Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

concentration for orders less than one, and is independent of initial concentration for reactions of first order.

Numerous variations of this procedure are possible. For instance, by having all but one component, say A in large excess, we can find the order with respect to that one component. For this situation the general expression reduces to

$$-\frac{dC_A}{dt} = \hat{k} C_A^a$$

where

$$\hat{k} = k(C_{B0}^b \cdots) \quad \text{and} \quad C_B \cong C_{B0}$$

And here is another variation of the half-life method.

Fractional Life Method t_F. The half-life method can be extended to any fractional life method in which the concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time t_F. The derivation is a direct extension of the half-life method giving

$$t_F = \frac{F^{1-n} - 1}{k(n-1)} C_{A0}^{1-n} \tag{33b}$$

في بعض التفاعل من الصعوبة الوصول الى زمن النصف بسهولة لذلك يمكن استبداله بقيمة ثانية

Thus, a plot of log t_F versus log C_{A0}, as shown in Fig. 3.5, will give the reaction order.

Example E3.1 illustrates this approach.

Irreversible Reactions in Parallel. Consider the simplest case, A decomposing by two competing paths, both elementary reactions:

تفاعلات غير انعكاسية متوازية

نفس المادة تعطى اكثر من ناتج

$$\left. \begin{array}{c} A \xrightarrow{k_1} R \\[1em] A \xrightarrow{k_2} S \end{array} \right\}$$
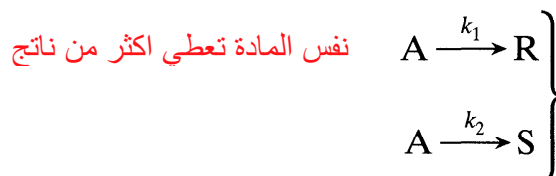
The rates of change of the three components are given by

$$-r_A = -\frac{dC_A}{dt} = k_1 C_A + k_2 C_A = (k_1 + k_2)C_A \tag{34}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A \tag{35}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A \tag{36}$$

This is the first time we have encountered multiple reactions. For these in general, if it is necessary to write N stoichiometric equations to describe what is happening, then it is necessary to follow the decomposition of N reaction components to describe the kinetics. Thus, in this system following C_A, or C_R, or C_S alone will not give both k_1 and k_2. At least two components must be followed. Then, from the stoichiometry, noting that $C_A + C_R + C_S$ is constant, we can find the concentration of the third component.

The k values are found using all three differential rate equations. First of all, Eq. 34, which is of simple first order, is integrated to give

$$-\ln \frac{C_A}{C_{A0}} = (k_1 + k_2)t \tag{37}$$

When plotted as in Fig. 3.6, the slope is $k_1 + k_2$. Then dividing Eq. 35 by Eq. 36 we obtain the following (Fig. 3.6).

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

which when integrated gives simply

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2} \tag{38}$$

This result is shown in Fig. 3.6. Thus, the slope of a plot of C_R versus C_S gives the ratio k_1/k_2. Knowing k_1/k_2 as well as $k_1 + k_2$ gives k_1 and k_2. Typical concentration-time curves of the three components in a batch reactor for the case where $C_{R0} = C_{S0} = 0$ and $k_1 > k_2$ are shown in Fig. 3.7.

Reactions in parallel are considered in detail in Chapter 7.

Homogeneous Catalyzed Reactions.   Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the uncatalyzed and catalyzed reactions,
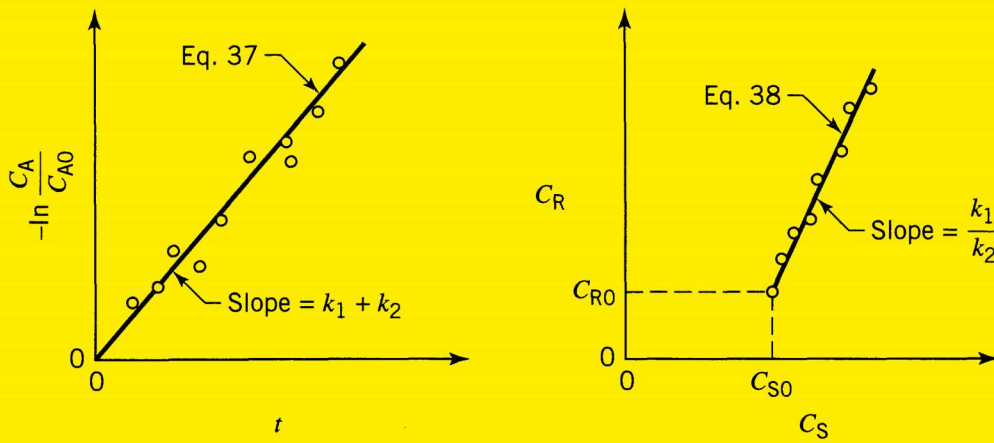
$$\left. \begin{array}{l} A \xrightarrow{k_1} R \\[2em] A + C \xrightarrow{k_2} R + C \end{array} \right\}$$
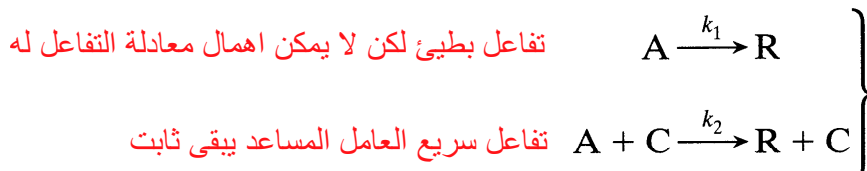
Figure 3.6 Evaluation of the rate constants for two competing elementary first-order reactions of the type $A \diagdown \begin{smallmatrix} R \\ S \end{smallmatrix}$.

with corresponding reaction rates

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A$$

$$-\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

This means that the reaction would proceed even without a catalyst present and that the rate of the catalyzed reaction is directly proportional to the catalyst concentration. The overall rate of disappearance of reactant A is then

$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_C = \underline{(k_1 + k_2 C_C)} C_A \qquad (39)$$

ثابت

On integration, noting that the catalyst concentration remains unchanged, we have

$$-\ln \frac{C_A}{C_{A0}} = -\ln (1 - X_A) = \underline{(k_1 + k_2 C_C)} t = k_{observed} t \qquad (40)$$

مشابهة لمعادلة الدرجة الاولى
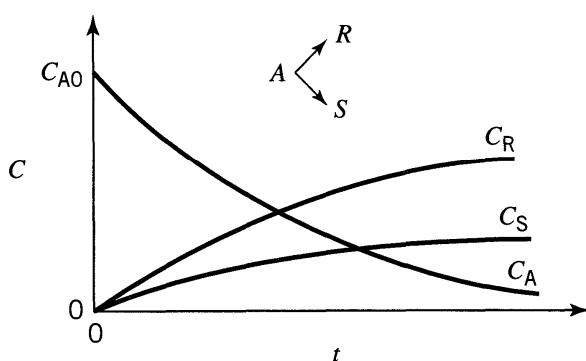
يمكن ايجاد قيمة الثوابت عن طريق تغيير قمية تركيز العامل المساعد يتتحول المعادلة الى معادلة خط مستقيم

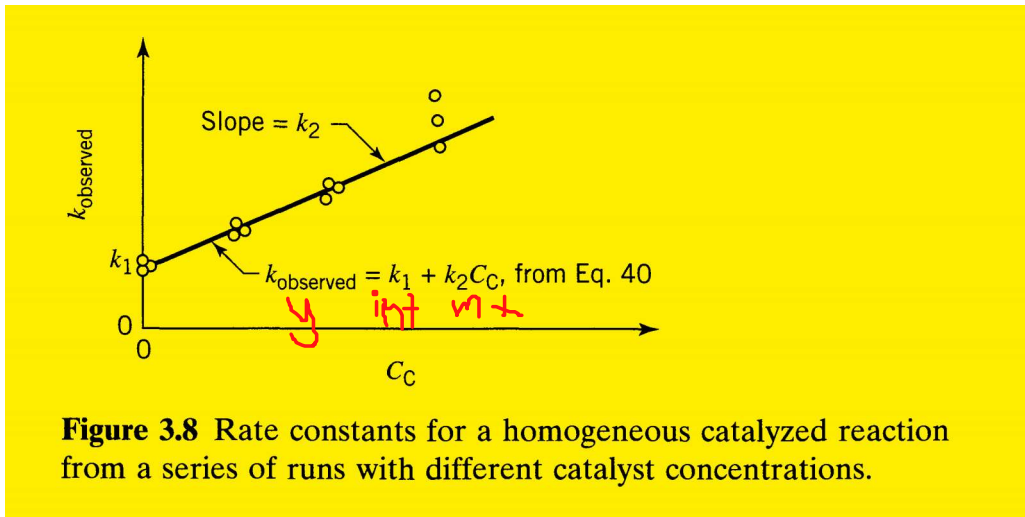**Figure 3.7** Typical concentration-time curves for competing reactions.

Figure 3.8 Rate constants for a homogeneous catalyzed reaction from a series of runs with different catalyst concentrations.

Making a series of runs with different catalyst concentrations allows us to find k_1 and k_2. This is done by plotting the observed k value against the catalyst concentrations as shown in Fig. 3.8. The slope of such a plot is k_2 and the intercept k_1.

Autocatalytic Reactions. A reaction in which one of the products of reaction acts as a catalyst is called an autocatalytic reaction. The simplest such reaction is

$$A + R \rightarrow R + R \tag{41a}$$

for which the rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R \tag{41b}$$

Because the total number of moles of A and R remain unchanged as A is consumed, we may write that at any time

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

Thus, the rate equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Rearranging and breaking into partial fractions, we obtain

$$-\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0}\left(\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A}\right) = k\,dt$$

which on integration gives

$$\ln\frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln\frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0 kt = (C_{A0} + C_{R0})\,kt \tag{42}$$
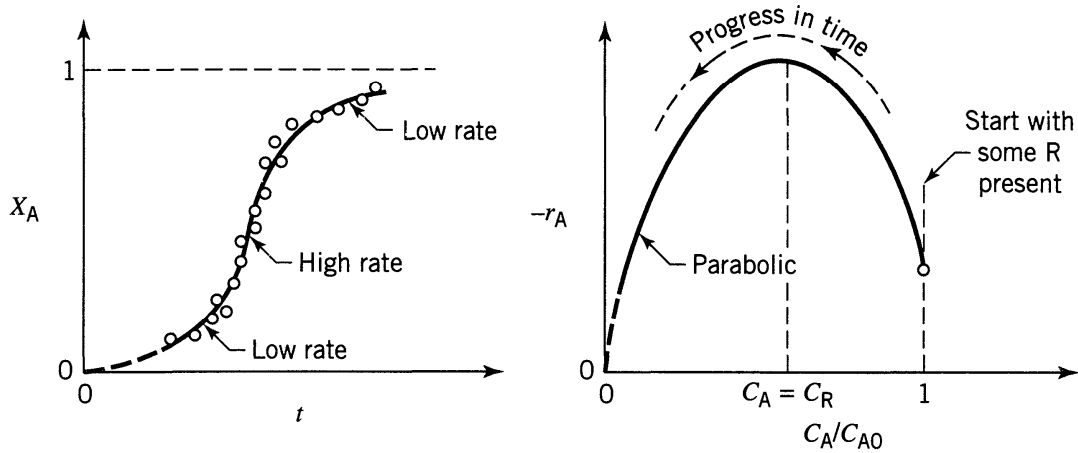
Figure 3.9 Conversion-time and rate-concentration curves for autocatalytic reaction of Eq. 41. This shape is typical for this type of reaction.

In terms of the initial reactant ratio $M = C_{R0}/C_{A0}$ and fractional conversion of A, this can be written as

$$\ln \frac{M + X_A}{M(1 - X_A)} = C_{A0}(M + 1)kt = (C_{A0} + C_{R0})kt \tag{43}$$

For an autocatalytic reaction in a batch reactor some product R must be present if the reaction is to proceed at all. Starting with a very small concentration of R, we see qualitatively that the rate will rise as R is formed. At the other extreme, when A is just about used up the rate must drop to zero. This result is given in Fig. 3.9, which shows that the rate follows a parabola, with a maximum where the concentrations of A and R are equal.

To test for an autocatalytic reaction, plot the time and concentration coordinates of Eq. 42 or 43, as shown in Fig. 3.10 and see whether a straight line passing through zero is obtained.

Autocatalytic reactions are considered in more detail in Chapter 6.

Irreversible Reactions in Series. We first consider consecutive unimolecular-type first-order reactions such as

تفاعل غير نعكاسي
$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$
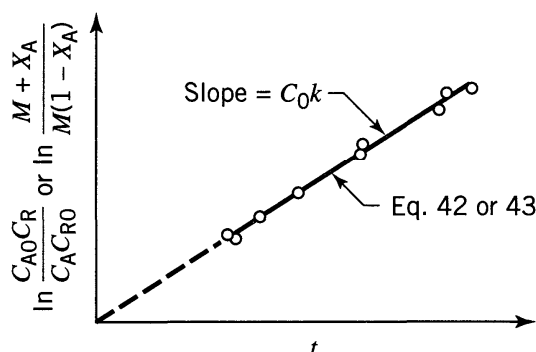المادة الاولى تتحول الى ثانية والثانية الى ثالثة

Figure 3.10 Test for the autocatalytic reaction of Eq. 41.

whose rate equations for the three components are

مادة متفاعلة ال rate لها سالب
لكن تم نقله الى الطرف الاخر

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \tag{44}$$

r يتكن من a لكن يستهلك r

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \tag{45}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \tag{46}$$

Let us start with a concentration C_{A0} of A, no R or S present, and see how the concentrations of the components change with time. By integration of Eq. 44 we find the concentration of A to be

$$-\ln \frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t} \tag{47}$$

To find the changing concentration of R, substitute the concentration of A from Eq. 47 into the differential equation governing the rate of change of R, Eq. 45; thus

$$\frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t} \tag{48}$$

which is a first-order linear differential equation of the form

$$\frac{dy}{dx} + Py = Q$$

By multiplying through with the integrating factor $e^{\int P \, dx}$ the solution is

$$y e^{\int P \, dx} = \int Q e^{\int P \, dx} \, dx + \text{constant}$$

Applying this general procedure to the integration of Eq. 48, we find that the integrating factor is $e^{k_2 t}$. The constant of integration is found to be $-k_1 C_{A0}/(k_2 - k_1)$ from the initial conditions $C_{R0} = 0$ at $t = 0$, and the final expression for the changing concentration of R is

$$C_R = C_{A0} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right) \tag{49}$$

Noting that there is no change in total number of moles, the stoichiometry relates the concentrations of reacting components by

كل التراكيز الناتجة هي بالاصل CA0

$$C_{A0} = C_A + C_R + C_S$$

which with Eqs. 47 and 49 gives

$$C_S = C_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right) \tag{50}$$

Thus, we have found how the concentrations of components A, R, and S vary with time.

Now if k_2 is much larger than k_1, Eq. 50 reduces to

$$C_S = C_{A0} (1 - e^{-k_1 t}), \qquad k_2 \gg k_1$$

In other words, the rate is determined by k_1 or the first step of the two-step reaction.

If k_1 is much larger than k_2, then

$$C_S = C_{A0} (1 - e^{-k_2 t}), \qquad k_1 \gg k_2$$

which is a first-order reaction governed by k_2, the slower step in the two-step reaction. Thus, in general, for any number of reactions in series it is the slowest step that has the greatest influence on the overall reaction rate.

As may be expected, the values of k_1 and k_2 also govern the location and maximum concentration of R. This may be found by differentiating Eq. 49 and setting $dC_R/dt = 0$. The time at which the maximum concentration of R occurs is thus

واجب

$$t_{max} = \frac{1}{k_{log\,mean}} = \frac{\ln (k_2/k_1)}{k_2 - k_1} \tag{51}$$

The maximum concentration of R is found by combining Eqs. 49 and 51 to give

$$\frac{C_{R,max}}{C_{A0}} = \left(\frac{k_1}{k_2} \right)^{k_2/(k_2 - k_1)} \tag{52}$$

Figure 3.11 shows the general characteristics of the concentration-time curves for the three components; A decreases exponentially, R rises to a maximum and then falls, and S rises continuously, the greatest rate of increase of S occurring where R is a maximum. In particular, this figure shows that one can evaluate k_1 and k_2 by noting the maximum concentration of intermediate and the time when this maximum is reached. Chapter 8 covers series reactions in more detail.

For a longer chain of reactions, say

$$A \rightarrow R \rightarrow S \rightarrow T \rightarrow U$$

the treatment is similar, though more cumbersome than the two-step reaction just considered. Figure 3.12 illustrates typical concentration-time curves for this situation.
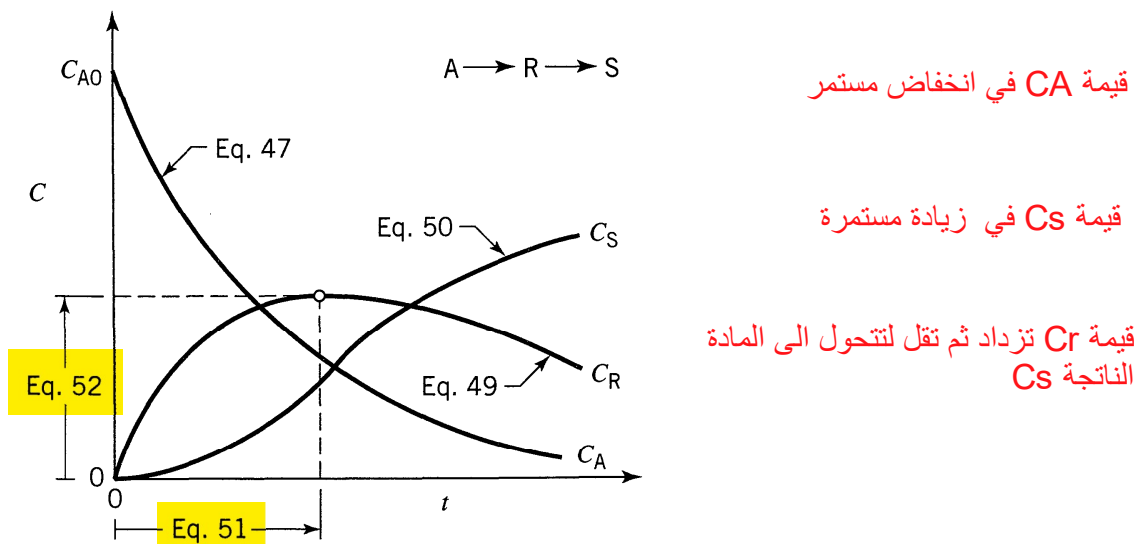
$A \longrightarrow R \longrightarrow S$

قيمة CA في انخفاض مستمر

قيمة Cs في زيادة مستمرة

قيمة Cr تزداد ثم تقل لتتحول الى المادة الناتجة Cs

Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

First-Order Reversible Reactions. Though no reaction ever goes to completion, we can consider many reactions to be essentially irreversible because of the large value of the equilibrium constant. These are the situations we have examined up to this point. Let us now consider reactions for which complete conversion cannot be assumed. The simplest case is the opposed unimolecular-type reaction

$$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R, \qquad K_C = K = \text{equilibrium constant} \qquad (53a)$$
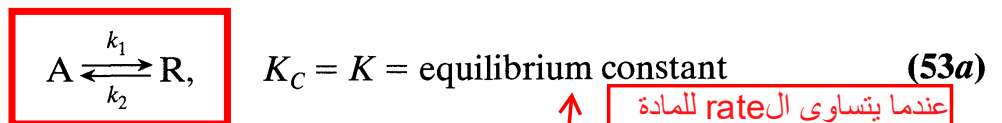
عندما يتساوى الrate للمادة A مع الrate للمادة R

Starting with a concentration ratio $M = C_{R0}/C_{A0}$ the rate equation is

سالب لان المادة R تتفاعل انعكاسياً لتستهلك ولتكون المادة A عنـــد K2

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = k_1 C_A - k_2 C_R \qquad (53b)$$

موجب لان المادة R تتكول من المادة A عنـــد K1

$$= k_1(C_{A0} - C_{A0}X_A) - k_2(MC_{A0} + C_{A0}X_A)$$

C_{R0}

المقدار المتحول من المادة A

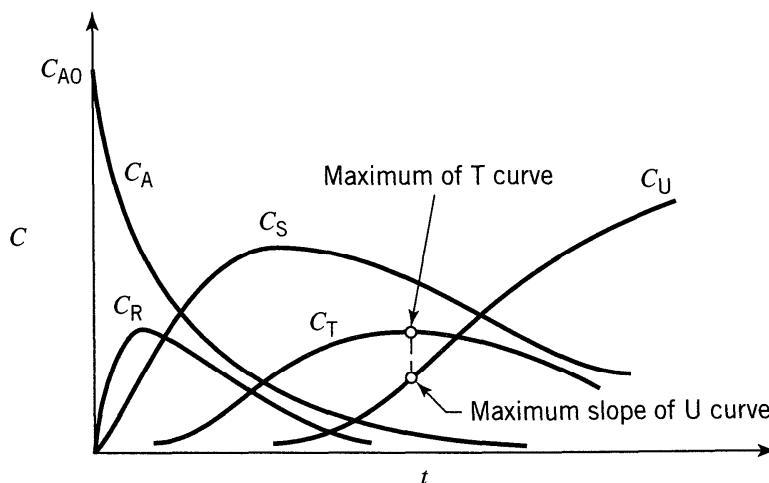Maximum of T curve

Maximum slope of U curve

Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.