate of Consumption ν_A ν_A is defined as: The absolute value of the rate of change of the amount of a reactant A in a unit volume,

$$v_A \overset{\text{def}}{=\!=} -\frac{1}{V} \frac{dn_A}{dt} \tag{7-5}$$

The unit of ν_A is the same as that of v. To assure a positive rate of consumption ν_A, a negative sign must be added because A is diminishing during the reaction. Similar to Eqs.(7-3) and (7-4),

$$v_A = -\frac{dc_A}{dt} - \frac{c_A}{V} \frac{dV}{dt} \tag{7-6}$$

$$v_A = -\frac{dc_A}{dt} \quad \text{(constant } V\text{)} \tag{7-7}$$

Rate of Formation ν_P ν_P is defined as: The rate of change of the amount of a product P in unit volume,

$$v_P \overset{\text{def}}{=\!=} \frac{1}{V} \frac{dn_P}{dt} \tag{7-8}$$

The unit of ν_P is the same as that of v. The rate of formation ν_P is naturally positive. Similar to Eqs.(7-3) and (7-4),

$$v_P = \frac{dc_P}{dt} + \frac{c_P}{V} \frac{dV}{dt} \tag{7-9}$$

$$v_P = \frac{dc_P}{dt} \quad \text{(constant } V\text{)} \tag{7-10}$$

Rate of Conversion $\dot{\xi}$ Different from the above formulae, irrelevant to a unit volume, $\dot{\xi}$ is simply defined as: The rate of change of ξ,

$$\dot{\xi} \overset{\text{def}}{=\!=} \frac{d\xi}{dt} = \frac{1}{\nu_B} \frac{dn_B}{dt} \tag{7-11}$$

The unit of $\dot{\xi}$ is mol·s^{-1}, in which min or h can also be used for the unit of time. The rate of conversion $\dot{\xi}$ is always positive.

Peculiarities and Mutual Relations of Various Rates   The reaction rate v and the rate of conversion $\dot{\xi}$ are defined on the basis of the reaction

extent ξ, independent of the selection of the substance B, therefore, they are standard definitions. Here v does not depend on the size of the reaction space (volume) while $\dot{\xi}$ is proportional to the size of the reaction space. The former is used more often than the latter and the rate equations are built primarily on v. Although depending on the selection of substance, the rate of consumption v_A and the rate of formation v_P are conveniently used in practical work and measurements. The mutual relations of various rates are:

$$v = -v_A/\nu_A = v_P/\nu_P = \dot{\xi}/V \tag{7-12}$$

For example, for the reaction of the synthesis of ammonia, we have

$$v = v_{N_2} = v_{H_2}/3 = v_{NH_3}/2 = \dot{\xi}/V$$

7.3   Reaction-Rate Equations

Reaction-Rate Equations   They are also called **Kinetic Equations**. In general, they are mathematical equations quantitatively describing the effect of concentrations of various substances on reaction rates when fixing the other factors. In a broad sense, besides concentrations, temperature and external fields are also included in the equations as factors to influence the rates. This section discusses primarily the former case. **Reaction-rate equations are irrelevant to the types and the sizes of the reactors**.

1. Elementary Reactions

Mass Action Law   The law was proposed by Waage P and Guldberg C M in 1867 and can be expressed in words as: Reaction rate is proportional to the power product of concentrations of various reactants. However, people at that time did not realize that this law is only applicable to elementary reactions.

Rate Equations   Rates of elementary reactions follow the mass action law at not too high concentrations and are not influenced by other reactions, products and inert substances, therefore, rate equations posses a form of a power function. The situation with higher concentration is more complicated and a possible choice is to adopt activities.

Unimolecular Reactions, $A \longrightarrow P$

$$v = kc_A \tag{7-13}$$

Bimolecular Reactions, $2A \longrightarrow P$, $A + B \longrightarrow P$

$$v = kc_A^2, \qquad v = kc_A c_B \qquad\qquad (7\text{-}14)$$

Trimolecular Reactions, $3A \longrightarrow P$, $2A + B \longrightarrow P$, $A + B + C \longrightarrow P$

$$v = kc_A^3, \qquad v = kc_A^2 c_B, \qquad v = kc_A c_B c_C \qquad (7\text{-}15)$$

Molecularity of Reaction   The molecularity with a symbol n of an elementary reaction is the number of reactant molecules in the corresponding chemical equation. Microscopically, it is the number of molecules colliding directly to react. Most of the elementary reactions are unimolecular and bimolecular. Trimolecular reactions are very rare. Quatemolecular reactions are almost impossible because of the negligible probability for the four molecules colliding together simultaneously.

Rate Constant   Parameter k in Eqs.(7-13, 7-14, 7-15) is called the rate constant which is the reaction rate with the concentrations of reactants all at 1mol·m^{-3} or 1mol·dm^{-3}. It is a characteristic property of the elementary reactions depending on temperature. The unit of k is $(\text{mol·m}^{-3})^{1-n} \cdot \text{s}^{-1}$ or $(\text{mol·dm}^{-3})^{1-n} \cdot \text{s}^{-1}$ where n is the molecularity.

2. Complex Reactions

Empirical Rate Equations   The empirical rate equations are usually induced from experimental data.

Theoretical Rate Equations   The theoretical rate equations are derived from reaction mechanisms.

(1) **Rate Equations of Power-Function Type**   Experiences indicate that for many chemical reactions, the relation between the rate and the concentrations c_A, c_B, c_C,… for various substances in reaction can be expressed with the following power function,

$$v = kc_A^\alpha c_B^\beta c_C^\gamma \cdots \qquad\qquad (7\text{-}16)$$

where A, B, C,… are reactants and catalysts in general as well as products and other substances.

Partial Orders   Parameters α, β, γ,… in Eq.(7-16) are called partial orders representing the extents of influence of the substances A, B, C,… on the reaction rate, respectively. They could be positive and negative integers or non-integers. Negative means that the substance retards the reaction.

Reaction Order   The sum of the partial orders is called the reaction

order. The symbol is n, the same as that of the molecularity, $n=\alpha+\beta+\gamma+\cdots$. The corresponding reaction is called a n-order reaction.

Rate Coefficient   Parameter k in Eq.(7-16) is called the rate coefficient which is the reaction rate with the concentrations of substances involved all at $1\,\text{mol}\cdot\text{m}^{-3}$ or $1\,\text{mol}\cdot\text{dm}^{-3}$. It is a characteristic property of the reactions depending on temperature. The unit of k is $(\text{mol}\cdot\text{m}^{-3})^{1-n}\cdot\text{s}^{-1}$ or $(\text{mol}\cdot\text{dm}^{-3})^{1-n}\cdot\text{s}^{-1}$ where n is the reaction order. The "coefficient" adopted here is to distinguish it from the "constant" of the elementary reactions.

Rate Equations Using Rate of Consumption or Rate of Formation Eq.(7-16) turns to

$$v_A = k_A c_A^{\alpha} c_B^{\beta} c_C^{\gamma}\cdots \tag{7-17}$$

$$v_P = k_P c_A^{\alpha} c_B^{\beta} c_C^{\gamma}\cdots \tag{7-18}$$

where k_A or k_P is also called the rate coefficient. According to Eq.(7-12), the relation among k_A, k_P and k is

$$k = -k_A/\nu_A = k_P/\nu_P \tag{7-19}$$

Partial Orders, **Reaction Order and Reaction Coefficient are Characteristic Properties of Reactions**   We should emphasize first that the partial orders can not be simply obtained directly from the stoichiometric numbers in the chemical equation. We can not simply write $\alpha=-\nu_A$, $\beta=-\nu_B,\ldots$ For example, $2N_2O_5\rightarrow4NO_2+O_2$, it is a first order reaction because the rate equation is $v = kc_{N_2O_5}$ by experiment. For another example, $CH_3CHO\rightarrow CH_4+CO$, the rate equation by experiment is $v = kc_{CH_3CHO}^{3/2}$ at the initial time without product indicating a 1.5 order, and $v = kc_{CH_3CHO}^2$ afterwards, a second order reaction. The rate coefficients in the two rate equations are different because of different orders. In short, partial orders, reaction orders and rate coefficients are obtained primarily by experiment. They are possibly to be derived theoretically only if the reaction mechanism is clear and the corresponding molecularities and rate constants of all elementary reactions are known.

(2) **Rate Equations of Non-Power-Function Type**   The most common form is

$$v = \frac{kc_A^{\alpha} c_B^{\beta}\cdots}{1+k' c_A^{\alpha'} c_B^{\beta'}\cdots} \tag{7-20}$$

For example, $H_2+Br_2\rightarrow 2HBr$, referring to 7.13,

$$v = \frac{kc_{H_2}c_{Br_2}^{1/2}}{1+k'\ c_{HBr}c_{Br_2}^{-1}} \qquad (7\text{-}21)$$

On this occasion, it is meaningless to talk about partial orders and the reaction order. Parameters k or k' can be called the rate equation coefficient. This type of equations always indicates a complex reaction mechanism.

7.4   Integrated Reaction-Rate Equations

Because the reaction rate, the rate of consumption and the rate of formation are all first order derivatives, the rate equations are therefore a first order differential equation. After integration, we can obtain relations for the change of concentrations with time which are called integrated reaction-rate equations. The equations show intuitively the characteristics of reaction processes and have many practical applications. The concrete form of an integrated reaction-rate equation depends on the type of the reactor, referring to 8.9 of the next chapter. As shown by experiment, many chemical reactions have orders of simple positive integers, therefore, we will discuss situations when n=0, 1, 2,… at first.

Batch Reactor   In this chapter, to derive the equations, primarily we adopt the batch reactor. Its distinguishing feature is to feed reactants only once then to obtain products after reaction. Other types of reactor will be discussed in 7.10.2 and 8.9. We further suppose a constant volume of the reactor, therefore, Eqs.(7-4, 7-7, 7-10) are used to express the rates,

$$v = \frac{1}{\nu_B}\frac{dc_B}{dt} \quad , \quad v_A = -\frac{dc_A}{dt} \quad , \quad v_P = \frac{dc_P}{dt}$$

In the following derivations, we use v_A for convenience. The concentrations of A at initial time (t=0) and at t are c_{A0} and c_A, respectively.

Concentration of Reactant A Consumed at time t   The symbol adopted is x. It is often used in kinetics and is defined by

$$x \overset{def}{=\!=} c_{A0} - c_A \qquad (7\text{-}22)$$

Half Life $t_{1/2}$ The half life is the time needed to consume one half of the reactant A. It is also often used in kinetics.

1. Zeroth Order Reactions, $n=0$

Rate Equation of the Zeroth Order Reaction　For a reaction with a one-way forward direction, $a\mathrm{A}+b\mathrm{B}\rightarrow p\mathrm{P}$, the zeroth order rate equation is

$$v_\mathrm{A} = -\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}t} = \frac{\mathrm{d}x}{\mathrm{d}t} = k_\mathrm{A} \tag{7-23}$$

Integrated Rate Equation　Rearranging Eq.(7-23) and integrating,

$$-\int_{c_{\mathrm{A}0}}^{c_\mathrm{A}} \mathrm{d}c_\mathrm{A} = k_\mathrm{A}\int_0^t \mathrm{d}t$$

we obtain the integrated rate equation,

$$c_{\mathrm{A}0} - c_\mathrm{A} = x = k_\mathrm{A}t \tag{7-24}$$

Characteristics of Zeroth Order Reactions　Zeroth order reactions are observed mostly in catalytic reactions and in reactions subject to external fields. There are the following characteristics:

(1) Plotting c_A against t, a straight line is obtained indicating that the rate is independent of concentrations. Eq.(7-24) shows that k_A is the negative value of the slope of the line.

(2) Dimension of k_A is $\mathrm{NL^{-3}T^{-1}}$, where N, L, T are the dimension symbols of fundamental physical quantities, the amount of substance, length and time, respectively. The unit of k_A is $\mathrm{mol \cdot m^{-3} \cdot s^{-1}}$ or $\mathrm{mol \cdot dm^{-3} \cdot s^{-1}}$.

(3) Half life $t_{1/2}$ is proportional to the initial concentration $c_{\mathrm{A}0}$ and inversely proportional to k_A. Substitution of $c_\mathrm{A}=c_{\mathrm{A}0}/2$ into Eq.(7-24) yields

$$t_{1/2} = c_{\mathrm{A}0}/2k_\mathrm{A} \tag{7-25}$$

Example　Experimental data of the formation of Cl_2 from the reaction of CCl_4 and H_2O acted by ultrasonic wave are listed in Table 7-1. Figure 7-1 is a corresponding plot of c_{Cl_2} against t showing a straight line indicating a zeroth order reaction. The rate equation and the corresponding integrated form expressed by the product Cl_2 are:
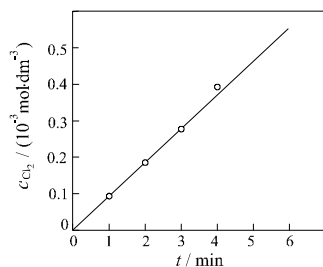

Figure 7-1　Variation of c_{Cl_2} with time

Table 7-1 Variation of c_{Cl_2} with time

t/min	$c_{Cl_2}/10^{-3}\mathrm{mol \cdot dm^{-3}}$
0	0.000
1	0.090
2	0.170
3	0.265
4	0.385

$$v_{Cl_2} = dc_{Cl_2}/dt = k_{Cl_2}, \quad c_{Cl_2} - c_{Cl_2,0} = k_{Cl_2}t$$

Because the initial concentration of Cl_2 is zero, $c_{Cl_2,0} = 0$, the straight line starts with the origin of the coordinates, the slope is k_{Cl_2}. In this example, $k_{Cl_2} = 0.095 \times 10^{-3} mol \cdot dm^{-3} \cdot min^{-1}$.

2. First Order Reactions, $n=1$

Rate Equation of the First Order Reaction　　For a reaction with a one-way forward direction, $a A + b B \rightarrow p P$, if it is first order, we can write,

$$v_A = -\frac{dc_A}{dt} = k_A c_A = \frac{dx}{dt} = k_A(c_{A0} - x) \qquad (7\text{-}26)$$

Integrated Rate Equation　　Rearranging Eq.(7-26) and integrating,

$$-\int_{c_{A0}}^{c_A} \frac{1}{c_A} dc_A = \int_0^t k_A dt$$

we obtain the integrated rate equation,

$$\ln\{c_A\} = \ln\{c_{A0} - x\} = -k_A t + \ln\{c_{A0}\} \qquad (7\text{-}27)$$

or
$$k_A = \frac{1}{t} \ln \frac{c_{A0}}{c_A} = \frac{1}{t} \ln \frac{c_{A0}}{c_{A0} - x} \qquad (7\text{-}28)$$

Characteristics of First Order Reactions

(1) Plotting $\ln\{c_A\}$ against t, a straight line is obtained. Eq.(7-27) shows that k_A is the negative value of the slope of the line.

(2) Dimension and unit of k_A are T^{-1} and s^{-1}, respectively. The value of k_A is independent of the unit of concentration.

(3) Half life $t_{1/2}$ is inversely proportional to k_A independent of c_{A0}. Substitution of $c_A = c_{A0}/2$ into Eq.(7-27) yields

$$t_{1/2} = \ln 2/k_A \qquad (7\text{-}29)$$

Example The experimental kinetic data of the formation of tertiary butyl alcohol by hydrolysis of tertiary butyl bromide in a mixed solvent acetone and 10% of water are listed in Table 7-2. The chemical equation is

Table 7–2 Variation of c_A of $(CH_3)_3CBr$ with t in a mixed solvent of acetone and 10% of water at 25℃

t/h	0	3.15	6.20	10.0	13.5	18.3	26.0	30.8	37.3	43.8
$c_A \times 10^3/(mol \cdot dm^{-3})$	103.9	89.6	77.6	63.9	52.9	35.8	27.0	20.7	14.2	10.1

$$(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$$

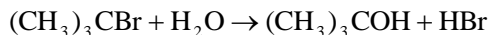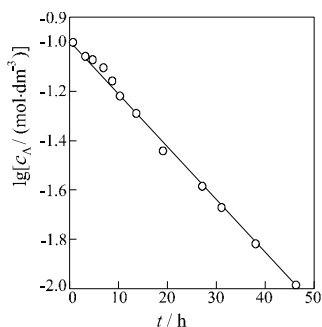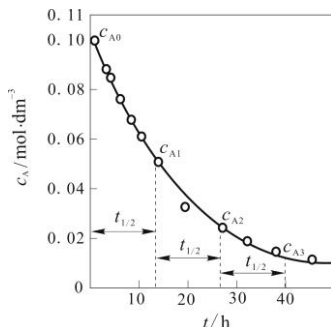Figure 7-2 is a plot of $\ln\{c_A\}$ against t showing a straight line indicating a first order reaction. Rate equation is $v_A = k_A c_A$, with $k_A = 5.18 \times 10^{-2} h^{-1}$ obtained from the slope of the line. Figure 7-3 is a plot of c_A against t

Figure 7–2 $\lg\{c_A\}\sim t$ for hydration of $(CH_3)_3CBr$ Figure 7–3 $c_A\sim t$ for hydration of $(CH_3)_3CBr$

showing that if we take $c_{A1}= c_{A0}/2$, $c_{A2}= c_{A1}/2$, $c_{A3}= c_{A2}/2,\ldots$, the time intervals are the same indicating that the half life is independent of the initial concentration of the tertiary butyl bromide. From Eq.(7-29), $t_{1/2}=13.3h$.

3. Second Order Reactions, $n=2$

Rate Equation of the Second Order Reaction   For a reaction with a one-way forward direction, $aA+bB\rightarrow pP$, if it is second order, the rate equation has two forms,

$$v_A = -\frac{dc_A}{dt} = k_A c_A^2 = \frac{dx}{dt} = k_A(c_{A0} - x)^2 \tag{7-30}$$

$$v_A = -\frac{dc_A}{dt} = k_A c_A c_B = \frac{dx}{dt} = k_A(c_{A0} - x)\left(c_{B0} - \frac{b}{a}x\right) \tag{7-31}$$

Notice that $c_{B0} - c_B = (c_{A0} - c_A)b/a$. In the following, we distinguish five different cases to discuss:

(A) **Rate Equation is** $v_A = k_A c_A^2$

Integrated Rate Equation   Rearranging Eq.(7-30) and integrating,

$$-\int_{c_{A0}}^{c_A} \frac{1}{c_A^2} dc_A = \int_0^t k_A dt$$

we obtain the integrated rate equation,

$$\frac{1}{c_A} - \frac{1}{c_{A0}} = \frac{1}{c_{A0} - x} - \frac{1}{c_{A0}} = k_A t \tag{7-32}$$

or

$$k_A = \frac{c_{A0} - c_A}{tc_{A0}c_A} = \frac{x}{tc_{A0}(c_{A0} - x)} \tag{7-33}$$

Characteristics of Second Order Reactions (A)

(1) Plotting $1/c_A$ against t, a straight line is obtained. From Eq.(7-32), k_A is the slope of the line.

(2) Dimension and unit of k_A are $L^3N^{-1}T^{-1}$ and $mol^{-1} \cdot m^3 \cdot s^{-1}$ or $mol^{-1} \cdot dm^3 \cdot s^{-1}$, respectively.

(3) Half life $t_{1/2}$ is inversely proportional to the product of k_A and c_{A0}. Substitution of $c_A = c_{A0}/2$ into Eq.(7-32) yields

$$t_{1/2} = 1/(k_A c_{A0}) \qquad (7\text{-}34)$$

Example   The experimental kinetic data for the conversion of ammonium cyanate into an isomer urea in aqueous solution at 65°C are listed in Table 7-3. The chemical equation is
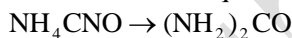
$$NH_4CNO \rightarrow (NH_2)_2CO$$

Figure 7-4 $c_A^{-1} \sim t$ for isomerization of ammonium cvanate

Table 7-3   Variation of c_A of ammonium cyanate versus t in aqueous solution at 65℃

t/min	0	20	50	65	150
c_A / $(mol \cdot dm^{-3})$	0.381	0.265	0.180	0.156	0.086

Figure 7-4 is a plot of $1/c_A$ against t showing a straight line indicating a second order reaction. From the slop, we have

$$k_A = 5.88 \times 10^{-2} dm^3 \cdot mol^{-1} \cdot min^{-1}$$

$$t_{1/2} = [1/(5.88 \times 10^{-2} \times 0.381)] \ min = 44.6 \ min$$

(B) **Rate Equation is $v_A = k_A c_A c_B$, $a = b$, $c_{A0} = c_{B0}$**

At any time, $c_A = c_B$, Eq.(7-31) returns to Eq.(7-30), therefore, the results are completely the same as that of the case (A).

(C) **Rate Equation is $v_A = k_A c_A c_B$, $a \neq b$, $c_{A0}/c_{B0} = a/b$**

At any time, $c_A/c_B = a/b$, substitution into Eq.(7-31) yields

$$v_A = (b/a)k_A c_A^2 \qquad (7\text{-}35)$$

By defining $k_A' = (b/a)k_A$, all results of case (A) can be applied.

(D) **Rate Equation is $v_A = k_A c_A c_B$, $a = b$, $c_{A0} \neq c_{B0}$**

Integrated Rate Equation   Rearranging Eq.(7-31) and integrating,

$$\frac{1}{(c_{A0} - x)(c_{B0} - x)} dx = k_A dt \qquad (7\text{-}36)$$

$$\frac{1}{c_{A0} - c_{B0}} \int_0^x \left(\frac{1}{c_{B0} - x} - \frac{1}{c_{A0} - x} \right) dx = k_A \int_0^t dt$$

we obtain the integrated rate equation,

$$\frac{1}{c_{A0} - c_{B0}} \ln \frac{c_{B0}(c_{A0} - x)}{c_{A0}(c_{B0} - x)} = k_A t$$

or $$k_A = \frac{1}{t(c_{A0} - c_{B0})} \ln \frac{c_{B0}(c_{A0} - x)}{c_{A0}(c_{B0} - x)} \tag{7-37}$$

Characteristics of Second Order Reactions (D)

(1) Plotting $\ln(c_A/c_B)$ or $\ln(c_{B0}c_A/c_{A0}c_B)/(c_{A0} - c_{B0})$ against t, a straight line is obtained. In the latter case, according to Eq.(7-37), the line starts with the origin of the coordinates.

(2) Dimension and unit of k_A are the same as those of the case (A).

Example   The reaction of bromo-isobutane with sodium ethoxide in ethanol solution forming sodium bromide and ethyl isobutyl ether at 95.15 ℃ belongs to this type.

(E) **Rate Equation is** $v_A = k_A c_A c_B$, $a \neq b$, $c_{A0} \neq c_{B0}$

Integrated Rate Equation   Rearranging Eq.(7-31) and integrating, we obtain a most common equation,

$$k_A = \frac{a}{t(bc_{A0} - ac_{B0})} \ln \frac{c_{B0}c_A}{c_{A0}c_B} \tag{7-38}$$

4. nth Order Reactions

Rate Equation of the nth Order Reaction   The simplest form is

$$v_A = -\frac{dc_A}{dt} = k_A c_A^n = \frac{dx}{dt} = k_A(c_{A0} - x)^n \tag{7-39}$$

Integrated Rate Equation   Rearranging Eq.(7-39) and integrating,

$$\int_0^x (c_{A0} - x)^{-n} dx = \int_0^t k_A dt$$

we obtain the integrated rate equation,

$$\frac{1}{n-1}\left[\frac{1}{(c_{A0} - x)^{n-1}} - \frac{1}{c_{A0}^{n-1}}\right] = k_A t \tag{7-40}$$

$$k_A = \frac{1}{t(n-1)}\left[\frac{1}{(c_{A0} - x)^{n-1}} - \frac{1}{c_{A0}^{n-1}}\right] \tag{7-41}$$

Except $n=1$, Eqs.(7-40, 7-41) can be used for reactions of any other orders.

**Characteristics of nth Order Reactions**

(1) Plotting c_A^{1-n} or $(c_{A0} - x)^{1-n}$ against t, a straight line is obtained according to Eq.(7-40).

(2) Dimension of k_A is $L^{3(n-1)}N^{(1-n)}T^{-1}$. As for the unit, refer to 7.3.2(1).

(3) Half life $t_{1/2}$ is inversely proportional to the product of k_A and the initial concentration c_{A0} raise to a power of $n–1$. Substitution of $x=c_{A0}/2$ into Eq.(7-40) yields an equation suitable for reactions of any orders except $n=1$,

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k_A c_{A0}^{n-1}} \qquad (7\text{-}42)$$

Examples   In fact, reactions with $n>2$ are rare. Besides some atomic recombination reactions, it was found that NO reacting with O_2, Cl_2, Br_2 and H_2 are third order reactions, the general chemical equation is

$$2NO + X_2 \rightarrow 2NOX$$
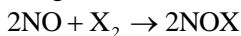
where X represents O, Cl, Br and H. The rate equation is $v = kc_{NO}^2 c_{X_2}$.

5. Applications of Rate Equations

Rate equations can be used to calculate reaction rates, variation of the conversion with time, and the size (volume) of reactors.

Example   The chemical equation of the conversion of sucrose (cane sugar) (A) into glucose and fructose is

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\ H^+\ } C_6H_{12}O_6(\text{Fructose}) + C_6H_{12}O_6(\text{Glucose})$$
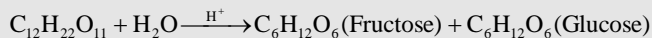
Experimental rate equation is $v_A= k_A c_A$, k_A=0.0193min^{-1}, with a concentration of 0.1mol·dm^{-3} for the catalyst HCl and a temperature of 48℃. Now we have a sucrose solution with a concentration of 0.200 mol·dm^{-3} in a reactor with an effective volume of 2 dm^3 reacting at the above condition. (1) What is the initial rate? (2) How much glucose and fructose can be obtained after 20 min? (3) What is the conversion of the sucrose at 20 mim?

Solution: (1) $t = 0$, $c_{A0} = 0.200$ mol·dm^{-3}. Substituting into rate equation,

$$v_{A0} = k_A \times c_{A0} = (0.0193 \times 0.200)\text{mol} \cdot \text{dm}^{-3}\text{min}^{-1} = 0.00386\text{mol} \cdot \text{dm}^{-3}\text{min}^{-1}$$

(2) Substituting t =20 min into Eq. (7-27) $\ln\{c_A\} = -k_A t + \ln\{c_{A0}\}$,

$\ln(c_A/\text{mol·dm}^{-3})$=–0.0193×20+ln0.200, c_A=0.136 mol·dm^{-3}

$c_{glucose}= c_{fructose}= c_{A0}- c_A$=(0.200–0.136) mol·dm^{-3}=0.064 mol·dm^{-3}

Volume of reactor V=2dm^3. By $n_i =c_iV$, $n_{glucose}= n_{fructose}$=(0.064×2)mol=0.128mol. Given the output, the effective volume of the reactor can be calculated. This is one of the bases of the reactor design.

(3) $\alpha_A = \dfrac{0.200-0.136}{0.200} = 0.32$, conversion is 32%.

7.5   Opposite Reactions

Opposite Reactions   When a reaction is the reverse to another reaction, the combination of the two reactions is called an opposite reaction. In principle, all reactions are opposite reactions, only on some occasions, the

reverse reaction is so slow that can be neglected. In this section, we discuss those reactions where the forward and the reverse reactions both proceed in notable rates, such as synthesis of ammonia, $N_2+3H_2 \rightleftarrows 2NH_3$, transformation of carbon mono-oxide, $CO+H_2O \rightleftarrows CO_2+H_2$, etc. The forward and reverse reactions can be either elementary reactions, or complex reactions.

First Order Opposite Reactions   For an opposite reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$,

when the forward and reverse reactions are both first order, it is the simplest one called a first order opposite reaction. The forward and reverse are signed by subscripts 1 and –1, respectively. Here $v_A = v_B = v$. At the beginning, the concentrations of reactant A and product B are c_{A0} and zero. At a time t, the concentration of A consumed is x which is transformed to B, therefore, the concentrations of A and B are $c_A = c_{A0} - x$ and $c_B = x$, respectively.

Rate Equation of the First Order Opposite Reaction   Rate equations of the forward and reverse reactions are $v_1 = k_1 c_A$ and $v_{-1} = k_{-1} c_B$, respectively, the difference of them is the total rate. The rate equation is

$$v = -\frac{dc_A}{dt} = \frac{dx}{dt} = v_1 - v_{-1} = k_1 c_A - k_{-1} c_B = k_1 c_{A0} - (k_1 + k_{-1})x \quad (7\text{-}43)$$

Integrated Rate Equation of the First Order Opposite Reaction
Integrating the above equation, we obtain the integrated rate equation,

$$\int_0^x \frac{1}{k_1 c_{A0} - (k_1 + k_{-1})x} dx = \int_0^t dt \qquad (7\text{-}44)$$

$$\ln c_{A0} - \ln\left(c_{A0} - \frac{k_1 + k_{-1}}{k_1} x \right) = (k_1 + k_{-1})t \qquad (7\text{-}45)$$

Carrying out an opposite reaction for a long time will result in a dynamic equilibrium with the rates of the forward and reverse reactions approaching counterbalanced because the former continuously slowing down with the decrease of the reactant concentration while the latter gradually rising up with the increase of the product concentration. At equilibrium, $dx/dt=0$, concentrations of the product and the reactant are x_e and $c_{A0}-x_e$, respectively. Substitution into Eq.(7-43) and the integrated form Eq.(7-45) yields

$$k_1 (c_{A0} - x_e) = k_{-1} x_e \qquad (7\text{-}46)$$

$$c_{A0} = (k_1 + k_{-1})x_e/k_1 \qquad (7\text{-}47)$$

$$\ln\frac{x_e}{x_e - x} = (k_1 + k_{-1})t \qquad (7\text{-}48)$$

Characteristics of First Order Opposite Reactions

(1) $\ln\{x_e - x\}$ against t shows linear relation according to Eq.(7-48).

(2) The time needed for consuming $x_e/2$ of the concentration of the reactant A is $\ln2/(k_1+k_{-1})$ obtained by substituting $x = x_e/2$ into Eq.(7-48).

Example   Kinetic data for the transformation of hydroxyl butyric

Table 7-4 Kinetic data for the transformation of hydroxyl butyric acid into lactone in water at 25 ℃

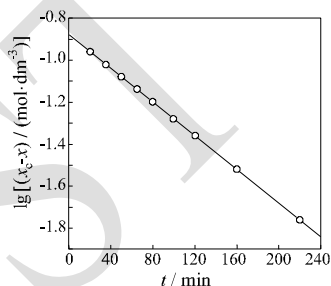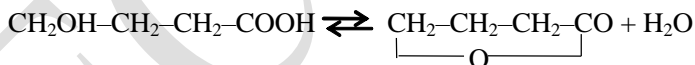| $\dfrac{t}{\min}$	$\dfrac{c_{\text{lactone}}, x}{\text{mol}\cdot\text{dm}^{-3}}$	$\dfrac{x_e - x}{\text{mol}\cdot\text{dm}^{-3}}$	$\lg\{x_e - x\}$
21	0.0241	0.1086	-0.964
36	0.0373	0.0954	-1.020
50	0.0499	0.0828	-1.082
65	0.0610	0.0717	-1.144
80	0.0708	0.0619	-1.208
100	0.0811	0.0516	-1.287
120	0.0900	0.0427	-1.369
160	0.1035	0.0292	-1.534
220	0.1155	0.0172	-1.764
47h	0.1328 (x_e)		
60h	0.1326 (x_e)		

Figure 7-5 Kinetic curve for the

transformation of hydroxyl butyric acid

acid into lactone in water at 25 ℃ are listed in Table 7-4. The chemical reaction is

$$CH_2OH\text{–}CH_2\text{–}CH_2\text{–}COOH \rightleftarrows CH_2\text{–}CH_2\text{–}CH_2\text{–}CO + H_2O$$
$$\underset{O}{\underline{\qquad\qquad\qquad\qquad}}$$

The initial concentration of hydroxyl butyric acid, $c_{A0}=0.1823$ mol·dm^{-3}. Figure 7-5 plots $\lg\{x_e - x\}$ listed in the Table against t showing a straight line indicating a first order opposite reaction. However, from the slope of the line, we can only calculate k_1+k_{-1}. If we want k_1 and k_{-1} separately, the equilibrium constant K_c of the opposite reaction should be used. Because

$$K_c = x_e/(c_{A0} - x_e) \qquad (7\text{-}49)$$

Substitution into Eq.(7-46) yields a relation between K_c and k_1, k_{-1},

$$K_c = k_1/k_{-1} \qquad (7\text{-}50)$$

The Equilibrium Constant K_c is Equal to the Ratio of the Rate Constants (Coefficients) of the Forward and the Reverse Reactions.

Opposite Reactions with Other Orders   Similar rate equations and

integrated rate equations can be established.

Most Favorable Temperature of Exothermic Opposite Reactions

Substitution of Eq.(7-50) into Eq.(7-43) yields

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k_1(c_{A0} - x) - \frac{k_1}{K_c}x \qquad (7\text{-}51)$$

Both k_1 and K_c in the equation depend on temperature, the former always increases with increasing temperature, while the latter decreases with increasing temperature for an opposite reaction with its forward component exothermic. On this occasion, the two terms on the right side of Eq.(7-51) both increase with increasing temperature resulting in a maximum for the temperature dependence of the reaction rate at a given conversion because the larger K_c at low temperature leading to a greater contribution by the first term while at a higher temperature, the smaller K_c leading to a larger contribution by the second term.

Example Figure 7-6 shows the temperature dependence of the relative rate of $SO_2 + \frac{1}{2}O_2 \rightleftarrows SO_3$ at different conversions. Each curve with a maximum corresponds to a definite conversion. The corresponding temperature T_m at the maximum is called the most favorable temperature at this conversion which decreases with the increasing conversion. In industry, to try all efforts to carry out this sort of reactions the closer to T_m the possible, the multi-stage heat-exchange type reactors are always adopted, where the reaction mixture left from each stage will be cooled in a heat exchanger by the cold import gas. Figure 7-7 shows a four-stage heat-exchange type reactor and the corresponding operation sketch diagram. The dash line in Figure 7-6 is the most favorable temperature line.

Figure 7-6 Temperature dependence of relative reaction rate of SO_2 at different conversions

The a_1b_1 line demonstrates that the temperature and the conversion increase simultaneously when passing through the first-stage catalyst, b_1a_2 displays the decrease of temperature when passing through the heat exchanger,…,
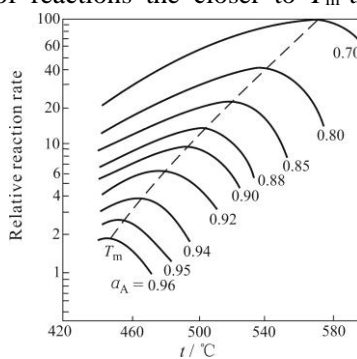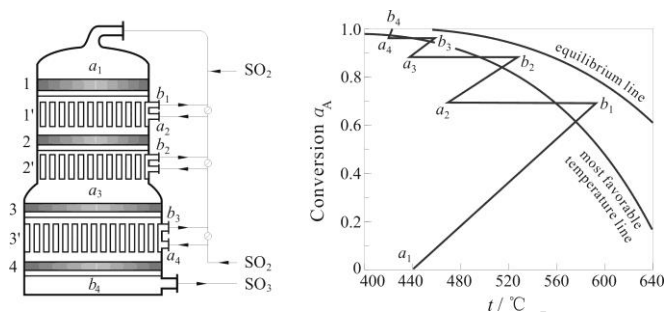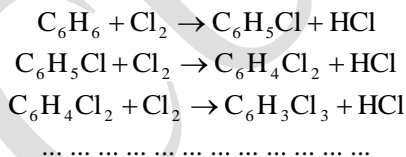
Figure 7-7 A four-stage reactor for the oxidation of SO_2 and the corresponding operation sketch diagram.   1, 2, 3, 4- catalyst layers, 1', 2', 3'- heat exchanger

a_4b_4 shows that the conversion reaches 99% after the fourth-stage catalyst.

7.6   Consecutive Reactions

Consecutive Reactions   When a certain product of a reaction is a reactant of another reaction (the later is not the reverse reaction of the former), the combination of these reactions is called a consecutive reaction. For example, the chlorination of benzene in liquid phase is a combination of the following reactions,

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl$$
$$C_6H_5Cl + Cl_2 \rightarrow C_6H_4Cl_2 + HCl$$
$$C_6H_4Cl_2 + Cl_2 \rightarrow C_6H_3Cl_3 + HCl$$
$$... ... ...$$

The product chloro-benzene of the first reaction is the reactant of the second reaction and the product dichloro-benzene of the second reaction is the reactant of the third reaction… Each step could be either an elementary reaction or a complex reaction.

First Order Consecutive Reactions   For a consecutive reaction

$$A \xrightarrow{\ k_1\ } B \xrightarrow{\ k_2\ } C$$
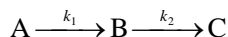
when both the reactions 1 and 2 are first order, it is the simplest one called a first order consecutive reaction. Here $v_A = v_B = v_C = v$. At initial time $t=0$, concentrations of the reactant A, the intermediate B and the product C are c_{A0} and $c_{B0} = c_{C0} = 0$, respectively.

Rate Equations of the First Order Consecutive Reaction   For the three substances in the above reaction, we can write respectively,

$$v_A = -\frac{dc_A}{dt} = k_1 c_A \tag{7-52}$$

$$v_B = \frac{dc_B}{dt} = k_1 c_A - k_2 c_B \tag{7-53}$$

$$v_C = \frac{dc_C}{dt} = k_2 c_B \tag{7-54}$$

Only two of the three equations are independent because $v_B = v_A - v_C$.

Integrated Rate Equation of the First Order Consecutive Reaction

Integrating Eq.(7-52) first, we obtain

$$c_A = c_{A0} e^{-k_1 t} \tag{7-55}$$

Substitution into Eq.(7-53) yields

$$\frac{dc_B}{dt} + k_2 c_B = k_1 c_{A0} e^{-k_1 t} \tag{7-56}$$

This is a first order linear differential equation which can be solved by standard procedure. Combining with $c_A + c_B + c_C = c_{A0}$, we obtain

$$c_B = c_{A0} \frac{k_1}{k_2 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{7-57}$$

$$c_C = c_{A0} \left(1 - \frac{k_2 e^{-k_1 t} - k_1 e^{-k_2 t}}{k_2 - k_1} \right) \tag{7-58}$$

Eqs.(7-55, 7-57, 7-58) are the integrated rate equations expressing variations of c_A, c_B and c_C with t.

Variations of Concentrations with Time   Referring to Figure 7-8, at the beginning stage of the reaction, the rate of formation is greater than the rate of consumption for the intermediate B because of the larger concentration of A and the smaller concentration of B. With the gradually consumption of A and accumulation of B, the rate of consumption is gradually greater than the rate of formation for B resulting in an appearance of a maximum of the concentration of the intermediate B. This is the most remarkable peculiarity of consecutive reactions. At the maximum, $c_B = c_{B,max}$, $dc_B/dt=0$, $t=t_{max}$, differentiating Eq.(7-57) against t, we obtain

$$\frac{dc_B}{dt} = c_{A0} k_1 \frac{k_2 e^{-k_2 t_{max}} - k_1 e^{-k_1 t_{max}}}{k_2 - k_1} = 0 \tag{7-59}$$

$$t_{max} = \frac{\ln(k_2/k_1)}{k_2 - k_1} \tag{7-60}$$

Substitution into Eq.(7-57) yields

$$c_{B,max} = c_{A0}\left(\frac{k_1}{k_2}\right)^{\frac{k_2}{k_2-k_1}} \tag{7-61}$$

Using Eqs.(7-60, 7-61), k_1 and k_2 can be obtained by t_{max} and $c_{B,max}$ at the maximum of c_B.

Stable and Unstable Intermediates   As shown in Eq.(7-61), the ratio of the maximum value $c_{B,max}$ and c_{A0} is determined by k_1/k_2. When k_1/k_2 is larger, $c_{B,max}/c_{A0}$ is larger too, indicating a higher concentration of B in a broad time interval. In this case, B can be viewed as a stable intermediate.
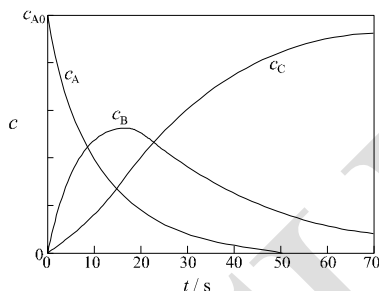

Figure 7-8 Variations of concentrations of A, B and C   Figure 7-9   Kinetic curves of a consecutive
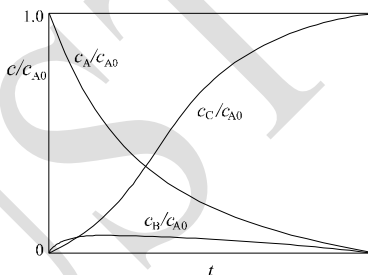   with time for a first order consecutive reaction.   reaction when forming an unstable intermediate.

When k_1/k_2 is smaller, $c_{B,max}/c_{A0}$ is smaller too, indicating a lower concentration of B because it participates in the other reaction soon after its formation. In this case, B can be looked at as an unstable intermediate. Figure 7-8 describes the former while the latter is sketched in Figure 7-9. For the case of unstable intermediate B, because of the small value, c_B can be treated approximately as unchanged with time at a broad time interval,

$$\frac{dc_B}{dt} \approx 0 \tag{7-62}$$

Substitution into Eq.(7-53), we obtain

$$k_1 c_A = k_2 c_B \tag{7-63}$$

This equation indicates that the intermediate B is at a steady state with the rate of formation counterbalancing the rate of consumption. This is a typical situation for a complex reaction composed of several elementary reactions. Eq.(7-62) can be used to derive a theoretical rate equation from the reaction mechanism, referring to 7.12(2), the steady-state approximation.

Example   For the stable intermediates, the alkylation reaction of cumene (isopropyl benzene) and n-butene in the presence of a catalyst HF is an example.

$$i - C_3H_7 - C_6H_5 \rightarrow i - C_3H_7 - C_6H_4 - (s - C_4H_9) \rightarrow$$
$$i - C_3H_7 - C_6H_3 - (s - C_4H_9)_2$$
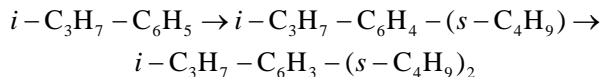
For the unstable one, the hydration of diphenyl chloromethane with a very small concentration of the intermediate is an example.

$$(C_6H_5)_2CHCl \rightarrow (C_6H_5)_2CH^+ \rightarrow (C_6H_5)_2CHOH$$

Consecutive Reactions with Other Orders   Similar rate equations and integrated forms can be established.
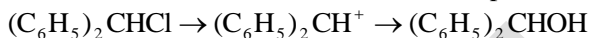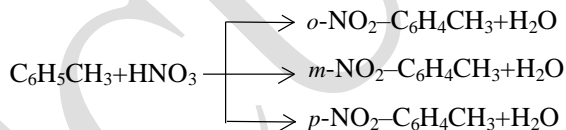
7.7   Parallel Reactions

Parallel Reactions   When the reactants participate in two or more reactions independently and simultaneously, the combination of these reactions is called a parallel reaction. For example, the nitration of toluene forms ortho-, meta- and para-nitrotoluene,

$$C_6H_5CH_3 + HNO_3 \longrightarrow \begin{cases} o\text{-}NO_2\text{-}C_6H_4CH_3 + H_2O \\ m\text{-}NO_2\text{-}C_6H_4CH_3 + H_2O \\ p\text{-}NO_2\text{-}C_6H_4CH_3 + H_2O \end{cases}$$

Generally, the reaction with higher rate and more products formed is called the principal reaction. Correspondingly, the others are called side reactions. They could be either elementary reactions or complex reactions.

First Order Parallel Reactions   When the two component reactions are both first order, it is the simplest one called a first order parallel reaction,

$$A \begin{cases} \xrightarrow{k_1} B \\ \xrightarrow{k_2} C \end{cases}$$
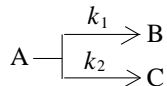
Here $v_A = v_B = v_C = v$. At initial time, the concentration of the reactant A is c_{A0}, those of the products are usually supposed to be zero, $c_{B0} = c_{C0} = 0$.

Rate Equations of the First Order Parallel Reaction   For the above two reactions, we can write respectively,

$$v_B = \frac{dc_B}{dt} = k_1 c_A \qquad (7\text{-}64)$$

$$v_C = \frac{dc_C}{dt} = k_2 c_A \tag{7-65}$$

$$v_A = -\frac{dc_A}{dt} = v_B + v_C = (k_1 + k_2)c_A \tag{7-66}$$

Integrated Rate Equation of the First Order Parallel Reaction
Rearranging Eq.(7-66) and integrating, we have

$$c_A = c_{A0} e^{-(k_1+k_2)t} \tag{7-67}$$

Substituting into Eqs.(7-64) and (7-65) respectively and integrating, we have

$$c_B = c_{A0}(1 - e^{-(k_1+k_2)t}) k_1/(k_1 + k_2) \tag{7-68}$$

$$c_C = c_{A0}(1 - e^{-(k_1+k_2)t}) k_2/(k_1 + k_2) \tag{7-69}$$

Eqs.(7-67, 7-68, 7-69) are the integrated rate equations expressing the variation of c_A, c_B and c_C with t.

Characteristics of the First Order Parallel Reactions   From Eqs.(7-68, 7-69),

$$c_B/c_C = k_1/k_2 \tag{7-70}$$

The ratio of the product concentrations of the principal and the side reactions equals the ratio of their rate coefficients. Combining Eq.(7-70) and k_1+k_2 obtained from Eq.(7-67), k_1 and k_2 can be solved.

Parallel Reactions with Other Orders   The above results can be extended. For the following parallel reaction,

$$A+B \underset{k_2}{\overset{k_1}{\longrightarrow}} \begin{matrix} E \\ F \end{matrix} \qquad \begin{matrix} v_E = k_1 c_A^{\alpha_1} c_B^{\beta_1} \\ v_F = k_2 c_A^{\alpha_2} c_B^{\beta_2} \end{matrix}$$

if the reactants A and B have the same partial orders for the two component reactions, $\alpha_1=\alpha_2$, $\beta_1=\beta_2$, similar to Eq.(7-70), the characteristics exist also,

$$c_E/c_F = k_1/k_2 \tag{7-71}$$

Example   Nitration of toluene has the following rate equations,

$$dc_{ortho}/dt = k_{ortho} c_{toluene} c_{nitric\ acid}\ ,\ \ dc_{meta}/dt = k_{meta} c_{toluene} c_{nitric\ acid}$$

$$dc_{para}/dt = k_{para} c_{toluene} c_{nitric\ acid}$$

Experimental results show that the ratio of the concentrations of the three products keeps constant during the reaction process (ortho-, meta- and para-nitrotoluene are 58.5%, 4.4% and 36.8%, respectively). For the nitration of other substituted derivatives of benzene, although the nature of

Table 7-5 Compositions of nitration product of various substituted derivatives of benzene

Substituting group on benzene ring		F	Cl	Br	I	CH_3	CH_2Cl	$CHCl_2$	$COOC_2H_5$	COOH
Composition of product, %	ortho	12.4	30.1	37.6	41.1	58.8	40.9	23.3	28.3	18.5
	meta	trace	trace	trace	trace	4.4	4.2	38.8	68.4	80.2
	para	87.2	69.9	62.4	58.7	36.8	54.9	42.9	3.3	1.3

the derivatives has notable influence on the composition of the nitration products, the same rule also exist, referring to Table 7-5.

7.8　Effect of Temperature on Reaction Rates

Works in Earlier Stage by Van′t Hoff et al　Temperature is a very sensitive factor to influence the reaction rates mainly by changing the rate constants or coefficients. Van't Hoff J H found that in the vicinity of the ambient temperature, for an increase of $10\,°C$, the rate coefficients of ordinary reactions increase by two- to four-fold of the original value,

$$k_{t+10°C}/k_t \approx 2 \sim 4 \tag{7-72}$$

This is known as the Van′t Hoff rule. In 1884, by analogy with the equilibrium constant, he further proposed the following equations,

$$\frac{d\ln\{k\}}{dT} = \frac{E_a}{RT^2} \tag{7-73}$$

$$k = Ae^{-E_a/RT} \tag{7-74}$$

These equations can describe more accurately the temperature dependence of k. However, the meanings of parameters E_a and A in the equations were not clear at that time. Earlier in 1862, Berthelot P E M also proposed an equation with an exponential function,

$$k = Ae^{DT} \tag{7-75}$$

Besides, in 1895, Harcourt A G V and Esson W, who had made great contributions towards the establishment of rate equations, proposed an empirical equation with a power-function form,

$$k = AT^m \tag{7-76}$$

In 1893, Kooij D M, a student of Van′t Hoff, recommended further the following equation which is more accurate than the above equations,

$$k = AT^m e^{-E_0/RT} \tag{7-77}$$

Concept of Activated Molecules　In 1889, Arrhenius S proposed

that not all the molecules but only those activated ones with activation energy E_a can participate in the reaction. The reason of the increase of reaction rate with rising temperature is not because of the strengthening of the average translational velocities of molecules but mainly because of the increase of the number of the activated molecules. There is an equilibrium relation existing between the activated molecules and those ordinary molecules, therefore, the temperature dependence of the rate constant can be described by using the relation between equilibrium constant and temperature with the fraction of the activated molecules determined by the exponential term of Eq.(7-74). This idea gives a clear physical meaning for the empirical equation Eq.(7-74).

Arrhenius Equation   Because of the above correct analysis, Eqs.(7-73, 7-74) are now called the Arrhenius equation which not only can accurately describe the temperature effect on the rate constant, also is consistent with the thermodynamic theory by satisfying the restriction of $K_c=k_1/k_{-1}$ at equilibrium. What is more is that the exponential factor can be derived by the modern rate theories based on statistical mechanics and correspondingly, the factor is now called **Boltzmann factor**. If only the correlation of the experimental results of the temperature dependence of the rate constant is concerned, among those equations Eqs.(7-74), (7-75) and (7-76), empirically, the last one is the most favorable because it can use $\ln\{k\}$ against $\ln\{T\}$ to plot while the former two is using $\ln\{k\}$ against $1/T$ or T, and as known the double logarithm is easier to obtain straight lines than the single logarithm. However, the commonly accepted relation at present for the temperature dependence is Eq.(7-74) or the more accurate Eq.(7-77). This is because of the contribution of Arrhenius.

Pre-Exponential Factor   Parameter A in Eq.(7-74) is called the pre-exponential factor, also called the **frequency factor**.

Arrhenius Activation Energy   Parameter E_a in Eqs.(7-73, 7-74) is called the Arrhenius activation energy defined by

$$E_a \overset{\text{def}}{=\!=} RT^2 \frac{\mathrm{d}\ln\{k\}}{\mathrm{d}T} \tag{7-78}$$

Its physical meaning is: The difference between the average molar energy of the activated molecules of reactants and that of the total reactant molecules.

The larger E_a, the more serious temperature effect, the reaction rate will accelerate more notably when raising temperature. If the variation of temperature is not so large that E_a can be treated as a constant, according to Eqs.(7-73, 7-74),

$$\ln\{k\} = -\frac{E_a}{RT} + \ln\{A\} \quad \text{or} \quad \ln\frac{k_2}{k_1} = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (7\text{-}79)$$

Plotting $\ln\{k\}$ against $1/T$ should give a straight line with a slope of $-E_a/R$ and an intercept of $\ln\{A\}$. If the temperature range is large, E_a will be temperature dependent. Differentiating the more accurate Eq.(7-77) with respect to T yields

$$\frac{\mathrm{d}\ln\{k\}}{\mathrm{d}T} = \frac{E_0 + mRT}{RT^2} \quad (7\text{-}80)$$

E_0 is the activation energy at 0K. Comparing with the definition of E_a,

$$E_a = E_0 + mRT \quad (7\text{-}81)$$

Example　Experimental data of $N_2O_5 \rightarrow N_2O_4 + \frac{1}{2}O_2$ at different temperatures are listed in Table 7-6. Figure 7-10 gives a corresponding

Table 7-6　Rate coefficients of the decomposition of N_2O_5 at various temperatures

$T\,/\,K$	273	298	303	313	328	338
$k \times 10^5\,/\,s^{-1}$	0.0787	3.46	13.5	49.8	150	487
$(1/T) \times 10^3\,/\,K^{-1}$	3.663	3.357	3.247	3.145	3.048	2.959
$\ln\{k\}$	-14.05	-10.27	-8.910	-7.605	-6.502	-5.325

$\ln\{k\}\sim 1/(T/K)$ plot showing a straight line with a slope of -12.40×10^3 and an intercept of 31.36. The Arrhenius activation energy and the pre-exponential factor calculated are respectively,

E_a=12.40 $\times$ 10^3K $\times$ R=103.1kJ·mol^{-1},
A=e$^{31.36}$s^{-1}=4.16$\times10^{13}$ s^{-1}

Figure 7-10　$\ln\{k\}\sim 1/T$ plot for the decomposition of N_2O_5

Other Examples　Table 7-7 lists values of activation energy E_a for several reactions, generally 40~400kJ·mol^{-1}, but mostly 60~250 kJ·mol^{-1}.

Various Types of the Temperature Dependence of the Reaction Rate Coefficients　Refer to Figure 7-11. Type I with exponential temperature dependence is the most commonly met. For type II, the rate
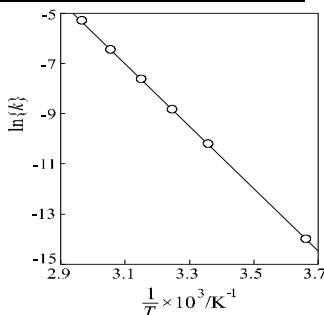
Table 7-7   Arrhenius activation energies for several reactions

Reaction	$E_a /(kJ \cdot mol^{-1})$
$2HI \rightarrow H_2 + I_2$	183
$H_2 + I_2 \rightarrow 2HI$	167
$2NH_3 \rightarrow N_2 + 3H_2$	~330
$2NOCl \rightarrow 2NO + Cl_2$	98.7
$2NO_2 \rightarrow 2NO + O_2$	112
$2H_2O_2 \rightarrow 2H_2O + O_2$	75.3
$CH_3CHO \rightarrow CH_4 + CO$	190
$H_2 + C_2H_4 \rightarrow C_2H_6$	180
$C_2H_5OC_2H_5 \rightarrow C_2H_6 + CO + CH_4$	224
$Cl + NOCl \rightarrow NO + Cl_2$	4.2
$H_2 + Cl_2 \rightarrow 2HCl(photochemial\ reaction)$	25
$2N_2O \rightarrow 2N_2 + O_2$	245
$CH_2I \cdot COO^- + OH^- \rightarrow CH_2OHCOO^- + I^-$	93.7
$C_2H_5Br + OH^- \rightarrow C_2H_5OH + Br^-$	89.5
$CH_3Br + I^- \rightarrow CH_3I + Br^-$	76.1
$CH_3I + OH^- \rightarrow CH_3OH + I^-$	92.9
$C_6H_5N(CH_3)_2 + CH_3I \rightarrow C_6H_5N(CH_3)_3I$	49

Stark J G, Wallace H G, Chemistry Data Book. 2nd. Ed. London: John Murrary, 1982.
86.   Ashmore P G, Principles of Reaction Kinetics. London: W Heffer, 1965. 29.
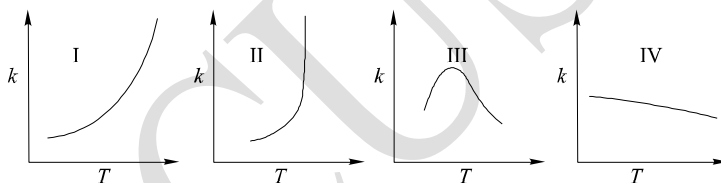
Figure 7-11 Various types of the temperature dependence of the rate coefficients

coefficient increases sharply and suddenly when the temperature rising to a certain value. The reactions of this type are called explosion reactions, referring to 8.5 of the next chapter. For type III, the rate rises at earlier stage then decreases later with the increase of temperature appearing a maximum. Enzyme reactions are typical example, referring to 8.7. As for type IV, reaction rate decreases with increasing temperature. This case is very rare, the formation of NO_2 from NO and O_2 is one of the very few examples.

   Generalized Rate Equations   Substitution of Eq.(7-74) into Eq.(7-16) yields a generalized rate equation representing effects of not only concentrations but also temperature on reaction rates,

$$v = kc_A^{\alpha} c_B^{\beta} c_C^{\gamma} \cdots = Ae^{-E_a/RT} c_A^{\alpha} c_B^{\beta} c_C^{\gamma} \cdots \qquad (7-82)$$

where E_a, A, k and α, β, γ are characteristic parameters of the reaction, and k is determined by E_a and A.

II.   Characteristic Parameters in Chemical Kinetics

7.9   Experimental Methods in Chemical Kinetics

Kinetics Experiment   The basic task of kinetics experiment is to monitor or determine the variations of concentrations of reactants or products with time. After obtaining the kinetics data, using the methods introduced in the next section, those characteristic parameters E_a, A, k, α, β and γ of reactions can be obtained.

Chemical Analysis Methods   Adopting chemical analysis is the most direct way in the experiment. Sampling from the reactor and analyzing at a certain time interval, the time dependence of concentrations of reactants or products can be obtained. To avoid continuously running of reactions after sampling, some measures should be used such as suddenly cooling, rapid diluting, adding retarding agents, or separating the catalyst to cease the reaction. The limitations of these methods are: (1) Many compounds, especially organic ones, are hardly to be determined quantitatively by chemical analysis. (2) Larger reactors are used because large amount of samples are needed. (3) Determinations are of very much time consuming.

Physicochemical Analysis Methods   Time dependence of some physical properties of the reaction system with time is monitored and determined. The properties should have simple relations with concentrations of reactants and products and have notable change before and after the reaction. The most commonly used are electric conductance, optical rotation, absorbance, refractive index, vapor pressure, viscosity, pressure and volume of gas, specific volume of dilute solution, etc. These methods are widely used because of the simplicity and high efficiency.

Relation between Concentrations and Physical Properties Suppose a reaction $a\text{A} + b\text{B} \rightarrow p\text{P}$ with a very large equilibrium constant, the reactant A can be regarded as completely consumed if the time is long enough. Now we have determined values Y_0, Y_t and Y_∞ for a physical property Y at times 0, t and ∞, respectively. If the contributions of various

substances to Y are proportional to or are linear to their concentrations, respectively, and are additive, then the physical property Y of the whole system at different times has the following intuitive relations with the concentration of A,

$$\frac{c_{A0}}{c_{A0} - x} = \frac{Y_\infty - Y_0}{Y_\infty - Y_t} \tag{7-83}$$

$$\frac{x}{c_{A0} - x} = \frac{Y_t - Y_0}{Y_\infty - Y_t} \tag{7-84}$$

where $x = c_{A0} - c_A$. The essentials of these two equations are: The variation of the concentration of A is proportional to the variation of the physical property Y. For instance, when time changes from t to ∞, the concentration of A changes from c_A to 0, the change of A is $c_A = c_{A0} - x$, correspondingly, the change of Y is $Y_\infty - Y_t$.

7.10   Data Processing in Chemical Kinetics

1. Integration Method

It is also called the **trying method**. Substituting the experimental data of a reaction into integrated rate equations of various orders, if the k values calculated kept unchanged within a certain error range for one of those equations, the order of the equation is the order of the reaction. An alternative is the graphic method. For instance, when the various reactants having the same stoichiometric number and the same initial concentration, plot in term of the following four patterns with different orders,

Zero order: plotting c_A against t,   First order: plotting $\ln\{c_A\}$ against t,
 Second order: plotting $1/c_A$ against t,   Third order: plotting $1/c_A^2$ against t.

If one of them exhibiting a straight line, the order of the pattern is the order of the reaction.The rate coefficient or constant can be obtained by the slope of the straight line.

Peculiarities and Limitations   The integration method is always selected because of simplicity and convenience when the reaction order is a simple positive integer. The demerit is that it is not sensitive enough especially for narrower concentration range of experiment resulting in difficulty to distinguish the different orders. Also it can not be used when

the order is a non-integer including a fraction, or a negative value.

Example 1   The chemical equation of a gas phase decomposition of peroxy-ditertiary butyl is $(CH_3)_3COOC(CH_3)_3 \rightarrow C_2H_6 + 2CH_3COCH_3$. Pure peroxy-ditertiary butyl is filled in an isothermal reactor with constant volume. The total pressure of the system increases when the reaction proceeds. The Table lists the total pressure data measured at different times. Determine the reaction order and the rate coefficient.

t/min	0.0	2.5	5.0	10.0	15.0	20.0
p/kPa	1.00	1.40	1.67	2.11	2.39	2.59

Solution: The total pressure p is the relevant physical property Y in this example. If it is a zero order reaction, from Eqs.(7-24) and (7-84), we have

$$k_A = \frac{x}{t} = \frac{c_{A0}(p_t - p_0)}{(p_\infty - p_0)t} \qquad \text{or} \qquad p_t = p_0 + \frac{p_\infty - p_0}{c_{A0}}k_A t \qquad (7\text{-}85)$$

If it is a first order reaction, from Eqs.(7-28) and (7-83), we have

$$k_A = \frac{1}{t}\ln\frac{c_{A0}}{c_{A0}-x} = \frac{1}{t}\ln\frac{(p_\infty - p_0)}{(p_\infty - p_t)} \qquad (7\text{-}86)$$

When the reaction proceeds to the end, the total pressure is three times as large as the initial pressure, $p_\infty = 3p_0$, Eq.(7-86) turns to

$$\ln 2p_0 - \ln(3p_0 - p_t) = k_A t$$

If it is a second order reaction, from Eqs.(7-33) and (7-84) and substituting $p_\infty = 3p_0$, we have

$$k_A = \frac{x}{tc_{A0}(c_{A0}-x)} = \frac{(p_t - p_0)}{tc_{A0}(p_\infty - p_t)} = \frac{(p_t - p_0)}{tc_{A0}(3p_0 - p_t)}$$

or

$$\frac{1}{3p_0 - p_t} - \frac{1}{2p_0} = \frac{c_{A0}k_A t}{2p_0}$$

Therefore, plotting p_t or $\ln[2p_0/(3p_0-p_t)]$ or $1/(3p_0-p_t)$ against t, respectively, the order can be decided by which one exhibiting a straight line. Figure 7-12(a)(b)(c) is the

(a) $p_t \sim t$ plot   (b) $\ln[2p_0/(3p_0 - p_t)] \sim t$ plot   (c) $1/(3p_0 - p_t) \sim t$ plot
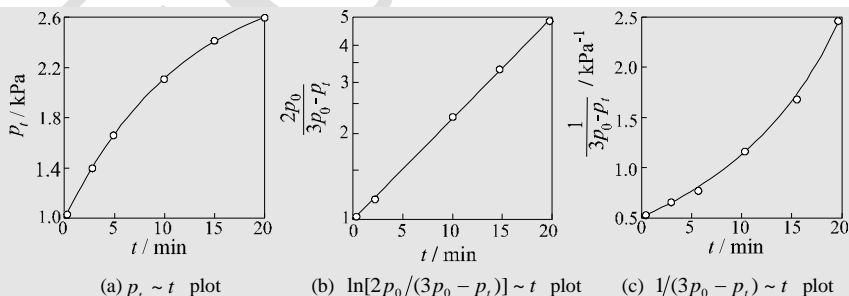
Figure 7-12 Determination of rate equation for example 1 by integration method

corresponding plot indicating that it is a first order reaction and the rate coefficient $k_A = 0.08 \text{min}^{-1}$ is obtained by the slope of the straight line of Figure 7-12(b).

Note: If the reactant A is partially decomposed at $t=0$, $p_\infty = 3p_0$ is invalid. In this case, the experimentally determined p_∞ should be used.

Example 2   The conversion of sucrose can be monitored by measuring the angle of optical rotation of a plane-polarized light passing through the solution. Example in 7.4 has written the chemical equation in which the reactant sucrose is dextro-rotated while

the product fructose and glucose mixture is levo-rotated. As the hydrolysis proceeds, the dextrorotatory angle decreases continuously, and at the end of the reaction, the system converts into levo and reaches a maximum levorotatory angle. The hydrolysis of sucrose is therefore called conversion. The Table presents data of hydrolysis of a 20% aqueous sucrose solution in the presence of $0.5 \text{mol} \cdot \text{dm}^{-3}$ lactic acid measured at 25 ℃

t/min	a_t /(°)	$(a_t - a_\infty)$/(°)	$k_A \times 10^5$ / min^{-1}
0	34.50(α_0)	45.27	—
1435	31.10	41.87	5.44
4315	25.00	35.77	5.46
7070	20.16	30.93	5.39
11360	13.98	24.75	5.32
14170	10.61	21.38	5.29
16935	7.57	18.34	5.34
19815	5.08	15.85	5.30
29925	−1.65	9.12	5.35
∞	−10.77	0.00	—

where α_0, α_t and α_∞ are angles of optical rotation at the initial time, time t, and the end of the hydrolysis, respectively. Determine the reaction order and the rate coefficient.

Solution: Here the angle of rotation is the relevant physical property Y. Suppose it is a first order reaction, according to Eqs.(7-28) and (7-83),

$$k_A = \frac{1}{t}\ln\frac{c_{A0}}{c_{A0}-x} = \frac{1}{t}\ln\frac{\alpha_0-\alpha_\infty}{\alpha_t-\alpha_\infty} \qquad (7\text{-}87)$$

Note that the angle of dextro is positive and that of levo is negative. Calculation results are listed in the Table showing that those calculated k_As are almost kept unchanged within an accepted error indicating a first order for the sucrose conversion. The average value of k_A is $5.36 \times 10^{-5} \text{min}^{-1}$. Figure 7-13 is the corresponding plot of $\ln\{\alpha_t-\alpha_\infty\}$ listed in the Table against t showing a straight line. From the slope of the line,

$$k_A = 5.37 \times 10^{-5} \text{min}^{-1}.$$

Figure 7-13 $\ln\{\alpha_t-\alpha_\infty\}\sim t$ plot for the conversion of sucrose

Note: For the first order reactions, the initial point can start at any time. For instance, taking t=4315min (71.92h) as t=0, the straight line in Figure 7-13 translates toward left with the slope unchanged.

Example 3 For the reaction $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$, mix equal volumes of $CH_3COOC_2H_5$ and NaOH solutions with the same concentration of $0.0200 \text{ mol} \cdot \text{dm}^{-3}$. The reaction can be monitored by measuring the electrical conductance G of the reaction mixture because of the large difference between the conductivities of reactants and products also because of the proportionality between the conductivity and the concentration of substance in dilute solution. Data are listed in the Table. Determine the reaction order and the rate coefficient.

t/min	0	5	9	15	20	25	∞
$G \times 10^3$ /S	2.400	2.024	1.836	1.637	1.530	1.454	0.861
k_A /$\left(\text{dm}^3 \cdot \text{mol}^{-1} \cdot \text{min}^{-1}\right)$		6.47	6.43	6.55	6.50	6.38	

Solution: Here the conductance G is the relevant physical property Y. Suppose it is a second order reaction. According to Eqs.(7-33) and (7-84),

$$k_A = \frac{x}{tc_{A0}(c_{A0}-x)} = \frac{G_0-G_t}{tc_{A0}(G_t-G_\infty)} \qquad (7\text{-}88)$$

c_{A0}=(0.0200/2)mol·dm^{-3}=0.0100 mol·dm^{-3}, the concentration is reduced by half because of the equal volume mixing. Substituting c_{A0} and data listed into the above equation, rate coefficients k_As obtained are written in the same Table showing that they are almost kept
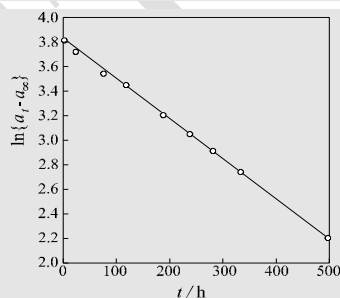
unchanged within an accepted error indicating a second order reaction. The average value of k_A is 6.47 $dm^3 \cdot mol^{-1} \cdot min^{-1}$.

Note: Different from the first order, for the second order reactions, c_{A0} should be provided to calculate k_A when using physical properties to replace the concentration.

2. Differential Method

Suppose the rate equation is $v_A = -dc_A/dt = k_A c_A^n$. Taking logarithm for the both sides, we have

$$\lg\{v_A\} = n\lg\{c_A\} + \lg\{k_A\} \tag{7-89}$$

Plotting $\lg\{v_A\}$ against $\lg\{c_A\}$ should give a straight line. The reaction order n and the rate coefficient k_A are obtained by the slope and the intercept, respectively. The order is not limited by positive integer. This is called the differential method because the rate $v_A = -dc_A/dt$ is a derivative.

(1) **Initial Rate Method**   Running a series of kinetics experiments with different initial concentrations, determining the corresponding initial rates by the graphic method, substituting into Eq.(7-89), the order obtained is called the **true order** n_c. The advantage of this method is that the rate determination will not be disturbed by the products.

(2) **One Run Method**   Using a whole $c_A \sim t$ curve given by one run of kinetics experiment, adopting the graphic method or making correlation by polynomial, the rates v_{AS} can be obtained by the absolute values of the slopes at various times. Substituting v_{AS} into Eq.(7-89), the order obtained is expressed by n_t. If $n_t > n_c$, it means that the products play retarding effect. If $n_t < n_c$, it predicts that the products play accelerating effect. The latter case is usually called the auto-catalytic reaction.

(3) **Isolating Variables Method**   Suppose the rate equation is $v_A = k_A c_A^\alpha c_B^\beta$. Making one of the reactants for example B in great excess, then we measure the variation of concentration of the other reactant A with time. In this case, the rate equation is simplified to $v_A = k_A' c_A^\alpha$. The reaction is then called a pseudo α order reaction. k_A' and α can be obtained by the differential method.

(4) **Differential Reactors**   For the differential method, it is needed to take derivatives for the relation of the variation of concentration with time resulting in an enhancement of error in the data procession. In the differential reactors, by keeping concentrations unchanged with time and in

space, the reactors can avoid the demerit brought by the derivation but still have the advantage of the differential method. Those ordinary reactors with changing concentrations in space and with time are correspondingly called the **integral reactors**. The following are two types of differential reactors:

Continuous Tank Reactor   This reactor is mostly used for studying rates of liquid phase reactions, referring to the left of Figure 7-14. The volume of the inflow material in unit time is the flow rate q_V and the concentration of the reactant is c_{A0}. To make the liquid stuff in the tank homogeneous, strong stirring is

Figure 7-14 Differential reactors

applied. After reaching steady state, both the concentration of the reactant in the tank and that of the outflow are c_A. If the volume of the liquid stuff in the reactor V_R is kept unchanged, the rate of consumption is

$$v_A = q_V \frac{c_{A0} - c_A}{V_R} \qquad (7\text{-}90)$$

Refer to Eq.(8-40) of the next chapter,

Continuous Tubular Reactor with a Loop   Referring to the right of Figure 7-14, because of the strong back mixing formed due to that the majority of the materials just flows out from the reactor flows back into the reactor again along a loop build from the outlet to the inlet with the help of a pump installed, the concentration gradient in the tubular reactor disappears keeping a homogeneous state. The rate of consumption of A is also calculated by Eq.(7-90). The reactor is usually used for studying gas phase reactions including gas-solid catalytic reactions.

Example 4   Under isochoric and isothermal (599K) conditions, partial pressures of butadiene and their variation rates at different times for the dimerization reaction of butadiene $2C_4H_6 \rightarrow (C_4H_6)_2$ are listed in the Table. Determine the rate equation.

t/min	10	30	50	70	85
$p_{C_4H_6}$ / kPa	73.6	58.0	48.3	41.7	37.9
$(-dp_{C_4H_6}/dt)/(kPa \cdot min^{-1})$	0.96	0.59	0.40	0.29	0.27

Solution: Suppose they are ideal gases, $p \propto c$. v_A in Eq.(7-89) is replaced by

$-dp_{C_4H_6}/dt$. Take two points arbitrarily from the Table,

$$n = \frac{\lg(v_{10}/v_{30})}{\lg(p_{10}/p_{30})} = \frac{\lg(0.96/0.59)}{\lg(73.6/58.0)} = 2.2 \quad , \quad n = \frac{\lg(v_{30}/v_{70})}{\lg(p_{30}/p_{70})} = \frac{\lg(0.59/0.29)}{\lg(58.0/41.7)} = 2.1$$

$n \approx 2$, it is a second order reaction. Plotting $\lg\{v_A\}$ against $\lg\{c_A\}$, a straight line is obtained. The slope is the order $n=2$. The intercept gives $k_A=0.85 \mathrm{dm^3 \cdot mol^{-1} \cdot min^{-1}}$ by using $c_A = p_A/RT$. The rate equation is

$$v_A = 0.85 \mathrm{dm^3 \cdot mol^{-1} \cdot min^{-1}} \cdot c_A^2$$

3. Half-Life Method

Suppose the rate equation is $v_A = -dc_A/dt = k_A c_A^n$, according to Eq.(7-42), the half life is expressed by $t_{1/2} = (2^{n-1}-1)/[(n-1)k_A c_{A0}^{n-1}]$ except $n=1$. Taking logarithm for the both sides,

$$\lg\{t_{1/2}\} = (1-n)\lg\{c_{A0}\} + \lg\left\{\frac{2^{n-1}-1}{k_A(n-1)}\right\} \tag{7-91}$$

Plotting $\lg\{t_{1/2}\}$ against $\lg\{c_{A0}\}$ gives a straight line. The reaction order n and the rate coefficient k_A can be obtained by the slope and the intercept of the line, respectively.

# III. Reaction Mechanisms

7.13   Reaction Mechanisms and Rate Equations

The pattern or sequence of elementary reactions in composing a complex reaction is called the reaction mechanism. We should emphasize first that the reaction mechanism is still a macroscopic concept which does not involve the microscopic mechanism of the change of molecules and the microscopic chemical kinetics.

1. Two Categories of Reaction Mechanisms

(1) **Reaction Mechanisms Composed of Limited Elementary Reactions**   Composing forms are mainly the opposite reaction, the consecutive reaction and the parallel reaction that have introduced above.
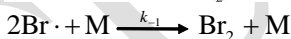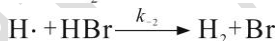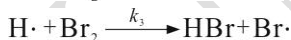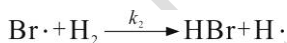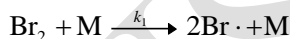
Example   Reaction of ozone decomposition to oxygen $2O_3 \rightarrow 3O_2$ is composed of the following three steps,

$$O_3 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_2 + O + M$$

$$O + O_3 \xrightarrow{k_2} 2O_2$$
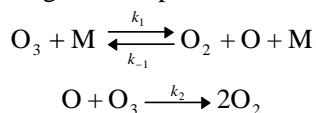
These elementary reactions are numbered by 1, 2,… according to the sequence from earlier to later, correspondingly, –1, –2,… for the reverse reactions. In this example, 1 and –1 compose an opposite reaction and M in reaction 1 could be any molecule which collides with a O_3 molecule to make the O_3 excited and decomposed. 1 and 2 are bi-molecular reactions composing a consecutive reaction. –1 is a tri-molecular reaction.

(2) **Chain Reaction Mechanisms Composed of Unlimited Elementary Reactions**   Composing forms still include the opposite reaction, the consecutive reaction and the parallel reaction but they can be transferred one by one infinitely as a chain.

Example The formation of hydrogen bromide from hydrogen and bromine $H_2 + Br_2 \rightarrow 2HBr$ in gas phase is composed of the following steps. These elementary reactions are also numbered by 1, 2,…, –1, –2,…

$$Br_2 + M \xrightarrow{k_1} 2Br \cdot + M$$
$$Br \cdot + H_2 \xrightarrow{k_2} HBr + H \cdot$$
$$H \cdot + Br_2 \xrightarrow{k_3} HBr + Br \cdot$$
$$H \cdot + HBr \xrightarrow{k_{-2}} H_2 + Br$$
$$2Br \cdot + M \xrightarrow{k_{-1}} Br_2 + M$$

Chain Initiation   In the elementary reaction 1, a Br_2 molecule is excited by colliding with any other molecule M creating two Br atoms. The Br atom with a symbol Br· is called a free radical because of the unpaired electron '·'. It is this free radical that makes the reaction proceeds further. This reaction of creating free radicals is called the chain initiation.

Chain Propagation   In elementary reactions 2, 3 and –2, a new free radical and a new molecule are formed by the reaction between a free radical such as Br· or H· and a molecule such as H_2, Br_2 or HBr. This new free radical can react with another molecule making the chain transfer infinitely. These reactions are therefore called the chain propagation. In the above example of ozone decomposition, O is also a free radical but it disappears soon because of its reaction with O_3 forming O_2. On the contrary, in the chain propagation of this example, the free radical does not vanish all along. Chain propagation is an unlimited consecutive reaction, and 2, –2 compose an opposite reaction. Besides free radicals, the propagation of

chain can also be bore by cations, anions and some active groups.

Chain Termination　In the elementary reaction –1, two Br· free radicals combine forming a Br_2 molecule and transferring energy to another molecule M leading to the vanishing of the free radical. This reaction is then called the chain termination. The reaction –1 is a tri-molecular reaction and composes a consecutive reaction with 1.

2. Establishment of Rate Equations of Complex Reactions from Reaction Mechanisms

Complex reactions are composed of a series of elementary reactions through the forms of the opposite, consecutive and parallel reactions. By using the methods introduced in 7.5, 7.6 and 7.7, the rate equations can be derived in principle. However, concise expressions are always difficult to obtain because of the increasing complexities with the number of elementary reactions. In practice, the following effective approximate methods have been developed.

(1) **Pre-Equilibrium Approximation**　Among all the elementary reactions in a reaction mechanism, if one of them has very slow reaction rate comparing with others, this elementary reaction is then in a controlling position and can be called the rate-controlling step. The reaction rate of this controlling step can be considered equal to the rate of the complex reaction approximately with all other elementary reactions almost reaching equilibrium.

Example 1　A reaction A+B→C+D has the following mechanism,

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + C + M \quad , \quad I + B \xrightarrow{k_2} D$$

where I is an intermediate. Reaction 2 is the controlling step. Its rate can be considered to be equal to the rate of the complex reaction,

$$-\frac{dc_B}{dt} = \frac{dc_D}{dt} = k_2 c_I c_B \tag{7-100}$$

The opposite reaction 1 and –1 can be considered as in equilibrium approximately. From the corresponding equilibrium constant K, we have

$$K = \frac{k_1}{k_{-1}} = \frac{c_I c_C}{c_A} \quad \text{or} \quad c_I = \frac{k_1 c_A}{k_{-1} c_C} \tag{7-101}$$

Substitution into Eq.(7-100) yields rate equation for the complex reaction,

$$v = \frac{dc_D}{dt} = \frac{k_1 k_2}{k_{-1}} \frac{c_A c_B}{c_C} \tag{7-102}$$

Example 2   For the reaction of decomposition of O_3 to O_2 mentioned above in an atmosphere of enough oxygen, suppose the reaction 2 of the intermediate O and O_3 is a rate controlling step, $v_2 = k_2 c_O c_{O_3}$. However, because c_O of the intermediate atom O is very low, dc_O/dt is also small, every O consumed by reaction 2 should be replenished by one O_3 through reaction 1 to maintain the approximate equilibrium between reactions 1 and −1, the rate should be multiplied by 2. Consider alternatively, because of $dc_O/dt = k_1 c_{O_3} - k_{-1} c_{O_2} c_O - k_2 c_{O_3} c_O \approx 0$, $k_1 c_{O_3} - k_{-1} c_{O_2} c_O \approx k_2 c_{O_3} c_O$, we can write, $-dc_{O_3}/dt = k_1 c_{O_3} - k_{-1} c_{O_2} c_O + k_2 c_{O_3} c_O \approx 2 k_2 c_{O_3} c_O$. (This is consistent with the steady state approximation in next paragraph.) The decomposition reaction rate of O_3 is therefore written as

$$-\frac{dc_{O_3}}{dt} = 2 k_2 c_O c_{O_3} \tag{7-103}$$

Substituting the equilibrium relation $K = c_O c_{O_2} / c_{O_3}$ between reactions 1 and −1 into Eq.(7-103), we obtain the rate equation,

$$c_O = \frac{K c_{O_3}}{c_{O_2}} = \frac{k_1 c_{O_3}}{k_{-1} c_{O_2}} \tag{7-104}$$

$$v_{O_3} = -\frac{dc_{O_3}}{dt} = \frac{2 k_1 k_2}{k_{-1}} \frac{c_{O_3}^2}{c_{O_2}} \tag{7-105}$$

The rate equation is consistent with that obtained by experiment, the latter is

$$v_{O_3} = k \frac{c_{O_3}^2}{c_{O_2}} \tag{7-106}$$

Comparing with Eq.(7-105), $k = 2 k_1 k_2 / k_{-1}$, indicating partial orders of 2 and −1 for O_3 and O_2, respectively, O_2 has a retarding effect on the reaction.

Example 3   Experiment showed that $H_2 + I_2 \rightarrow 2HI$ is a second order reaction. This is consistent with the rate equation $v = k c_{H_2} c_{I_2}$ deduced from the mass action law leading to an understanding for a long time that it would be mainly a bi-molecular elementary reaction. This view has been changed later. In 1967, Suillivan J H proved by experiment that this reaction can be accelerated by photo radiation with a wave length of 578nm in the temperature range of 418K~520K. This radiation can only dissociate I_2 but

not H_2 indicating that I atom must be involved in the reaction mechanism under photo radiation. On the other hand, the activation energy of the photo chemical reaction of H_2 and 2I showing no difference with that of the same elementary reaction of the thermal reaction at 633 K～730K indicating that the mechanisms of the reaction with and without photo radiation should be the same. The following mechanism is then proposed,

(a) $I_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2I \cdot + M$, $K = k_1/k_{-1}$

(b) $H_2 + 2I \cdot \xrightarrow{k_2} 2HI$
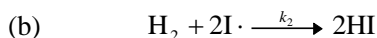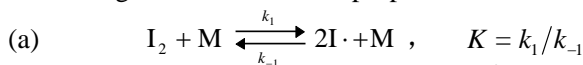
where M represents those H_2 and I_2 molecules existing in the gas phase. At the experimental temperature, k_2 is far less than k_1, therefore reaction (b) is the controlling step with the following rate equation,

$$v = k_2 c_{H_2} c_{I.}^2$$

Reaction (a) is close to equilibrium with $c_{I.}^2 = K c_{I_2}$. Substituting into the above equation with $k=k_2K$,

$$v = k_2 K c_{H_2} c_{I_2} = k c_{H_2} c_{I_2}$$

This result indicates a second order but not a bi-molecular reaction.

(2) **Steady State Approximation**   If the intermediates of the reaction are very active. They will have a very low concentration because once formed, they react with other molecules soon. The concentrations of them can then be considered as unchanged with time, referring to 7.6. The intermediates are then at a steady state. The rate of formation equals the rate of consumption approximately for them when the reaction proceeds.

Example 1   A reaction A+B→C+D has the following mechanism,

$$A + M \xrightarrow{k_1} I + C + M ,   I + C + M \xrightarrow{k_{-1}} A + M$$

$$I + B \xrightarrow{k_2} D$$
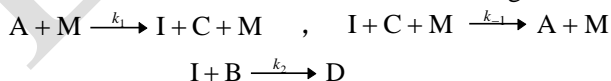
where M represents any arbitrary molecule and I is an active intermediate at a steady state. According to Eq.(7-62),

$$dc_I/dt = k_1 c_A c_M - k_2 c_I c_B - k_{-1} c_I c_C c_M = 0 \tag{7-107}$$

$$c_I = \frac{k_1 c_A c_M}{k_2 c_B + k_{-1} c_C c_M} \tag{7-108}$$

Because $v = -dc_B/dt = dc_D/dt = k_2 c_I c_B$, substitution of Eq.(7-108) yields a rate equation,

$$v = \frac{\mathrm{d}c_D}{\mathrm{d}t} = \frac{k_1 k_2 c_A c_B c_M}{k_2 c_B + k_{-1} c_C c_M} \tag{7-109}$$

It is interesting that if $k_2 c_B$ is very small and negligible, Eq.(7-109) is consistent with Eq.(7-102). This is not surprising because in terms of Eq.(7-107), we have $k_1 c_A c_M - k_{-1} c_I c_C c_M \approx 0$, it is just the pre-equilibrium approximation. However, this approximation can not be simply regarded as a special case of the steady state approximation because neither the low concentration c_I of the intermediate nor $\mathrm{d}c_I/\mathrm{d}t = 0$ is needed for the pre-equilibrium approximation.

Example 2   For the reaction of decomposition of O_3 mentioned above, the rate of accumulation of the intermediate O atoms is

$$\mathrm{d}c_O/\mathrm{d}t = k_1 c_{O_3} c_M - k_{-1} c_{O_2} c_O c_M - k_2 c_O c_{O_3} \tag{7-110}$$

In terms of the steady state approximation, $\mathrm{d}c_O/\mathrm{d}t = 0$, combining with Eq.(7-110), the concentration of O atoms is obtained as

$$c_O = \frac{k_1 c_{O_3} c_M}{k_{-1} c_{O_2} c_M + k_2 c_{O_3}} \tag{7-111}$$

Because $-\mathrm{d}c_{O_3}/\mathrm{d}t = k_1 c_{O_3} c_M - k_{-1} c_{O_2} c_O c_M + k_2 c_O c_{O_3}$, substitution of Eq.(7-111) yields the rate equation,

$$v_{O_3} = -\frac{\mathrm{d}c_{O_3}}{\mathrm{d}t} = 2k_1 k_2 \frac{c_{O_3}^2 c_M}{k_{-1} c_{O_2} c_M + k_2 c_{O_3}} \tag{7-112}$$

When the oxygen is sufficient, $c_{O_2} \gg c_{O_3}$, $k_2 c_{O_3}$ in the denominator can be neglected. On this occasion, Eq.(7-112) is consistent with Eq.(7-105) obtained by the pre-equilibrium approximation. If it is the decomposition of pure ozone, at the initial time, $c_{O_2} \approx 0$. In this case, M is O_3. Eq.(7-112) turns to a second order rate equation,

$$v_{O_3} = 2k_1 c_{O_3}^2 \tag{7-113}$$

Example 3   For the reaction of the formation of HBr from H_2 and Br_2, the rate equation can be established by applying this approximation. In terms of the mechanism introduced above, the rate of formation of HBr is

$$\frac{\mathrm{d}c_{HBr}}{\mathrm{d}t} = k_2 c_{Br \cdot} c_{H_2} + k_3 c_{H \cdot} c_{Br_2} - k_{-2} c_{H \cdot} c_{HBr} \tag{7-114}$$

where Br· and H· are free radicals. They are both active intermediates. In terms of the steady state approximation,

$$\frac{dc_{Br\cdot}}{dt} = 2k_1 c_{Br_2} c_M - k_2 c_{Br\cdot} c_{H_2} + k_3 c_{H\cdot} c_{Br_2} + k_{-2} c_{H\cdot} c_{HBr} - 2k_{-1} c_{Br\cdot}^2 c_M = 0 \quad (7\text{-}115)$$

$$\frac{dc_{H\cdot}}{dt} = k_2 c_{Br\cdot} c_{H_2} - k_3 c_{H\cdot} c_{Br_2} - k_{-2} c_{H\cdot} c_{HBr} = 0 \quad\quad\quad (7\text{-}116)$$

The steady-state concentrations of Br· and H· can be obtained by solving these simultaneous equations,

$$c_{Br\cdot} = (k_1/k_{-1})^{1/2} c_{Br_2}^{1/2} \quad\quad\quad (7\text{-}117)$$

$$c_{H\cdot} = k_2 (k_1/k_{-1})^{1/2} \frac{c_{H_2} c_{Br_2}^{1/2}}{k_3 c_{Br_2} + k_{-2} c_{HBr}} \quad\quad\quad (7\text{-}118)$$

Subtracting Eq.(7-116) from Eq.(7-114) and substituting Eq.(7-118),

$$\frac{dc_{HBr}}{dt} = \frac{2k_2 (k_1/k_{-1})^{1/2} c_{H_2} c_{Br_2}^{1/2}}{1 + (k_{-2}/k_3) c_{HBr} c_{Br_2}^{-1}} \quad\quad\quad (7\text{-}119)$$

Comparing with Eq.(7-21) obtained by experiment, the two equations are fully consistent with the following relations,

$$k = 2k_2 (k_1/k_{-1})^{1/2} \quad , \quad\quad k' = k_{-2}/k_3$$

If HBr were directly formed by H_2 and Br_2, the activation energy estimated would be 190kJ·mol^{-1}. For the above chain mechanism, $c_{HBr}=0$ at the beginning, the denominator on the right side of Eq.(7-119) degenerates to 1, the activation energy $E_a = E_{a,2} + (E_{a,1} - E_{a,-1})/2$. Experiment gave

$$E_{a,2} = 72\text{kJ·mol}^{-1}, \quad E_{a,1} = 192\text{kJ·mol}^{-1}, \quad E_{a,-1} = 0\text{kJ·mol}^{-1}$$
$$E_a = (72 + 192/2)\text{kJ·mol}^{-1} = 168 \text{ kJ·mol}^{-1},$$

E_a obtained is notably less than 190kJ·mol^{-1}. This leads to the conclusion that the chain mechanism is more reasonable.

(3) **A Revised Method**　　To illustrate the method, take a simplest reaction A→D for example, it has the following mechanism,

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I \quad , \quad\quad I \xrightarrow{k_2} D$$
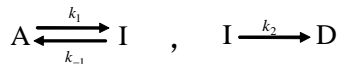
By material balance, among the rates of A, I and D, there is the following relation,

$$-\frac{dc_A}{dt} - \frac{dc_I}{dt} = \frac{dc_D}{dt} = k_2 c_I \quad\quad\quad (7\text{-}120)$$

Applying steady state approximation, $dc_I/dt = k_1 c_A - k_2 c_I - k_{-1} c_I = 0$,

$$c_{\mathrm{I}} = \frac{k_1}{k_{-1} + k_2} c_{\mathrm{A}} \qquad , \qquad \frac{\mathrm{d}c_{\mathrm{I}}}{\mathrm{d}t} = \frac{k_1}{k_{-1} + k_2} \frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} \qquad (7\text{-}121)$$

Here the approximation is relaxed, $\mathrm{d}c_{\mathrm{I}}/\mathrm{d}t$ is not truly zero. Substitution of both c_{I} and $\mathrm{d}c_{\mathrm{I}}/\mathrm{d}t$ in the approximate Eq.(7-121) into Eq.(7-120) yields

$$-\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t}\left(1 + \frac{k_1}{k_{-1} + k_2}\right) = k_2 \frac{k_1}{k_{-1} + k_2} c_{\mathrm{A}} \qquad , \qquad -\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = \frac{k_1 k_2}{k_1 + k_{-1} + k_2} c_{\mathrm{A}}$$

$$-\frac{\mathrm{d}c_{\mathrm{A}}}{\mathrm{d}t} = k c_{\mathrm{A}} \qquad , \qquad k = \frac{k_1 k_2}{k_1 + k_{-1} + k_2} \qquad (7\text{-}122)$$

k is a phenomenological rate coefficient.

If adopting pre-equilibrium approximation, $k = k_1 k_2 / k_{-1}$, if adopting steady state approximation, $k = k_1 k_2 / (k_{-1} + k_2)$. Because the above mechanism can be solved strictly, we can compare (1) pre-equilibrium, (2) steady state, and (3) the revised method. Results are as follows:

When $k_1 : k_{-1} : k_2 = 10^2 : 10^4 : 10^2$,   (1), (2), (3) are all satisfactory.

$k_1 : k_{-1} : k_2 = 1 : 10^2 : 10^2$,   (2) and (3) satisfactory, (1) unsatisfactory.

$k_1 : k_{-1} : k_2 = 10^2 : 10^2 : 1$,   (1) and (3) satisfactory, (2) unsatisfactory.

$k_1 : k_{-1} : k_2 = 1 : 10^{-2} : 1$,   (3) not bad, (1) and (2) are unsatisfactory.

The revised method shows superiority. The results indicate that the pre-equilibrium approximation and the steady state approximation have their own applicable ranges, respectively.

3. Distinguishing the Intermediates

If the theoretical rate equation derived from the mechanism supposed is consistent with that obtained from experiment, we can make a preliminary positive judgment. But the final conclusion still remains to be found. The key is to distinguish the intermediates. For stable intermediates, we should make efforts to separate them. For unstable intermediates especially those molecular fragments, groups or free radicals, the following methods are usually adopted.

(1) **Chemical Methods**   For example, methyl group CH_3 can react with Zn, Cd, Bi, Tl, Pb, etc. forming $M(CH_3)_n$ where n is the valence of the metal M. For another example, methylene group $(-CH_2-)$ can react with Te forming poly formaldehyde telluride $(CH_2Te)_x$. Coating the metal on the inner wall of a glass tube, a thin film forms called a metal mirror. If the
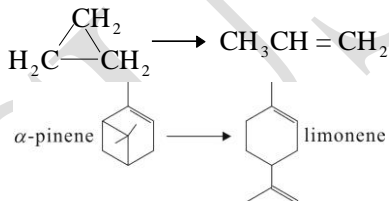
mirror is displaced when the reaction gas passes through the tube at a higher temperature, the existence of the above mentioned groups can be proved.

(2) **Spectroscopy Methods**   Using ultra violet spectrum, ultra red spectrum, nuclear magnetic resonance, electron spin resonance, etc., we can predict the existence of some molecules by their characteristic spectra. Also we can have information for many unstable radicals such as OH, NH, NH$_2$, CH, CN, C$_2$, HO$_2$, HCO, SH, BH, ClO, CF, etc.

(3) **Theoretical Analysis**   Quantum chemistry and structural chemistry are helpful to make valuable judgments.

7.14   Uni-Molecular Reactions

Many reactions are traditionally considered as uni-molecular reactions, for example,

$$Br_2 \longrightarrow 2Br \quad , \quad SO_2Cl_2 \longrightarrow SO_2 + Cl_2$$

$$\underset{H_2C \overline{\quad} CH_2}{\overset{CH_2}{\triangle}} \longrightarrow CH_3CH = CH_2$$

α-pinene ⟶ limonene

But they are not as simple as imagined at the beginning. Experiment showed that at higher temperature they are indeed first order reactions with the need of a certain activation energy. However, when lowering the pressure, reaction rate constants diminish and the reaction order turns from the first order to the second order. For $A^* \longrightarrow P$, the change of an excited molecule A^* to products P, the reaction can be considered as a true uni-molecular reaction. The problem is that if not colliding with other molecules, how can a molecule gain energy and turn into an excited molecule. As early as 1918, Perrin J proposed a radiation hypothesis which considers that the molecule gains energy from the wall of the reactor by radiation. But the hypothesis is not supported by experiment because according to this hypothesis, however low the pressure is, the reaction should remain first order and the rate constant should be unchanged. In 1921, Lindeman F L and Christiansen J A separately and independently proposed

a same theory for uni-molecular reactions by which many experimental phenomena could be interpreted.

Lindeman-Christiansen Theory   The reactant molecule A first turns to an activated molecule A^* with higher vibrational energy by collision. Then A^* adjusts its state internally to form products,

$$A + A \xrightarrow{\ k_1\ } A^* + A \quad , \quad A^* \xrightarrow{\ k_2\ } P$$

This second step is a true uni-molecular reaction which requires a certain time for internal adjustment. During this time interval, the activated molecule is possible to be deactivated by collision with another A molecule,

$$A^* + A \xrightarrow{\ k_{-1}\ } A + A$$
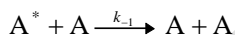
1 and -1 compose an opposite reaction. Because A^* is an active intermediate, we can use the steady state approximation,

$$\frac{dc_{A^*}}{dt} = k_1 c_A^2 - k_2 c_{A^*} - k_{-1} c_{A^*} c_A = 0 \qquad (7\text{-}120)$$

$$c_{A^*} = k_1 c_A^2 / (k_2 + k_{-1} c_A) \qquad (7\text{-}121)$$

$$-\frac{dc_A}{dt} = \frac{dc_P}{dt} = k_2 c_{A^*} = \frac{k_2 k_1 c_A^2}{k_2 + k_{-1} c_A} = k_A c_A \qquad (7\text{-}122)$$

where

$$k_A = \frac{k_2 k_1 c_A}{k_2 + k_{-1} c_A} \qquad (7\text{-}123)$$

When the gas pressure is higher, because of $k_{-1} c_A \gg k_2$,

$$k_A = k_2 k_1 / k_{-1} \qquad (7\text{-}124)$$

The so called uni-molecular reaction behaves as a first order reaction. When the gas pressure is lower, because of $k_2 \gg k_{-1} c_A$,

$$k_A = k_1 c_A \qquad (7\text{-}125)$$

The so called uni-molecular reaction behaves as a second order reaction with a smaller rate constant than that at higher pressure.

The above discussion indicates that those commonly called uni-molecular reactions are not true uni-molecular elementary reactions. They have complex mechanisms. However, we still follow the tradition call them uni-molecular reactions because the key step in the mechanism is a true uni-molecular reaction.

Progress   The opposite reaction $(1,-1)$ $A + A \rightleftharpoons A^* + A$ in the mechanism can be rewritten as

$$A + M \rightleftharpoons A^* + M$$
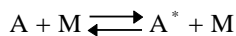
where M is an arbitrary molecule which can be A, or a product P, or other inert molecules. In section 7.13, the examples of HBr formation and O_3 decomposition all adopt this uni-molecular reaction mechanism involving M. However, we have to point out that although the Lindeman-Christiansen theory can explain the above behaviors of the so-called uni-molecular reactions qualitatively, the quantitative agreement is not good. Later, more advanced improvements appeared. In 1926, Hinshelwood C N considered the contribution of vibration and rotation and introduced the variation of k_1 of the reaction 1 with energy. From 1928 to 1951, RRKM theory (Rice O K, Ramsperger H C, Kassel L S, Marcus R A) was established. The theory delicately derived the variation of k_2 of the true uni-molecular reaction 2 with energy resulting in satisfactory quantitative predictions.

Brief History

　　　　Studies of chemical kinetics started with experimental determinations of reaction rates. As early as 18th century, there were observations concerning the relations between the speed of dissolution of metals in acids and the concentration of acids, and the time needed for the decomposition of hydrogen peroxide. However, the first scientist carried out quantitative studies is a French chemist Wilhelmy L F. He used polarimeter to study the rate of conversion of sucrose in the presence of acid and adopted differential equation to express the reaction progress. He also gave an empirical relation between rate and temperature. In 1862, French chemists Berthelot P E M (also referring to Chapters 1 and 5) and de Saint Gills L P (also referring to Chapter 5) studied the esterification of ethyl alcohol and acetic acid and the reverse reaction, the hydrolysis of ethyl acetate. They found that the rate of the former is proportional to the product of the concentration of the alcohol and that of the acid, and the rate of the latter is proportional to the concentration of the ester. They also found an exponential relation between rate and temperature. In 1836, enlightened by the work of Berthelot et al, a Norwegian chemist Waage P and a mathematician Guldberg C M (also referring to Chapter 5) proposed the mass action law: Reaction rate is proportional to the power product of concentrations (originally called effective masses) of various reactants. At equilibrium, $v_{forward} = v_{reverse}$, the equilibrium constant $K_c = k_{forward}/k_{reverse}$ can then be obtained.

　　　　Waage et al's studies are an important step bringing chemistry to a quantitative science. From 1865 to 1867, Harcourt A G V, a British chemist, determined in detail the relations between rates and concentrations for reactions of hydrogen peroxide and hydroiodic acid, and of potassium permanganate and oxalic acid. Their results were analyzed by a mathematician Esson W, who

obtained relations describing the variation of concentrations with time and distinguishing the first order reaction and the second order reaction. These studies can be viewed as the beginning of the modern establishment of rate equations. In 1884, Van′t Hoff J H of the Netherlands (also referring to the Introduction of the whole book and Chapters 4, 5 and 16) published a pioneering monograph concerning chemical equilibria. He proposed the equation named after him, Eq.(5-8), describing the relation between the equilibrium constant and temperature, and further extended to kinetics to relate the rate constant and temperature by constructing an empirical equation, Eq.(7-74) $k=k\exp(-E_a/RT)$.

In 1889, Arrhenius S, a Swedish chemist (also referring to Chapter 14, 16), probed into Eq.(7-74) and proposed the concept of activated molecules. Due to his correct analysis, Eq.(7-74) is now called the Arrhenius equation and the E_a in the exponential term is called the Arrhenius activation energy. Because of Arrhenius′ contribution to the development of chemistry by his dissociation theory of electrolytes, he won the Nobel Price of Chemistry in 1903.

The above works have laid the foundation of the modern chemical kinetics.

It is worth mentioning that Bodenstein M of Germany proposed the chain reaction mechanism in the study of photo synthesis of HCl. The study of free radical reactions of Семенов Н Н of the former Soviet Union and the study of heterogeneous catalytic kinetics (referring to 15.15) of Hinshelwood C N of the Great Britain have also made important influence. Because of their contributions to the chemical reaction mechanisms, Семенов and Hinshelwood won jointly the Nobel Prize of Chemistry in 1956.

Concluding Remarks

We have presented the fundamental contents of the chemical kinetics. It is more important than the chemical thermodynamics in a sense because not only discussing the possibilities but also studying how to turn the possibilities to realities. However, its theory is far less complete than that of chemical thermodynamics. At present, the principle content that has gained applications is the macroscopic chemical kinetics which mainly studies variations of reaction rates with concentrations and temperature, and focuses on reaction-rate equations. The rate equations have many different forms relevant to different situations, for instance, the elementary or the complex reactions, those with power-function forms such as the zeroth, the first, or the second order, or a fraction order, a single reaction or the opposite, the consecutive and the parallel reactions. They have different characteristics or rules. On the other hand, the rate equations include some characteristic parameters such as the order and partial orders, the rate constant or rate coefficient, the activation energy and the pre-exponential factor. They are characteristic properties of chemical reactions that can be obtained by experimental, semi-empirical and theoretical methods.

In reading different textbooks, you may find different treatments on the opposite, the consecutive and the parallel reactions. In some cases, they are discussed in the reaction mechanisms, the components of them are elementary reactions. In other cases, they are called 'complex reactions' distinguished from those simple zeroth order, first order and second order reactions. In fact, how to classify is not important, the key is learning methods. The rules of the opposite, the consecutive and the parallel reactions can be used in reaction mechanisms

for composing a complex reaction by elementary reactions, also can be used for composing a more complex reaction by several complex reactions. For example, the oxidation of ethanol to produce acetaldehyde in industry, as side reactions, the acetaldehyde can be oxidized to acetic acid, the latter can be further oxidized to CO_2, those ethanol, acetaldehyde and acetic acid can also be directly oxidized to CO_2. This is a kinetic net composed of several consecutive reactions and parallel reactions and each of them are also a complex reaction with complex mechanism. The knowledge introduced in this chapter provides a basis to study this net. In solving the coupled differential equations, we may adopt some special mathematical methods such as the determinant method, the Laplace transformation and the random sampling. If the number of reactions is too much to solve simultaneously, we can adopt **lumping** method by sorting out similar reactions.

This chapter is the fundamental content of the macroscopic chemical kinetics. In the next chapter, more types of real reactions such as polymerization reactions, explosion reactions, catalytic reactions, photo chemical reactions, oscillation reactions and continuous reactions will be introduced. As for the statistical theories of reaction rates on the microscopic level which can predict kinetic characteristic parameter theoretically, they will be further introduced in Chapter 14 after the quantum mechanics and statistical mechanics are studied.

General Problems

1．The rate of consumption v_A is the absolute value of the rate of change of the amount of the reactant A in a unit volume. Why should we take the absolute value? If A is an intermediate, what should we do? (Refer to 7.6)

2. In the following expressions, which of them is correct? Which of them is incorrect or conditional?

$$\text{(a) } v = dc_A/dt \quad, \quad \text{(b) } v = -dc_A/dt \quad, \quad \text{(c) } v = d\xi/dt$$
$$\text{(d) } v = -\frac{1}{V}\frac{dn_A}{dt}, \quad \text{(e) } v = -\frac{1}{v_A V}\frac{dn_A}{dt}, \quad \text{(f) } v = \frac{1}{v_A}\frac{dc_A}{dt}, \quad \text{(g) } v = -\frac{1}{v_A}\frac{dc_A}{dt}$$

3. Why are the rate equations irrelevant to the type of the reactor? Why do the integrated rate equations depend on the type of the reactor? (Refer to 8.9)

4. When the partial orders of the reaction are the same as those absolute values of the stoichiometric numbers of the chemical equation, we can judge that the reaction is an elementary reaction. Give comments on this statement.

5. In the establishment of the rate equations, we have mentioned several times that the reaction proceeds one-way forward. What is its implication?

6. In the example in 7.4, if $c_{A0}=0.400\,mol\cdot dm^{-3}$, what are the initial rate, the amount of the product in 20min and the conversion of the reactant?

7. Systematically induce the characteristics of the zeroth, the first and the second order reactions.

8. Establish the rate equation and the integrated rate equation for an opposite reaction in which the forward reaction is second order and the reverse reaction is first order.

9. For an opposite reaction in which the forward reaction is endothermic, how is the variation of reaction rate with temperature?

10. Establish the rate equation and the integrated rate equation for a consecutive reaction in which the first reaction is first order and the second one is second order.

11. Is the activation energy a constant?

12. Referring to 7.5, give another example of the variation of rate coefficient with temperature for the type III.

13. Derive Eqs.(7–83, 7–84),

$$c_{A0}/(c_{A0} - x) = (Y_\infty - Y_0)/(Y_\infty - Y_t) , \quad x/(c_{A0} - x) = (Y_t - Y_0)/(Y_\infty - Y_t)$$

14. In the Example 1 in 7.10, the decomposition of peroxy-ditertiary butyl, if the data at $t=0$ is not provided, can we obtain the first order rate coefficient? If we can, how is the reliability of the result? If part of the reactant has been decomposed at $t=0$, how to determine the reaction order and rate coefficient?

15. In the Example 3 in 7.10, the hydrolysis of ethyl acetate, if the initial concentrations of ethyl acetate and NaOH are not provided, can we obtain the reaction order and the rate coefficient?

16. What is a differential reactor? What is an integral reactor? What are their peculiarities, respectively?

17. Compare the batch reactor, the continuous tank reactor and the continuous tubular reactor? (Refer to 8.9)

18. Why can't the final conclusion be obtained if the theoretical rate equation derived by the mechanism with the pre-equilibrium or the steady state approximations selected is consistent with the experimental results?

19．When the pre-equilibrium approximation and the steady state approximation can obtain the same results? When do they obtain different results? Give examples and discussion.

20. Are there any relations between the principle of microscopic reversibility and the concept of equilibrium or non-equilibrium? Why is the principle of detailed equilibrium a part of the principle of microscopic reversibility?

Numerical Problems

1.   The decay rates of radio isotopes conform to the first order kinetics (the decay rate is proportional to the amount of the radio isotope). The α decay of ^{210}Po forms stable ^{206}Pb: $^{210}Po \rightarrow ^{206}Pb + ^4He$. Experiment obtained that the radioactivity decreases 6.85% after 14d. Calculate the decay rate coefficient, the half life and the time needed for a 90% decay for ^{210}Po.

2.   Mix equal volumes of $CH_3COOC_2H_5$ and NaOH solutions with the same concentration of $0.0400 mol \cdot dm^{-3}$ at 21℃. Take a sample of 100cm^3 after 25 min. The sample is neutralized by a HCl solution of 4.23 cm^3 with a concentration of 0.125 mol·dm^{-3}. Determine the second order rate coefficient at 21 ℃ of the reaction $CH_3COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$ and the conversion of ethyl acetate.

3.   The reaction $CH_3CH_2NO_2 + OH^- \rightarrow H_2O + CH_3CHNO_2^-$ is second order with $k=39.1$ dm$^3 \cdot$mol$^{-1} \cdot$min^{-1} at 0℃. Now we have $CH_3CH_2NO_2$ with a concentration of 0.004 mol·dm^{-3} and NaOH with a concentration of 0.005 mol·dm^{-3}. How much time is needed when 90% of nitro-ethane is reacted?

4.   A reaction $A + B \rightarrow P$ with equal initial concentrations of A and B, after 1h, 25% of A is reacted. Determine the amount of A remained after 2h. (1) The reaction is first order for A and zeoth order for B. (2) Both A and B are first order. (3) Both A and B are zeroth order.

5. An opposite reaction $A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} B$ with $k_1 = 0.006$ min^{-1} and $k_{-1} = 0.002$ min^{-1}, if only A exists at the beginning with a concentration of 1 mol$\cdot$dm^{-3}, determine: (1) The time needed when concentrations of A and B are equal. (2) Concentrations of A and B after 100min.

<u>6.</u>   The reaction of β-glucose changing to α-glucose $\beta - C_6H_{12}C_6 \rightleftharpoons \alpha - C_6H_{12}C_6$ is a first order opposite reaction with $k_1+k_{-1}=0,0016$ min^{-1} and an equilibrium constant $K_c=0.557$. Calculate k_1 and k_{-1}.

7. The reaction of hydrolysis of L-2,3-；4,6-diacetone guluronic acid ($C_{12}H_{18}O_6$) in acid solution forming ascorbic acid ($C_6H_8O_6$, Vitamin C),

$$C_{12}H_{18}O_6 \xrightarrow{k_1} C_6H_8O_6 \xrightarrow{k_2} \text{dissociation products}$$
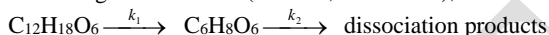
is a first order consecutive reaction with $k_1=4.2\times10^{-3}$ min^{-1}, $k_2=0.020\times10^{-3}$ min^{-1} at 50℃ and $k_1=410\times10^{-3}$ min^{-1}, $k_2=0.090\times10^{-3}$ min^{-1} at 60℃. Determine the most favorable reaction time and the corresponding maximum yield for the production of ascorbic acid.

<u>8.</u>   A parallel reaction of chlorobenzene and chlorine in a CS_2 solution,

$C_6H_5Cl+Cl_2{\rightarrow}HCl+o\text{-}C_6H_4Cl_2$, $C_6H_5Cl+Cl_2{\rightarrow}HCl+p\text{-}C_6H_4Cl_2$,

in the presence of iodine as catalyst, with the same initial concentrations of 0.5 mol$\cdot$dm^{-3} for C_6H_5Cl and Cl_2 at a constant temperature and a constant concentration of iodine, after 30 min, 15% of C_6H_5Cl transforms to $o\text{-}C_6H_4Cl_2$, 25% to $p\text{-}C_6H_4Cl_2$. Calculate the second order rate coefficients k_1 and k_2 for the two reactions.

9. For a first order consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$, prove: If $k_1 \gg k_2$, the rate of formation of C is determined by k_2 and if $k_2 \gg k_1$, by k_1. The slowest step is the controlling step of the formation of C.

<u>10.</u> The hydrolysis of sucrose in a dilute solution,

$$C_{12}H_{22}O_{11} + H_2O \longrightarrow C_6H_{12}O_6(\text{glucose}) + C_6H_{12}O_6(\text{fructose})$$

The reaction rate is proportional to the concentration of sucrose at a constant temperature and a constant acid concentration. For a solution with concentrations of 0.300 mol of $C_{12}H_{22}O_{11}$ and 0.1 mol of HCl in 1dm^3 solution, 32% of sucrose is hydrolyzed after 20 min at 48℃. (1) Calculate the rate coefficient. (2) Calculate the initial rate (t=0) and the rate at 20 min. (3) How much sucrose is hydrolyzed after 40 min? (4) What is the time needed for 60% of sucrose to be hydrolyzed? (5) What is the effective volume of the reactor if we want 6 kg of sucrose at a reaction time of 40 min?

<u>11.</u> The reaction of 2-nitropropane and a base in aqueous solution is second order. The temperature dependence is $\lg(k/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{min}^{-1})=11.90-3163/(T/\text{K})$ for the rate coefficient. If the initial concentrations of the two reactants are the same of 8.00×10^{-3} mol$\cdot$dm^{-3}, calculate the temperature when the conversion of 2-nitropropane is 70% within 15 min.

<u>12.</u> The half life of the thermal decomposition of N_2O at constant temperature is proportional to the initial pressure p_0. The Table lists the data of different temperatures. Guess the reaction order.

$t/℃$	694	757
p_0/kPa	39.2	48.0
$t_{1/2}/\text{s}$	1520	212

Determine: (1) Rate coefficients at the two temperatures in which the concentration and time are expressed by mol$\cdot$dm^{-3} and s. (2) Activation energy.

13. The decomposition of nitrogen dioxide is a second order reaction. The Table lists rate coefficients k at various temperatures. Determine the activation

T/K	592	603	627	652	656
$k/\text{dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$	0.522	0.755	1.700	4.020	5.030

energy E_a and the pre-exponential factor A.

14. Decomposition of diazo-benzene in iso amyl alcohol solution produces N_2. The Table

| t/min	0	100	200	300	410	∞
V/cm^3	0	15.76	28.17	37.76	45.88	69.84

lists data of the volumes of nitrogen measured at different times. Determine the reaction order and the rate coefficient.

15. The initial concentration of an aqueous sucrose solution containing 2.5 mol·dm^{-3} of formic acid is 0.44 mol·dm^{-3} at 30℃. The variation of angles of rotation α with time for the hydrolysis of sucrose is listed in the Table,

t/h	0	8	15	35	46	85	∞
α/(°)	57.90	40.50	28.90	6.75	−0.40	−11.25	−15.45

Determine the reaction order and the rate coefficient.

16. Tertiary butanol is formed from isobutylene in the presence of H^+ as catalyst,

$$CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + H_2O \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$$
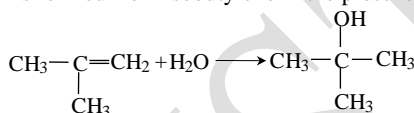
A capillary is connected with the vessel containing reaction mixture and the change of the meniscus in the capillary can be used to determine the rate coefficient (dilatometer method) because the volume is decreased with the reaction. The Table lists the data.

t / min	0	10	20	30	40	∞
Dilatometer reading R	18.84	17.91	17.19	16.56	16.00	12.16

Temperature is 25 ℃, $[HClO_4]=0.3974$ mol·dm^{-3}, $[i\text{-}C_4H_8]=0.00483$ mol·dm^{-3}, [ ] represents concentration. Determine the reaction order and the rate coefficient.

17. The following reaction proceeds at 22.6℃,

$$C_6H_5-CH=CH-CHCl_2 + C_2H_5OH \longrightarrow C_6H_5-\underset{\underset{OC_2H_5}{|}}{CH}-CH=CHCl + HCl$$
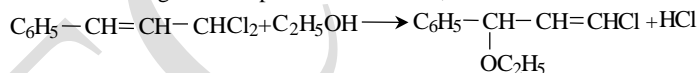
The reaction can be monitored by photo absorption method because of the conjugation of double bond and benzene ring in $C_6H_5-CH=CH-CHCl_2$ resulting in a strong absorption band at 260nm and no absorption for $C_6H_5-\underset{\underset{OC_2H_5}{|}}{CH}-CH=CHCl$ up to 210nm because of no conjugation. The Table lists data measured at 260nm where the absorbance $A=\lg(I_0/I)=\kappa l c$, κ is the molar absorption coefficient, l is the thickness of the solution layer, c is concentration. Determine the reaction order and the rate coefficient.

t/min	0	10	31	74	127	178	1000	∞
A	0.406	0.382	0.338	0.255	0.184	0.143	0.001	0

18. The thermal decomposition of gaseous acetaldehyde carries out at 518℃ in a closed vessel with an initial pressure of 48.39kPa, $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$. The Table lists the change of the value of pressure increase Δp with time.

t/s	42	105	242	840	1440
Δp/kPa	4.53	9.86	17.86	32.53	37.86

Determine the reaction order and the rate coefficient by using mol·dm^{-3} and s for the

units of concentration and time, respectively.

19. Dimer C_8H_{12} is formed by 1,3-butadiene at 326℃. Measuring the pressure versus time of a vessel filled with a certain amount of 1,3-butadiene, the data are listed in

t/min	0	12.18	24.55	42.50	68.05
p/kPa	84.26	77.88	72.90	67.90	63.27

the Table. Determine the reaction order and the rate coefficient.

20.   Reaction $C_6H_5COCH_2Br + C_5H_5N \longrightarrow C_6H_5COCH_2N^+C_5H_5 + Br^-$ carries out in a methanol solvent at 35.0℃ with the same initial concentration of 0.0385 mol·dm^{-3} for both reactants benzoyl methyl bromide and pyridine. The variation of resistance R of the solution with time measured is listed in the Table.

t/min	0	53	84	110	153	203	∞
R/Ω	78190	9200	6310	5100	3958	3220	801

Determine the reaction order and the rate coefficient. In dilute solutions, the electric conductance of the solution is linear to the concentration of the charged substances.
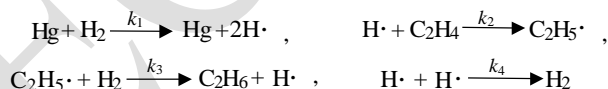
21. The rate equation of a solution reaction $2Fe(CN)_6^{3-} + 2I^- \rightarrow 2Fe(CN)_6^{4-} + I_2$ is

$$\frac{d[I_2]}{dt} = k\left[Fe(CN)_6^{3-}\right]^\alpha \left[I^-\right]^\beta \left[Fe(CN)_6^{4-}\right]^\gamma$$

Four sets of the initial rate of formation of I_2, d[I_2]/dt, with different compositions of the reaction mixture at 25℃ are measured and listed in the Table. Determine the partial orders α, β and γ by the data analysis of 1-2, 2-4, 1-3 set pairs.

Serial number	Concentration of reactant×10³/(mol·dm^{-3})			$\dfrac{(d[I_2]/dt)\times10^3}{mol\cdot dm^{-3}\cdot h^{-1}}$
	$Fe(CN)_6^{3-}$	I^-	$Fe(CN)_6^{4-}$	
1	1	1	1	1
2	2	1	1	4
3	1	2	2	1
4	2	2	1	8

22. In the presence of mercury vapor, the mechanism of the reaction $C_2H_4+H_2\rightarrow C_2H_6$ is as follows,

$$Hg + H_2 \xrightarrow{k_1} Hg + 2H\cdot \ , \qquad H\cdot + C_2H_4 \xrightarrow{k_2} C_2H_5\cdot \ ,$$

$$C_2H_5\cdot + H_2 \xrightarrow{k_3} C_2H_6 + H\cdot \ , \qquad H\cdot + H\cdot \xrightarrow{k_4} H_2$$

Suppose the concentrations of the intermediates H· and C_2H_5· are very low that the steady state approximation can be applied, write the rate of formation of C_2H_6 with respect to the rate constants of various elementary reactions and concentrations of Hg, H_2 and C_2H_4.
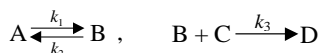
23. Reaction $C_2H_6+H_2\rightarrow 2C_2H_4$ has the following mechanism,

$$C_2H_6 \rightleftharpoons 2CH_3\cdot \ , \quad CH_3\cdot + H_2 \xrightarrow{k_1} CH_4 + H\cdot \ , \quad H\cdot + C_2H_6 \xrightarrow{k_2} CH_4 + CH_3\cdot$$

Suppose the first reaction reaches equilibrium with equilibrium constant K and H· is in the steady state, prove the following equation,

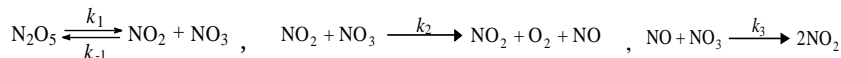$$d[CH_4]/dt = 2k_1 K^{1/2}\left[C_2H_6\right]^{1/2}\left[H_2\right]$$

24. The mechanism of a gaseous reaction $A + C \longrightarrow D$ is:

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B \ , \qquad B + C \xrightarrow{k_3} D$$

Write the rate equation for this complex reaction and prove that this reaction is first order
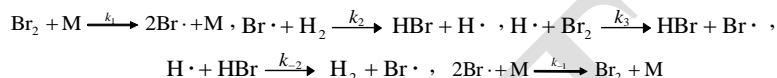
at a high pressure and second order at a low pressure. The concentration of the intermediate B is very small.

25. The rate equation measured by experiment for the gaseous decomposition of N_2O_5 is $-d[N_2O_5]/dt = k[N_2O_5]$. The reaction mechanism is

$$N_2O_5 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} NO_2 + NO_3 \quad, \quad NO_2 + NO_3 \xrightarrow{k_2} NO_2 + O_2 + NO \quad, \quad NO + NO_3 \xrightarrow{k_3} 2NO_2$$

where NO_3 and NO are active intermediates. (1) Derive the rate equation of this complex reaction by the steady state approximation. (2) If $k_{-1} \gg k_2$, write the relation between the activation energy E_a of the complex reaction and that of those elementary reactions.

26. The Mechanism of the gaseous reaction $H_2 + Br_2 \longrightarrow 2HBr$ is

$$Br_2 + M \xrightarrow{k_1} 2Br\cdot + M \, , \, Br\cdot + H_2 \xrightarrow{k_2} HBr + H\cdot \, , \, H\cdot + Br_2 \xrightarrow{k_3} HBr + Br\cdot \, ,$$

$$H\cdot + HBr \xrightarrow{k_{-2}} H_2 + Br\cdot \, , \, 2Br\cdot + M \xrightarrow{k_{-1}} Br_2 + M$$

The rate equation derived by the steady state approximation is

$$dc_{HBr}/dt = 2k_2 (k_1/k_{-1})^{1/2} c_{H_2} c_{Br_2}^{1/2} / \left[1 + (k_{-2}/k_3)c_{HBr}/c_{Br_2}\right]$$

Activation energies for elementary reactions are:

E_1=189kJ·mol^{-1}, E_2=73.6kJ·mol^{-1}, E_3=5.0kJ·mol^{-1}, E_{-2}=5.0kJ·mol^{-1}, E_{-1}=0.

Calculate the activation energy of the complex reaction: (1) at the very beginning. (2) when HBr is in large excess.

27. The rate coefficient of a reaction is derived as $k=k_3 K/(1+K)$ in which k_3 is the rate constant of the elementary reaction 3, $K=k_1/k_2$ is the ratio of rate constants or the equilibrium constant of two elementary reactions with opposite directions. Prove that the activation energy of the reaction is $E_a = E_3 + \Delta_r U_m^\ominus/(1+K)$ in which E_3 is the activation energy of the elementary reaction 3, $\Delta_r U_m^\ominus$ is the standard molar thermodynamic energy of reaction of the elementary reaction 1.

28. A parallel reaction
$$A + B \overset{k_1}{\underset{k_2}{\displaystyle\begin{array}{c} \nearrow E \text{ (principle)} \\ \searrow F \text{ (side)} \end{array}}}$$
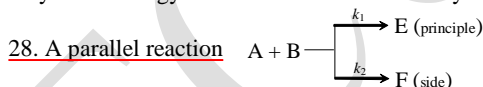
The principal reaction and the side reaction are both second order and their activation energies are E_1 and E_2, respectively. Prove that the activation energy of this parallel reaction is $E_a = (k_1 E_1 + k_2 E_2)/(k_1 + k_2)$.