University of Anbar

College of Engineering

Chemical and Petrochemical Engineering Department

Chemical Reacior Design

Third Year

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Lecture No.4:

Overall Order of Irreversible Reactions from the Half-Life $t_{,,}$. Sometimes, for the irreversible reaction

$$\alpha A + \beta B + \cdots \rightarrow products \qquad -r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b .$$

If the reactants are present in their stoichiometric ratios, they will remain at that ratio throughout the reaction. Thus, for reactants A and B at any time $C_B/C_A = \beta/\alpha$, and we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a \left(\frac{\beta}{\alpha} C_A\right)^b \cdots = \underbrace{k\left(\frac{\beta}{\alpha}\right)^b}_{\tilde{k}} \cdots \underbrace{C_A^{a+b+\cdots}}_{C_A^n}$$

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n$$

Integrating for $n \neq 1$ gives

$$C_A^{1-n} - C_{A0}^{1-n} = \tilde{k}(n-1)t \qquad \qquad \textbf{(24)}$$

Defining the half-life of the reaction, $t_{1/2}$, as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

$$\boxed{t_{1/2} = \frac{(0.5)^{1-n}-1}{\tilde{k}(n-1)} C_{A0}^{1-n}}$$
$$\textbf{(25)}$$

This expression shows that a plot of log $t_,$, vs. *log C_{Ao}* gives a straight line of slope *1 - n*, as shown in Fig. 3.5.
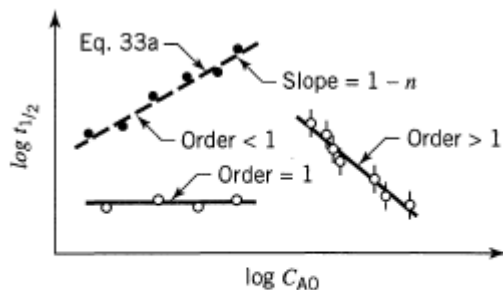

Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

The half-life method requires making a series of runs, each at a different initial concentration *fractional conversion* in a given time *rises **with increased concentration*** for **orders greater than one**, *drops* with *increased concentration* for **orders less than one**, and is *independent of initial concentration* for **reactions of first order**

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

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

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

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

$$\left. \begin{array}{l} A \xrightarrow{k_1} R \\[2mm] A \xrightarrow{k_2} S \end{array} \right\}$$

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

$$r_R = \frac{dC_R}{dt} = k_1 C_A \qquad (35)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_A \qquad (36)$$

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

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

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

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2} \qquad (38)$$

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.
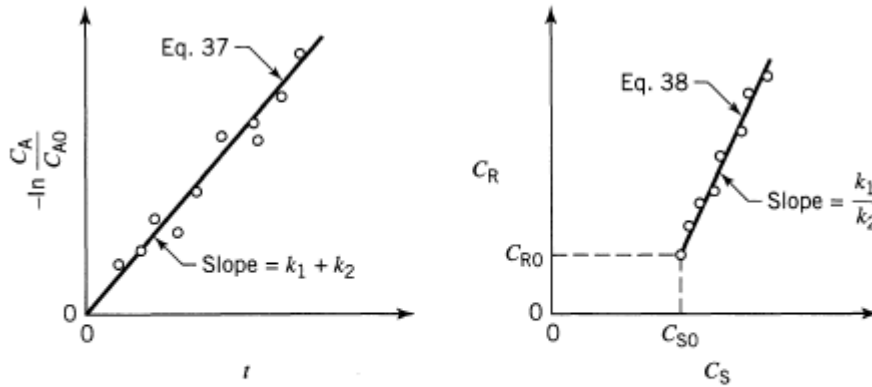
Figure 3.6 Evaluation of the rate constants for two competing elementary first-order reactions of the type $A \diagdown{}^{R}_{S}$.
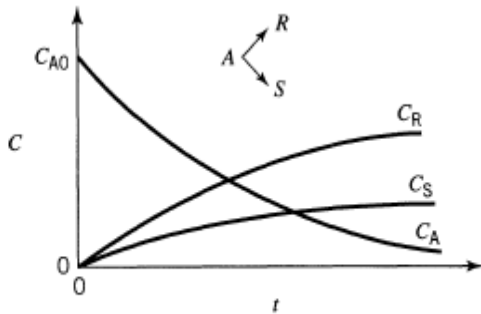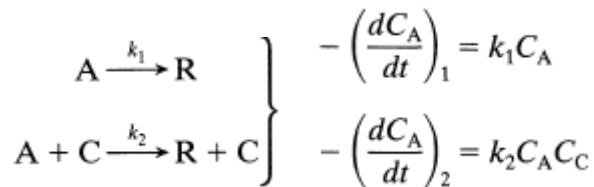

Figure 3.7 Typical concentration-time curves for competing reactions.

Homogeneous Catalyzed Reactions. Suppose the reaction rate for a homogeneous catalyzed system is the sum of rates of both the uncatalyzed and catalyzed reactions,

$$\left. \begin{array}{l} A \xrightarrow{k_1} R \\ \\ A + C \xrightarrow{k_2} R + C \end{array} \right\} \qquad \begin{array}{l} -\left(\dfrac{dC_A}{dt}\right)_1 = k_1 C_A \\ \\ -\left(\dfrac{dC_A}{dt}\right)_2 = k_2 C_A C_C \end{array}$$

The overall rate of disappearance of reactant A is then

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

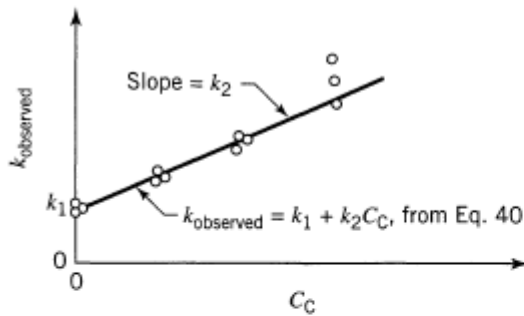$$-\ln \frac{C_A}{C_{A0}} = -\ln (1 - X_A) = (k_1 + k_2 C_C)t = k_{observed} \, t \qquad (40)$$

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

$$\ln \frac{C_{A0}(C_0 - C_A)}{C_A(C_0 - C_{A0})} = \ln \frac{C_R/C_{R0}}{C_A/C_{A0}} = C_0kt = (C_{A0} + C_{R0})\,kt \qquad (42)$$
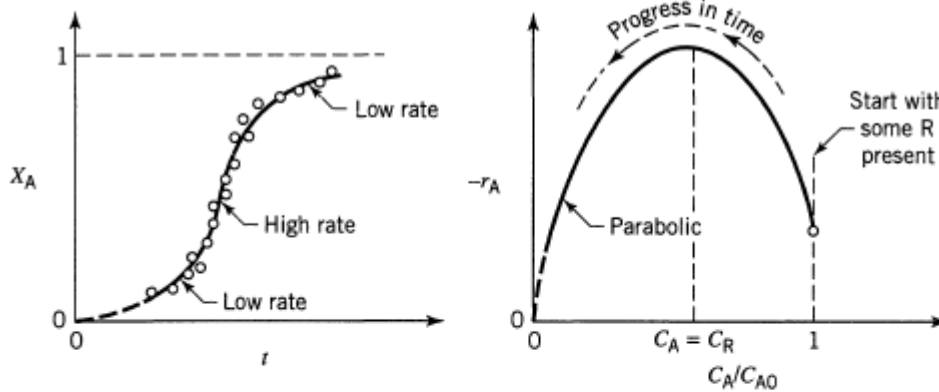

Figure 3.9 Conversion-time and rate-concentration curves for autocatalytic reaction of Eq. 41. This shape is typical for this type of reaction.

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

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

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.

Irreversible Reactions in Series. We first consider consecutive unimolecular type *first-order* reactions such as
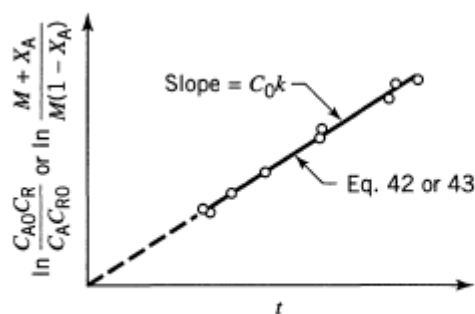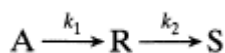
$$A \xrightarrow{k_1} R \xrightarrow{k_2} S$$

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

whose rate equations for the three components are

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \qquad\qquad (44)$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \qquad\qquad (45)$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \qquad\qquad (46)$$

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

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

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

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

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:
The integrating factor$=e^{K_2 t}$, The constant of integration$= -k_1 C_{Ao} / (k_1 - k_2)$ from the initial conditions $C_{R0} = 0$ at t = 0, the final expression for the changing concentration of R is

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

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

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

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

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

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

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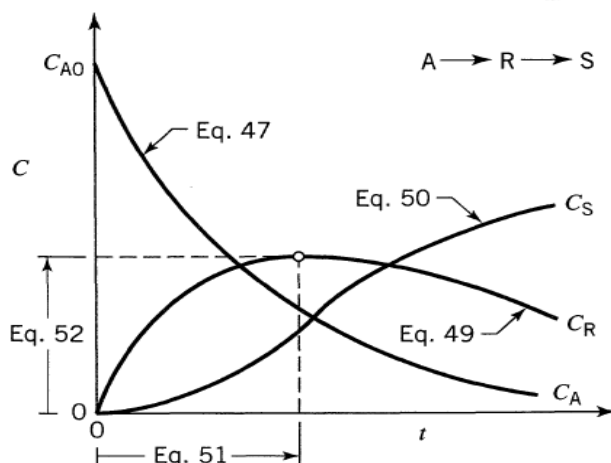

Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

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 raises 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.