BASIC CHEMICAL KINETICS

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Preface

This book is the outgrowth of the course Chemical Kinetics taught by S. H. Lin and H. Eyring and is intended for undergraduate seniors, graduate students, and researchers. The presentation is elementary and self-contained wherever possible. Both classical and quantal treatments are presented for comparison. Problems are presented to help the readers understand the material covered in this book. In view of the recent, rapid progress in photochemistry, photophysics, and photobiology, two chapters are used to present the elementary processes in these areas. Wherever derivations were too long to be included in detail, references are given to smooth the way.

Two of us, H. E. and S. H. L., would like to thank their wives, Winifred and Pearl, for their understanding, patience, and moral support; S. M. L. would like to thank Dr. R. E. Weston for his hospitality.

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Introduction

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In this chapter we briefly present some elementary mathematical methods that are frequently used in solving chemical kinetics problems. The application of these methods is demonstrated by solving some particular reactions. We also discuss the validity and limitations of the applications of steady-state approximation and equilibrium approximation to reaction kinetics.

1.1 METHOD OF SEPARATION OF VARIABLES

According to the law of mass action for the chemical reaction

$$aA + bB \longrightarrow cC + dD \tag{1.1}$$
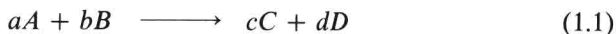
the rate of reaction is proportional to a product of concentrations of reactants,

$$\text{rate} = kC_A^a C_B^b \tag{1.2}$$

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where k is called the *rate constant*. The rate of reaction can be represented by $-(dC_A/dt)$ or $-(dC_B/dt)$ or (dC_C/dt) or (dC_D/dt). There exists a relation among these representations

$$-\frac{1}{a}\frac{dC_A}{dt} = -\frac{1}{b}\frac{dC_B}{dt} = \frac{1}{c}\frac{dC_C}{dt} = \frac{1}{d}\frac{dC_D}{dt} \tag{1.3}$$

assuming that the stoichiometry of reactions is also given by eq. 1.1.

Next we consider the simplest case

$$aA \longrightarrow \text{products} \tag{1.4}$$

In this case the rate of reaction is given by

$$-\frac{dC_A}{dt} = kC_A^a \tag{1.5}$$

This equation can be solved by using the method of separation of variables

$$-\frac{dC_A}{C_A^a} = k\,dt \tag{1.6}$$

If $a \neq 1$, we can carry out the integrations of both sides of eq. 1.6 independently to obtain

$$\frac{1}{a-1}\cdot\frac{1}{C_A^{a-1}} = kt + \frac{1}{a-1}\cdot\frac{1}{C_{A0}^{a-1}} \tag{1.7}$$

Here we have assumed that the initial concentration of A is C_{A0} (i.e., at $t = 0$, $C_A = C_{A0}$). Similarly, for $a = 1$, we have

$$\log C_A = -kt + \log C_{A0} \tag{1.8}$$

or

$$C_A = C_{A0}\exp(-kt) \tag{1.9}$$

It should be noticed that eq. 1.8 can be obtained from eq. 1.7 by using the l'Hospital rule.

Equation 1.7 indicates that the plot of $1/C_A^{a-1}$ versus t is linear with the slope of $(a-1)k$ and the intercept of $1/C_{A0}^{a-1}$. Similarly, eq. 1.8 shows that $\log C_A$ versus t is linear; the slope is $-k$ and the intercept is $\log C_{A0}$. These features provide us a method to determine the order of reactions and the rate constant. For reactions like those given by eq. 1.4, the half-life $t_{1/2}$, which is defined as the time required for the reactant concentration to reduce to one-half of its value, exists and can easily be found by setting $C_A = \frac{1}{2}C_{A0}$ in eqs. 1.7 and 1.8 to yield

$$t_{1/2} = \frac{2^{a-1} - 1}{(a-1)kC_{A0}^{a-1}} \tag{1.10}$$

for $a \neq 1$ and

$$t_{1/2} = \frac{\log 2}{k} \tag{1.11}$$

for $a = 1$, respectively.

Now we consider another simple case of eq. 1.1.

$$A + B \rightarrow \text{products} \tag{1.12}$$

If the initial concentrations of A and B are C_{A0} and C_{B0}, then at a particular instant $C_A = C_{A0} - \chi$ and $C_B = C_{B0} - \chi$. Thus the rate of reaction in this case can be written as

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = \frac{d\chi}{dt} = kC_A C_B = k(C_{A0} - \chi)(C_{B0} - \chi) \tag{1.13}$$

Separating the variables in eq. 1.13 and carrying out the partial fraction of the resulting expression yields

$$\frac{d\chi}{(C_{A0} - \chi)(C_{B0} - \chi)} = \frac{d\chi}{C_{B0} - C_{A0}} \left(\frac{1}{C_{A0} - \chi} - \frac{1}{C_{B0} - \chi} \right) = k \, dt \tag{1.14}$$

which can easily be integrated

$$\frac{1}{C_{B0} - C_{A0}} \log \frac{C_{B0} - \chi}{C_{A0} - \chi} = kt + \frac{1}{C_{B0} - C_{A0}} \log \frac{C_{B0}}{C_{A0}} \tag{1.15}$$

or

$$\frac{1}{C_{B0} - C_{A0}} \log \frac{C_B}{C_A} = kt + \frac{1}{C_{B0} - C_{A0}} \log \frac{C_{B0}}{C_{A0}} \tag{1.16}$$

Equation 1.13 can also be integrated by using the relation $C_B = C_{B0} - C_{A0} + C_A$

$$-\frac{dC_A}{dt} = kC_A(C_{B0} - C_{A0} + C_A) \tag{1.17}$$

and by carrying out the partial fraction of $1/C_A(C_{B0} - C_{A0} + C_A)$. Equation 1.16 indicates that for the reaction mechanism given by eq. 1.12 the plot of $\log(C_B/C_A)$ versus t is linear with the slope $k(C_{B0} - C_{A0})$ and the intercept $\log(C_{B0}/C_{A0})$. Notice that when $C_{A0} = C_{B0}$, eq. 1.13 reduces to eq. 1.15 for $a = 2$ and eq. 1.16 can be reduced to eq. 1.7 by using the l'Hospital rule. Other cases of eq. 1.1 can be discussed similarly (Benson, 1960; Cappellos and Bielski, 1972; Laidler, 1965).

1.2 DETERMINANT METHOD (EIGENVALUE METHOD)

To demonstrate this method let us consider the reaction

$$A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B \tag{1.18}$$

The rate equations are given by

$$\frac{dC_A}{dt} = -k_f C_A + k_b C_B \tag{1.19}$$

and

$$\frac{dC_B}{dt} = k_f C_A - k_b C_B \tag{1.20}$$

To solve these equations, we let

$$C_A = A_1 e^{-\lambda t}, \qquad C_B = A_2 e^{-\lambda t} \tag{1.21}$$

It follows that

$$\begin{aligned}
(\lambda - k_f)A_1 + k_b A_2 &= 0 \\
k_f A_1 + (\lambda - k_b)A_2 &= 0
\end{aligned} \tag{1.22}$$

In eq. 1.21, A_1, A_2, and λ are to be determined. For A_1 and A_2 to have non-trivial solutions, we must have

$$\begin{vmatrix} \lambda - k_f & k_b \\ k_f & \lambda - k_b \end{vmatrix} = 0 \tag{1.23}$$

This is usually called the secular determinant and λ is called the eigenvalue of this determinant. The two roots of eq. 1.23 are given by

$$\lambda_1 = 0, \qquad \lambda_2 = k_f + k_b \tag{1.24}$$

Thus the solutions of eq. 1.21 become

$$\begin{aligned}
C_A &= A_{11} e^{-\lambda_1 t} + A_{12} e^{-\lambda_2 t} \\
C_B &= A_{21} e^{-\lambda_1 t} + A_{22} e^{-\lambda_2 t}
\end{aligned} \tag{1.25}$$

Notice that for $\lambda = \lambda_1$, we have

$$(\lambda_1 + k_f)A_{11} + k_b A_{21} = 0 \tag{1.26}$$

or

$$A_{21} = \frac{k_f}{k_b} A_{11} \tag{1.27}$$

Similarly, for $\lambda = \lambda_2$

$$(\lambda_2 - k_f)A_{12} + k_b A_{22} = 0 \tag{1.28}$$

or

$$A_{22} = -A_{12} \tag{1.29}$$

Substituting eqs. 1.27 and 1.29 into eq. 1.28 yields

$$C_A = A_{11}e^{-\lambda_1 t} + A_{12}e^{-\lambda_2 t}$$
$$C_B = \frac{k_f}{k_b} A_{11}e^{-\lambda_1 t} - A_{12}e^{-\lambda_2 t} \tag{1.30}$$

Suppose at $t = 0$, $C_A = C_{A0}$ and $C_B = C_{B0}$,

$$C_{A0} = A_{11} + A_{12}$$

$$C_{B0} = \frac{k_f}{k_b} A_{11} - A_{12} = KA_{11} - A_{12} \tag{1.31}$$

where $K = k_f/k_b$, the equilibrium constant. Solving for A_{11} and A_{12}, we obtain

$$A_{11} = \frac{C_{A0} + C_{B0}}{1 + K}, \qquad A_{12} = \frac{KC_{A0} - C_{B0}}{1 + K} \tag{1.32}$$

Therefore the solutions given by

$$C_A = \frac{(C_{A0} + C_{B0})}{1 + K} + \frac{(KC_{A0} + C_{B0})}{1 + K} e^{-(k_f + k_b)t}$$

$$C_B = \frac{K(C_{A0} + C_{B0})}{1 + K} - \frac{(KC_{A0} - C_{B0})}{1 + K} e^{-(k_f + k_b)t} \tag{1.33}$$

Let $t \to \infty$. Equation 1.33 then reduces to

$$C_{Ae} = \frac{C_{A0} + C_{B0}}{1 + K}, \qquad C_{Be} = \frac{(K(C_{A0} + C_{B0})}{1 + K} \tag{1.34}$$

which of course represent the equilibrium concentrations of A and B.

One of the main purposes in chemical kinetics is to determine the rate constants. In the above discussed reversible reaction, two rate constants k_f amd k_b are involved and to be determined. Suppose that $k_f C_{A0} > k_b C_{B0}$. Then the reaction proceeds from the left to the right until the equilibrium is reached. In this case the concentration of A decreases with t, and the concentration of B increases with t. If we follow the reaction by measuring C_A

as a function of time t, then from the limiting value of $C_A = C_{Ae}$ as $t \to \infty$, we obtain one condition of $C_{Ae} = (C_{A0} + C_{B0})/(1 + K)$ (i.e., we determine the equilibrium constant) and from the slope of the plot of $\log(C_A - C_{Ae})$ versus t, we obtain $k_f + k_b$. These two conditions provide us enough information to determine k_f and k_b.

Although we have applied the determinant method to solve eqs. 1.19 and 1.20, actually eqs. 1.19 and 1.20 can be solved by using the method of separation of variables. Notice that

$$\frac{dC_A}{dt} + \frac{dC_B}{dt} = 0 \tag{1.35}$$

which indicates that $C_A + C_B$ is a constant, that is,

$$C_A + C_B = C_{A0} + C_{B0} \tag{1.36}$$

Using eq. 1.36, we can eliminate C_B from eq. 1.19 to obtain

$$\frac{dC_A}{dt} = -(k_f - k_b)C_A + k_b(C_{A0} + C_{B0}) \tag{1.37}$$

which can of course be easily solved by using the method of separation of variables.

The determinant method can be applied to solve a set of first-order equations or pseudo-first-order equations. If the set of reactions is first order, for example,

$$A$$
$$B \qquad C$$
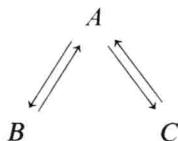
then among the three eigenvalues obtained, one of them will be zero; this eigenvalue corresponds to the equilibrium situation. In this case the concentration of, say A, can be expressed as

$$C_A = A_{11}e^{-\lambda_1 t} + A_{12}e^{-\lambda_2 t} + A_{13}e^{-\lambda_3 t} \tag{1.38}$$

where $\lambda_1 = 0$. Here A_{11}, A_{12}, A_{13}, λ_2, and λ_3 are related to the initial concentrations and the four rate constants. Now if we follow the reactions by measuring C_A versus t, we can determine A_{11}, A_{12}, A_{13}, λ_2, and λ_3, which can in turn be used to determine the four rate constants if we know the

initial concentrations of at least two reactants. On the other hand, for the set of reactions

$$
\begin{array}{c}
A \\
B \rightleftharpoons C
\end{array}
$$
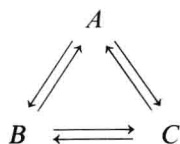
there are six rate constants to be determined and C_A is still given by eq. 1.38. In this case, if we measure C_A versus t and even if we know the initial concentrations of all the three reactants, we have only five relations A_{11}, A_{12}, A_{13}, λ_2, and λ_3 for six unknown rate constants. In other words, in this case we need another independent measurement to determine the six rate constants completely.

The determinant method has been applied to study the effect of vibrational relaxation on unimolecular reactions (Lin *et al.*, 1972; Lin and Eyring, 1974) and on molecular luminescence (Lin, 1972), the stochastic models of reaction kinetics (Widom, 1974; Bartis and Widom, 1974), and the kinetic Ising model (Lacombe and Simha, 1974).

1.3 LAPLACE TRANSFORM METHOD

In this section we discuss how to employ the Laplace transform method (cf. Appendix One) to solve chemical kinetic problems.

To begin with, we consider the reaction

$$
A \rightarrow \text{products}
$$

for which we have

$$
\frac{dC_A}{dt} = -kC_A \tag{1.39}
$$

Applying the Laplace transformation to eq. 1.39, we obtain

$$
-C_{A0} + P\bar{C}_A = -k\bar{C}_A, \qquad \bar{C}_A = \frac{C_{A0}}{k + P} \tag{1.40}
$$

Carrying out the inverse Laplace transformation of eq. 1.40 yields eq. 1.9 (see Appendix One).

Next we consider the reaction

$$
A \underset{k_b}{\overset{k_f}{\rightleftharpoons}} B \tag{1.41}
$$

The rate equations for this reaction are given by eqs. 1.19 and 1.20 and have been solved by using the determinant method. We solve these same equations by using the Laplace transform method.

Carrying out the Laplace transformation of eqs. 1.19 and 1.20, we obtain

$$P\bar{C}_A - C_{A0} = -k_f \bar{C}_A + k_b \bar{C}_B \tag{1.42}$$

and

$$P\bar{C}_B - C_{B0} = k_f \bar{C}_A - k_b \bar{C}_B \tag{1.43}$$

where $\bar{C}_A$ and $\bar{C}_B$ represent the Laplace transforms of C_A and C_B,

$$\bar{C}_A = \int_0^\infty e^{-Pt} C_A \, dt \tag{1.44}$$

and

$$\bar{C}_B = \int_0^\infty e^{-Pt} C_B \, dt \tag{1.45}$$

Solving for $\bar{C}_A$ and $\bar{C}_B$ from eqs. 1.42 and 1.43, we find

$$\bar{C}_A = \frac{C_{A0}(P + k_b) + k_b C_{B0}}{P(P + k_f + k_b)} \tag{1.46}$$

and

$$\bar{C}_B = \frac{C_{B0}(P + k_f) + k_f C_{A0}}{P(P + k_f + k_b)} \tag{1.47}$$

Noticing that

$$\frac{1}{P(P + k_f + k_b)} = \left(\frac{1}{P} - \frac{1}{P + k_f + k_b} \right) \frac{1}{k_f + k_b} \tag{1.48}$$

we can carry out the inverse transformation of eqs. 1.46 and 1.47 (see Appendix One)

$$C_A = \frac{C_{A0} + C_{B0}}{1 + K} + \frac{K C_{A0} - C_{B0}}{1 + K} \exp[-(k_f + k_b)t] \tag{1.49}$$

and

$$C_B = \frac{K(C_{A0} + C_{B0})}{1 + K} - \frac{(K C_{A0} - C_{B0})}{1 + K} \exp[-(k_f + k_b)t] \tag{1.50}$$

Next we show the application of the Laplace transform method to the diffusion problem (Crank, 1957). For this purpose we first derive the diffusion

equation for the one-dimensional case. Let us consider the points χ and $\chi + d\chi$. Then at a particular instant t if we let $J(\chi)$ and $J(\chi + d\chi)$ be the flux at χ and $\chi + d\chi$, respectively, the accumulation of mass between χ and $\chi + d\chi$ in the time interval dt causes the change in concentration dC,

$$[J(\chi) - J(\chi + d\chi)] \, dt = dC \, d\chi \tag{1.51}$$

Using the Taylor expansion, eq. 1.51 can be written as

$$\frac{\partial C}{\partial t} = -\frac{\partial J}{\partial \chi} \tag{1.52}$$

Now according to Fick's empirical law, we have $J(\chi) = -D(\partial C/\partial \chi)$, where D represents the diffusion coefficient. Inserting this relation into eq. 1.52, we obtain

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial \chi} \left(D \frac{\partial C}{\partial \chi} \right) \tag{1.53}$$

If D is independent of C, then eq. 1.53 reduces to

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial \chi^2} \tag{1.54}$$

For the three-dimensional case, it can easily be shown that the corresponding diffusion equation is given by

$$\frac{\partial C}{\partial t} = D\nabla^2 C \tag{1.55}$$

where

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}$$

As an example of the application of the Laplace transform method, we consider the problem of diffusion in a semiinfinite medium, $\chi > 0$, in which the boundary is kept at a constant concentration C_0, the initial concentration being zero throughout the medium. Thus we have

$$C = C_0, \qquad \chi = 0, \qquad t > 0 \tag{1.56}$$

and

$$C = 0, \qquad \chi > 0, \qquad t = 0 \tag{1.57}$$

Carrying out the Laplace transformation of eq. 1.54 yields,

$$P\bar{C}(p) = D \frac{d^2\bar{C}(P)}{d\chi^2} \tag{1.58}$$

which can easily be solved

$$\bar{C}(P) = A_1 \exp\left(-\chi\sqrt{\frac{P}{D}}\right) + A_2 \exp\left(\chi\sqrt{\frac{P}{D}}\right) \tag{1.59}$$

where A_1 and A_2 are the integration constants. As $C(P)$ is finite as $\chi \to \infty$, we find $A_2 = 0$. From eq. 1.56, we know that at $\chi = 0$,

$$\bar{C}(P) = \frac{C_0}{P} \tag{1.60}$$

by carrying out the Laplace transformation of eq. 1.56, that is, $A_1 = C_0/P$. It follows

$$\bar{C}(P) = \frac{C_0}{P} \exp\left(-\chi\sqrt{\frac{P}{D}}\right) \tag{1.61}$$

Inverting the transformation (see Appendix One) yields

$$C(\chi, t) = C_0 \frac{2}{\sqrt{\pi}} \int_{\frac{\chi}{2\sqrt{Dt}}}^{\infty} e^{-u^2} du = C_0 \operatorname{erfc} \frac{\chi}{2\sqrt{Dt}} \tag{1.62}$$

From eq. 1.62 we can see that in order to determine D, we need only measure the concentration at a particular χ and particular instant t.

To conclude this section of the Laplace transform method, it should be noted that as long as the rate equations are linear with respect to concentrations of reactants, this method can be used. Nonlinear rate equations can be made linear by making the concentrations of certain reactants in large excess in comparison with others. We return to the application of the Laplace transform method in unimolecular reactions.

1.4 MISCELLANEOUS METHODS

In this connection we discuss several methods of considerable generality. For other particular methods the literature may be consulted (Benson, 1952; Mowery, 1974; Kremer and Baer, 1974; Donohue, 1974). As usual we illustrate these methods by examples. First we consider

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{1.63}$$
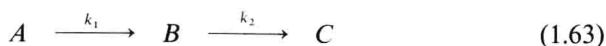
The rate equations in this case are given by

$$\frac{dC_A}{dt} = -k_1 C_A \tag{1.64}$$

$$\frac{dC_B}{dt} = k_1 C_A - k_2 C_B \tag{1.65}$$

$$\frac{dC_C}{dt} = k_2 C_B \tag{1.66}$$

These equations can of course be solved by using the determinant method and Laplace transform method. We can also solve these equations by starting with eq. 1.64. The solution of eq. 1.64 can easily be carried out

$$C_A = C_{A0} e^{-k_1 t} \tag{1.67}$$

where C_{A0} is the initial concentration. Substituting eq. 1.67 into eq. 1.65 yields

$$\frac{dC_B}{dt} + k_2 C_B = k_1 C_{A0} e^{-k_1 t} \tag{1.68}$$

This can be solved by noticing that the integration factor is $e^{k_2 t}$ (Frost and Pearson, 1961), that is,

$$\frac{d}{dt} (C_B e^{k_2 t}) = k_1 C_{A0} e^{t(k_2 - k_1)} \tag{1.69}$$

It follows that

$$C_B = \frac{k_1 C_{A0}}{k_1 - k_1} (e^{-k_1 t} - e^{-k_2 t}) \tag{1.70}$$

Here it has been assumed that $C_B = 0$ at $t = 0$. Equation 1.68 can also be solved by first finding the auxillary solution $C_B^{(a)}$ from

$$\frac{dC_B^{(a)}}{dt} + k_2 C_B^{(a)} = 0 \tag{1.71}$$

to yield

$$C_B^{(a)} = \alpha e^{-k_2 t} \tag{1.72}$$

where α is the integration constant. Next we have to find the particular solution $C_B^{(P)}$ from eq. 1.68 by letting $C_B^{(P)} = \beta e^{-k_1 t}$ to obtain

$$\beta = \frac{k_1 C_{A0}}{k_2 - k_1} \tag{1.73}$$

The general solution of eq. 1.68 is then

$$C_B = C_B^{(a)} + C_B^{(P)} = \alpha e^{-k_2 t} + \frac{k_1 C_{A0}}{k_2 - k_1} e^{-k_1 t} \tag{1.74}$$

The integration constant α can be determined by using the initial condition. This method can be applied to linear high-order differential equations. The term C_C can be found by noticing that $(dC_A/dt) + (dC_B/dt) + (dC/dt) = 0$ or $C_A + C_B + C_C$ is a constant.

Another method for solving the linear differential equations often appears in the literature. The essential point of the method is to replace simultaneous differential equations by a higher-order differential equation. For example, C_A can be eliminated by using eqs. 1.64 and 1.65 to yield

$$\frac{d^2 C_B}{dt^2} + (k_1 + k_2) \frac{dC_B}{dt} + k_1 k_2 C_B = 0 \tag{1.75}$$

which can easily be solved by letting $C_B = \beta e^{-\lambda t}$ to find $\lambda = k_1, k_2$, that is,

$$C_B = \beta_1 e^{-k_1 t} + \beta_2 e^{-k_2 t} \tag{1.76}$$

The integration constants β_1 and β_2 can be determined by using the initial conditions and by putting eq. 1.76 back into the original differential equations.

Next we consider (Weston and Schwarz, 1972)

$$A + C \xrightarrow{\ k_a\ } P \tag{1.77}$$

$$B + C \xrightarrow{\ k_b\ } Q \tag{1.78}$$

The corresponding rate equations are given by

$$\frac{dC_A}{dt} = -k_a C_A C_c \tag{1.79}$$

$$\frac{dC_B}{dt} = -k_b C_B C_c \tag{1.80}$$

$$\frac{dC_C}{dt} = -k_a C_A C_c - k_b C_B C_c \tag{1.81}$$

To solve these equations we take the ratio between eqs. 1.79 and 1.80

$$\frac{dC_A}{dC_B} = \frac{k_a C_A}{k_b C_B} \tag{1.82}$$

which can easily be integrated

$$\log \frac{C_A}{C_{A0}} = \frac{k_a}{k_b} \log \frac{C_B}{C_{B0}}, \qquad C_B = C_{B0} \left(\frac{C_A}{C_{A0}} \right)^r \tag{1.83}$$

where C_{A0} and C_{B0} are the initial concentrations and $r = k_b/k_a$. Since $dC_c/dt - dC_A/dt - dC_B/dt = 0$, we obtain

$$C_C = C_{C0} + (C_A - C_{A0}) + (C_B - C_{B0}) \qquad (1.84)$$

or

$$C_C = C_{C0} + C_A - C_{A0} - C_{B0}\left[1 - \left(\frac{C_A}{C_{A0}}\right)^r\right] \qquad (1.85)$$

Substituting eq. 1.85 into eq. 1.79 and carrying out the separation of variables, we find

$$\int_{C_A}^{C_{A0}} \frac{dC_A}{C_A\left[C_{C0} + C_A - C_{A0} - C_{B0}\left\{1 - \left(\frac{C_A}{C_{A0}}\right)^r\right\}\right]} = k_a t \qquad (1.86)$$

Analytical expressions of eq. 1.86 can be obtained only when r is $\frac{1}{2}$ or an integer. Otherwise the numerical calculation should be used.

1.5 STEADY-STATE AND EQUILIBRIUM APPROXIMATION

Although we have presented a number of mathematical methods to solve rate equations in chemical kinetics, very often one may run across rate equations so complicated that they cannot be solved analytically by using any of the conventional methods. In that case the steady-state approximation or equilibrium approximation are often used. To illustrate these approximations we consider the reactions given by eq. 1.63 and the Lindemann scheme for unimolecular decompositions.

$$A + M \; \underset{k_{-1}}{\overset{k_1'}{\rightleftarrows}} \; A^* + M \qquad (1.87)$$

$$A^* \; \xrightarrow{k_2} \; P \qquad (1.88)$$
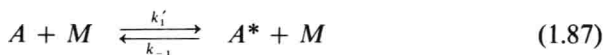
We shall assume that the concentration of M is much bigger than that of A. In that case we can conveniently rewrite eqs. 1.87 and 1.88 as

$$A \; \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \; B, \qquad B \; \xrightarrow{k_2} \; P \qquad (1.89)$$
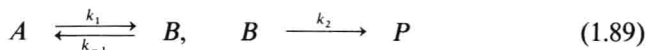
where $k_1 = k_1'M$, $k_{-1} = k_{-1}'M$ and $B = A^*$.

Let us first consider the reactions given by eq. 1.63. To test the validity of the steady-state approximation as applied to B, we compare the exact