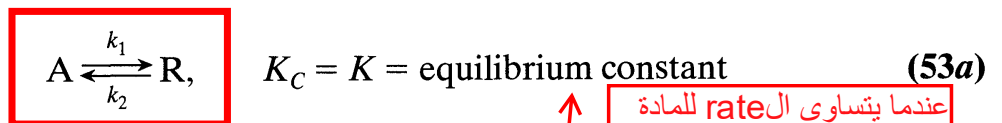


Figure 3.11 Typical concentration-time curves for consecutive first-order reactions.

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



عندما يتساوى ال rate للمادة R مع ال rate للمادة A

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

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

سالب لان المادة R تتفاعل انعكاسياً لتستهلك وتكون المادة A عند K2

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

موجب لان المادة R تتكون من المادة A عند K1

المقدار المتحول من المادة A

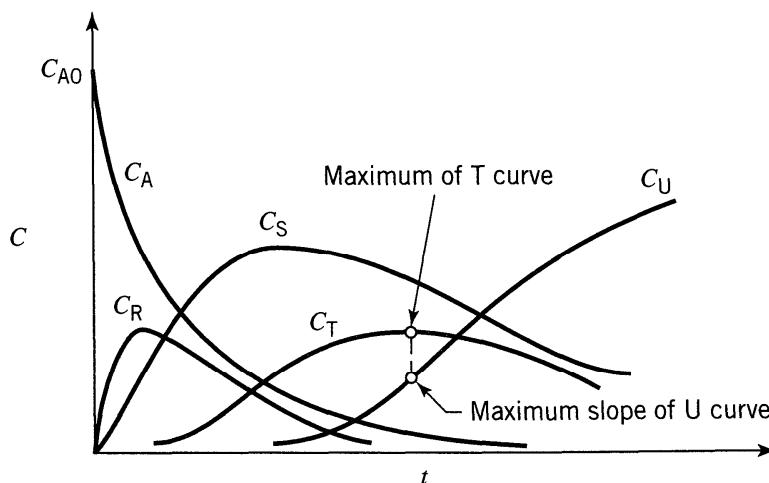


Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.

Now at equilibrium $dC_A/dt = 0$. Hence from Eq. 53 we find the fractional conversion of A at equilibrium conditions to be

تركيز النواتج على تركيز المتفاعلات عند
equilibrium conditions
$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

and the equilibrium constant to be

$$K_C = \frac{k_1}{k_2}$$

Combining the above three equations we obtain, in terms of the equilibrium conversion,

$$\frac{dX_A}{dt} = \frac{k_1(M+1)}{M+X_{Ae}}(X_{Ae} - X_A)$$

With conversions measured in terms of X_{Ae} , this may be looked on as a pseudo first-order irreversible reaction which on integration gives

$$\boxed{-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M+X_{Ae}}k_1t} \quad (54)$$

A plot of $-\ln(1 - X_A/X_{Ae})$ vs. t , as shown in Fig. 3.13, gives a straight line.

The similarity between equations for the first-order irreversible and reversible reactions can be seen by comparing Eq. 12 with Eq. 54 or by comparing Fig. 3.1 with Fig. 3.13. Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{Ae} = 0$, or $X_{Ae} = 1$, or $K_C = \infty$.

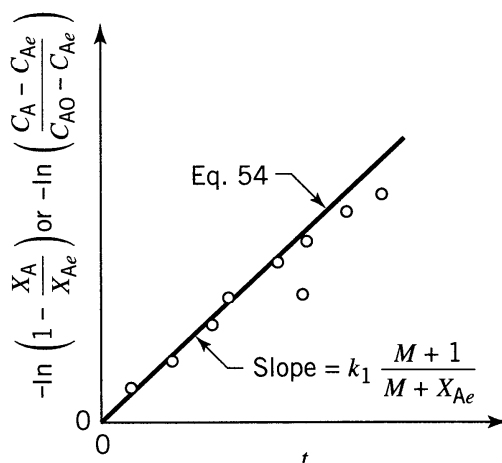
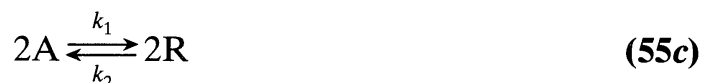


Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

Second-Order Reversible Reactions. For the bimolecular-type second-order reactions



with the restrictions that $C_{A0} = C_{B0}$ and $C_{R0} = C_{S0} = 0$, the integrated rate equations for A and B are all identical, as follows

$$\ln \frac{X_{Ae} - (2X_{Ae} - 1)X_A}{X_{Ae} - X_A} = 2k_1 \left(\frac{1}{X_{Ae}} - 1 \right) C_{A0}t \quad (56)$$

A plot as shown in Fig. 3.14 can then be used to test the adequacy of these kinetics.

Reversible Reactions in General. For orders other than one or two, integration of the rate equation becomes cumbersome. So if Eq. 54 or 56 is not able to fit the data, then the search for an adequate rate equation is best done by the differential method.

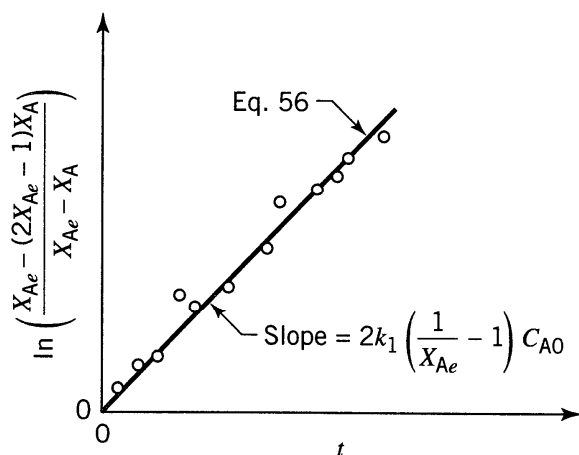


Figure 3.14 Test for the reversible bimolecular reactions of Eq. 55.

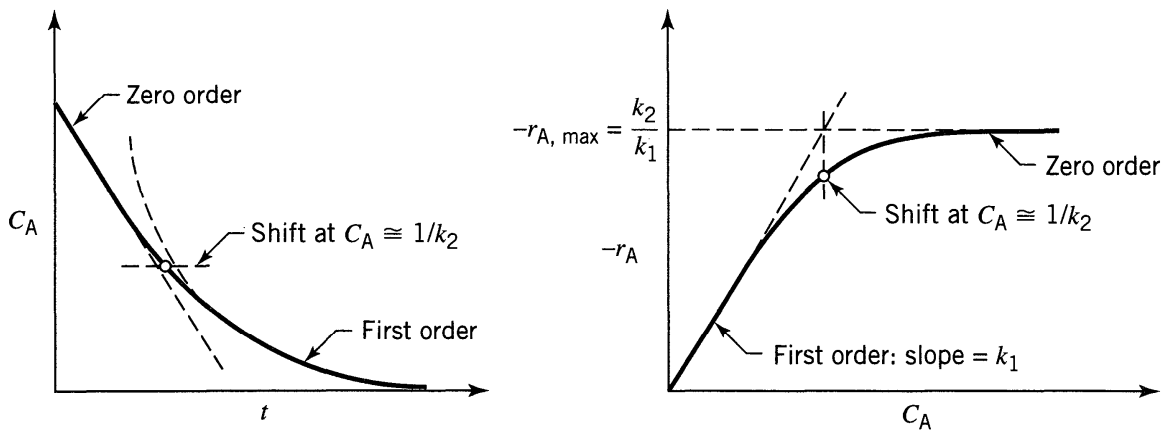
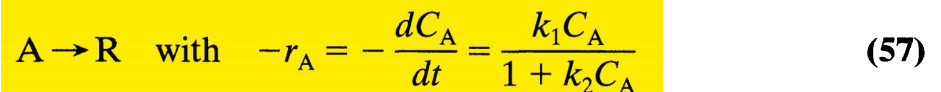


Figure 3.15 Behavior of a reaction that follows Eq. 57.

Reactions of Shifting Order. In searching for a kinetic equation it may be found that the data are well fitted by **one reaction order at high concentrations** but by **another order at low concentrations**. Consider the reaction



From this rate equation we see

At high C_A —the reaction is of zero order with rate constant k_1/k_2
(or $k_2 C_A \gg 1$)

At low C_A —the reaction is of first order with rate constant k_1
(or $k_2 C_A \ll 1$)

This behavior is shown in Fig. 3.15.

To apply the integral method, separate variables and integrate Eq. 57. This gives

$$\ln \frac{C_{A0}}{C_A} + k_2 (C_{A0} - C_A) = k_1 t \quad (58a)$$

To linearize, rearrange Eq. 58a to give

$$\frac{C_{A0} - C_A}{\ln (C_{A0}/C_A)} = -\frac{1}{k_2} + \frac{k_1}{k_2} \left(\frac{t}{\ln (C_{A0}/C_A)} \right) \quad (58b)$$

or

$$\frac{\ln (C_{A0}/C_A)}{C_{A0} - C_A} = -k_2 + \frac{k_1 t}{C_{A0} - C_A} \quad (58c)$$

Two ways to test this rate form are then shown in Fig. 3.16.

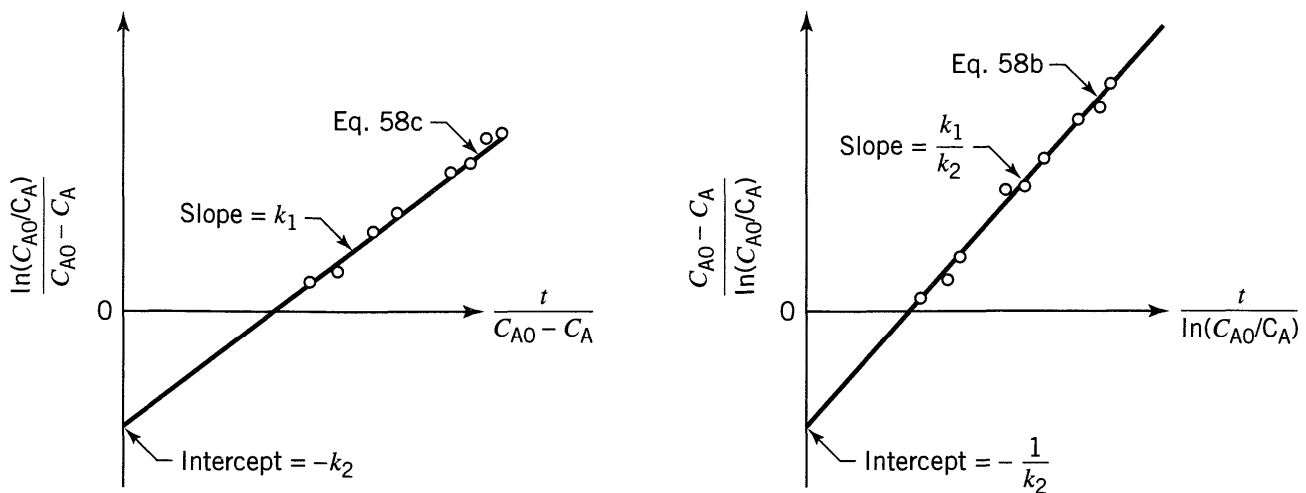


Figure 3.16 Test of the rate equation, Eq. 57, by integral analysis.

By similar reasoning to the above we can show that the general rate form

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{1 + k_2 C_A^n} \quad (59)$$

shifts from order $m - n$ at high concentration to order m at low concentration, the transition taking place where $k_2 C_A^n \cong 1$. This type of equation can then be used to fit data of any two orders.

Another form which can account for this shift is

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A^m}{(1 + k_2 C_A)^n} \quad (60)$$

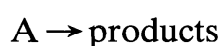
Mechanism studies may suggest which form to use. In any case, if one of these equation forms will fit the data, so will the other.

The rate form of Eq. 57 and some of its generalizations are used to represent a number of widely different kinds of reactions. For example, in homogeneous systems this form is used for enzyme-catalyzed reactions where it is suggested by mechanistic studies (see the Michaelis-Menten mechanism in Chap. 2 and in Chap. 27). It is also used to represent the kinetics of surface-catalyzed reactions.

In mechanistic studies, this form of equation appears whenever the rate-controlling step of a reaction is viewed to involve the association of reactant with some quantity that is present in limited but fixed amounts; for example, the association of reactant with enzyme to form a complex, or the association of gaseous reactant with an active site on the catalyst surface.

EXAMPLE 3.1 FIND A RATE EQUATION USING THE INTEGRAL METHOD

Reactant A decomposes in a batch reactor



The composition of A in the reactor is measured at various times with results shown in the following columns 1 and 2. Find a rate equation to represent the data.

Column 1	Column 2	Column 3	Column 4
Time t, s	Concentration $C_A, \text{mol/liter}$	$\ln \frac{C_{A0}}{C_A}$	$\frac{1}{C_A}$
0	$C_{A0} = 10$	$\ln 10/10 = 0$	0.1
20	8	$\ln 10/8 = 0.2231$	0.125
40	6	0.511	0.167
60	5	0.6931	0.200
120	3	1.204	0.333
180	2	1.609	0.500
300	1	2.303	1.000
Reported data		Calculated	

SOLUTION

Guess First-Order Kinetics. Start by guessing the simplest rate form, or first-order kinetics. This means that $\ln C_{A0}/C_A$ vs. t should give a straight line, see Eq. 11 or 12, or Fig. 3.1. So column 3 is calculated and the plot of Fig. E3.1a is made. Unfortunately, this does not give a straight line, so first-order kinetics cannot reasonably represent the data, and we must guess another rate form.

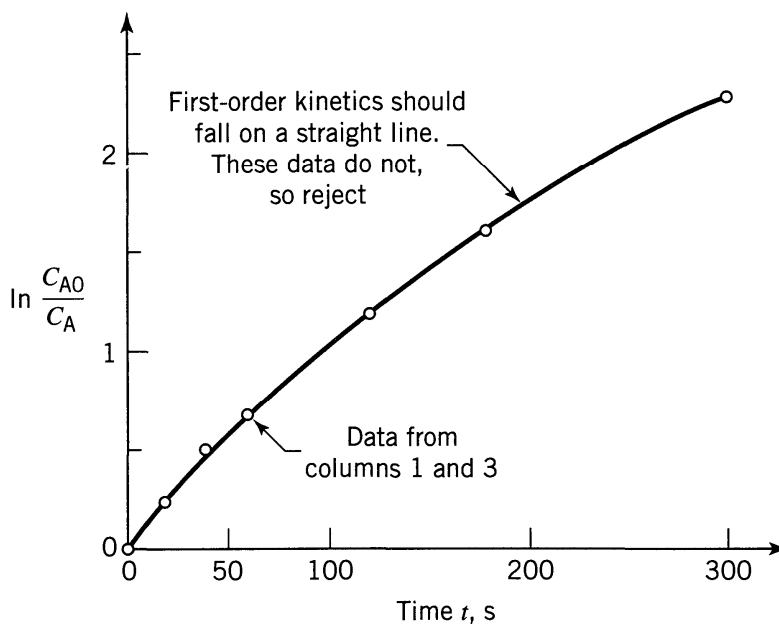
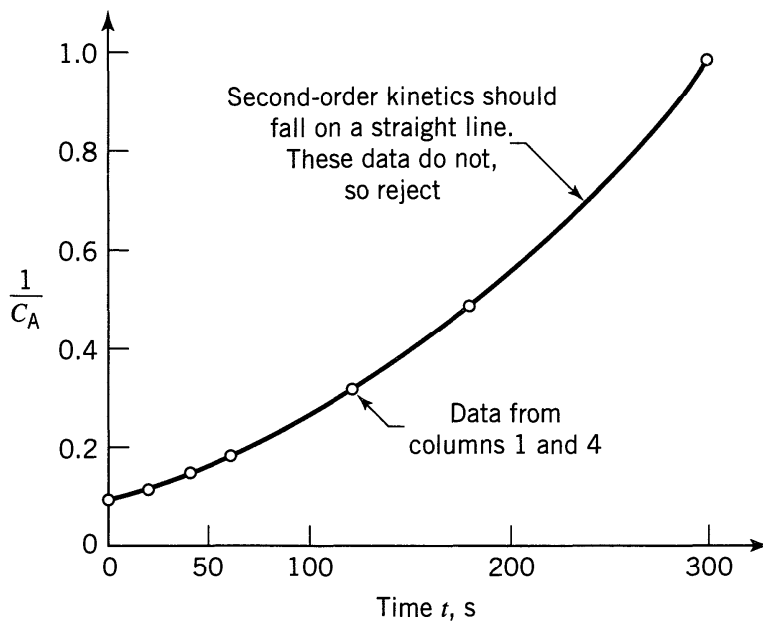


Figure E3.1a

Guess Second-Order Kinetics. Equation 16 tells that $1/C_A$ vs. t should give a straight line. So calculate column 4, plot column 1 vs. column 4, as shown in Fig. E3.1b. Again, this does not give a straight line, so a second-order kinetic form is rejected.


Figure E3.1b

Guess *n*-th-Order Kinetics. Let's plan to use the fractional life method with $F = 80\%$. Then Eq. 33b becomes

$$t_F = \frac{(0.8)^{1-n} - 1}{k(n-1)} C_{A0}^{1-n} \quad (\text{i})$$

Next take logarithms

$$\log t_F = \log \left(\frac{0.8^{1-n} - 1}{k(n-1)} \right) + (1-n) \log C_{A0} \quad (\text{ii})$$

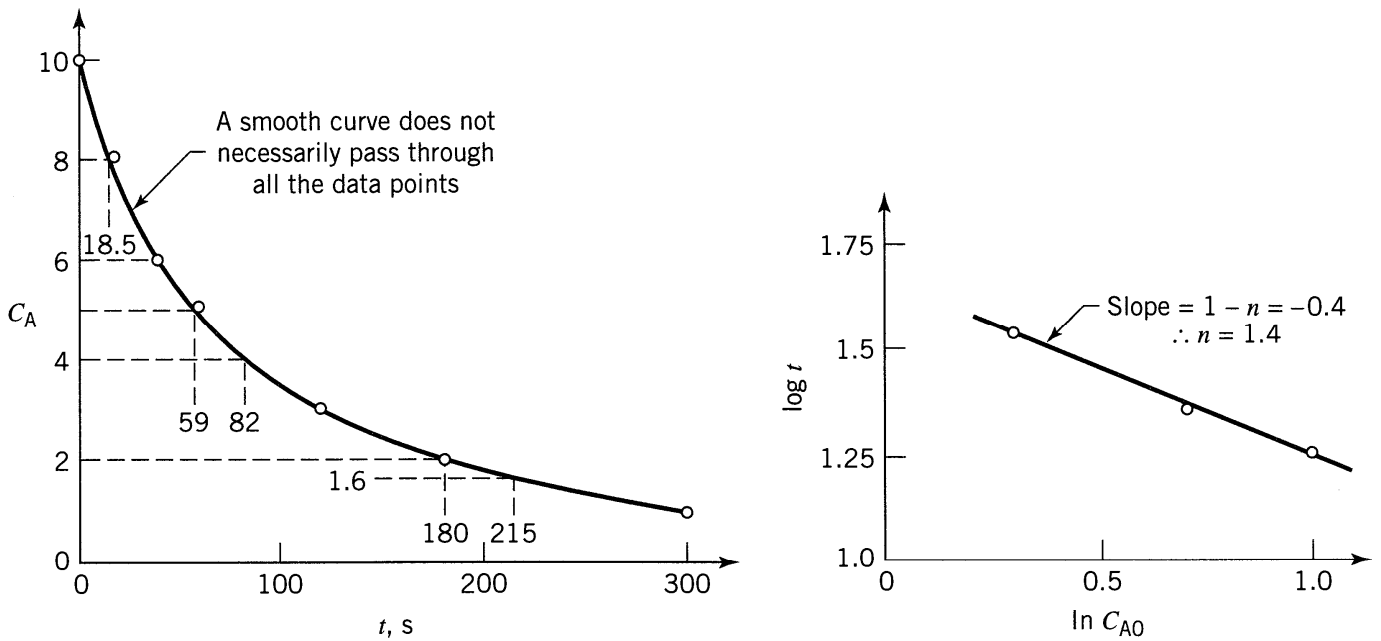
a constant
y
a
bx

The procedure is as follows. First accurately plot the C_A vs. t data, draw a smooth curve to represent the data (most important) as shown in Fig. E3.1c, then pick $C_{A0} = 10, 5,$ and 2 and fill in the following table from this figure.

C_{A0}	$C_{A \text{ end}}$ ($= 0.8C_{A0}$)	Time needed t_F, s	$\log t_F$	$\log C_{A0}$
10	8	$0 \rightarrow 18.5 = 18.5$	$\log 18.5 = 1.27$	1.00
5	4	$59 \rightarrow 82 = 23$	1.36	0.70
2	1.6	$180 \rightarrow 215 = 35$	1.54	0.30

From the curve, not the data

Next, plot $\log t_F$ vs. $\log C_{A0}$, as shown in Fig. E3.1d and find the slope.



Figures E3.1c and E3.1d

We now have the reaction order. To evaluate the rate constant, take any point on the C_A vs. t curve. Pick $C_{A0} = 10$, for which $t_F = 18.5$ s. Replacing all values into Eq. (i) gives

$$18.5 = \frac{(0.8)^{1-1.4} - 1}{k(1.4 - 1)} 10^{1-1.4}$$

from which

$$k = 0.005$$

Therefore, the rate equation that represents this reaction is

$$\underline{\underline{-r_A = \left(0.005 \frac{\text{liter}^{0.4}}{\text{mol}^{0.4} \cdot \text{s}}\right) C_A^{1.4}, \quad \frac{\text{mol}}{\text{liter} \cdot \text{s}}}}$$

Differential Method of Analysis of Data

The differential method of analysis deals directly with the differential rate equation to be tested, evaluating all terms in the equation including the derivative dC_i/dt , and testing the goodness of fit of the equation with experiment.

The procedure is as follows.

1. Plot the C_A vs. t data, and then by eye carefully draw a smooth curve to represent the data. This curve most likely will not pass through all the experimental points.
2. Determine the slope of this curve at suitably selected concentration values. These slopes $dC_A/dt = r_A$ are the rates of reaction at these compositions.

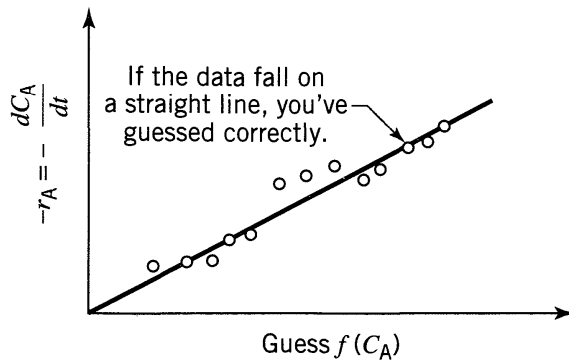


Figure 3.17 Test for the particular rate form $-r_A = kf(C_A)$ by the differential method.

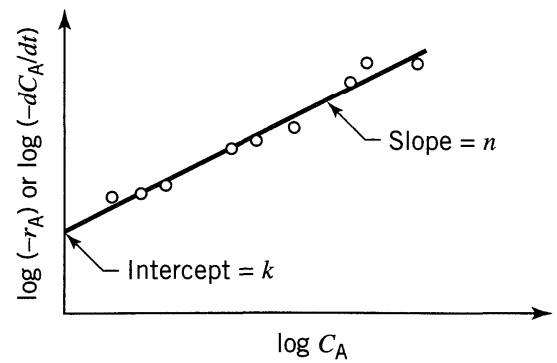


Figure 3.18 Test for an n th-order rate form by the differential method.

3. Now search for a rate expression to represent this r_A vs. C_A data, either by
- picking and testing a particular rate form, $-r_A = kf(C_A)$, see Fig. 17, or
 - testing an n th-order form $-r_A = kC_A^n$ by taking logarithms of the rate equation (see Fig. 3.18).

With certain simpler rate equations, however, mathematical manipulation may be able to yield an expression suitable for graphical testing. As an example, consider a set of C_A vs. t data to which we want to fit the M–M equation

$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A} \quad (57)$$

which has already been treated by the integral method of analysis. By the differential method we can obtain $-r_A$ vs. C_A . However, how do we make a straight-line plot to evaluate k_1 and k_2 ? As suggested, let us manipulate Eq. 57 to obtain a more useful expression. Thus, taking reciprocals we obtain

$$\frac{1}{(-r_A)} = \frac{1}{k_1 C_A} + \frac{k_2}{k_1} \quad (61)$$

and a plot of $1/(-r_A)$ vs. $1/C_A$ is linear, as shown in Fig. 3.19.

Alternatively, a different manipulation (multiply Eq. 61 by $k_1(-r_A)/k_2$) yields another form, also suitable for testing, thus

$$(-r_A) = \frac{k_1}{k_2} - \frac{1}{k_2} \left[\frac{(-r_A)}{C_A} \right] \quad (62)$$

A plot of $-r_A$ vs. $(-r_A)/C_A$ is linear, as shown in Fig. 3.19.

Whenever a rate equation can be manipulated to give a linear plot, this becomes a simple way of testing the equation. So, with any given problem we must use good judgment in planning our experimental program.

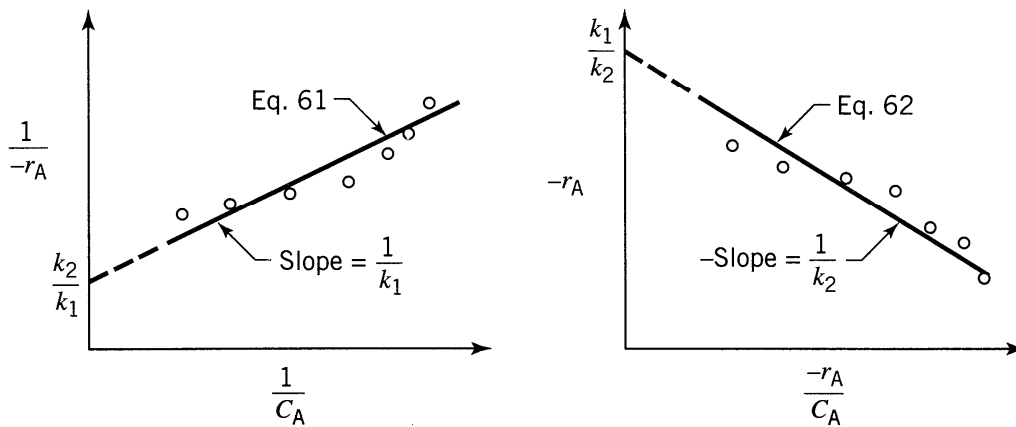


Figure 3.19 Two ways of testing the rate equation $-r_A = k_1 C_A / (1 + k_2 C_A)$ by differential analysis.

EXAMPLE 3.2 FIND A RATE EQUATION TO FIT A SET OF DATA USING THE DIFFERENTIAL METHOD

Try to fit an n th-order rate equation to the concentration vs. time data of Example 3.1.

SOLUTION

The data are tabulated in the following columns 1 and 2 and are plotted in Fig. E3.2a.

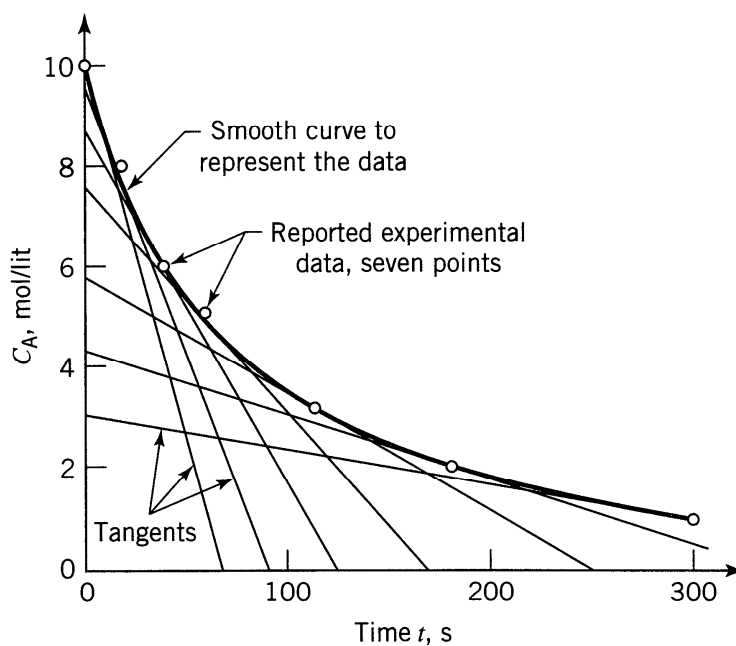


Figure E3.2a

Column 1	Column 2	Column 3	Column 4	Column 5
Time t, s	Concentration $C_A, \text{mol/liter}$	Slope, from Fig. E3.2a (dC_A/dt)	$\log_{10}(-dC_A/dt)$	$\log_{10} C_A$
0	10	$(10 - 0)/(0 - 75) = -0.1333$	-0.875	1.000
20	8	$(10 - 0)/(-3 - 94) = -0.1031$	-0.987	0.903
40	6	$(10 - 0)/(-21 - 131) = -0.0658$	-1.182	0.778
60	5	$(8 - 0)/(-15 - 180) = -0.0410$	-1.387	0.699
120	3	$(6 - 0)/(-10 - 252) = -0.0238$	-1.623	0.477
180	2	$(4 - 1)/(24 - 255) = -0.0108$	-1.967	0.301
300	1	$(3 - 1)/(-10 - 300) = -0.0065$	-2.187	0.000

Now carefully draw a smooth curve to represent the data and at $C_A = 10, 8, 6, 5, 3, 2, 1$, draw tangents to the curve, and evaluate them (see column 3).

Next, to fit an n th-order rate equation to this data, or

$$-r_A = -\frac{dC_A}{dt} = kC_A^n$$

take logarithms of both sides (see columns 3 and 4), or

$$\log_{10}\left(-\frac{dC_A}{dt}\right) = \log_{10}k + n\log_{10}C_A$$

y
 x

intercept
slope

and plot as in Fig. E3.2b. The slope and intercept of the best line gives n and k (see Fig.E3.2b). So the rate equation is

$$\underline{\underline{-r_A = -\frac{dC_A}{dt} = \left(0.005 \frac{\text{liter}^{0.43}}{\text{mol}^{0.43} \cdot \text{s}}\right) C_A^{1.43}, \frac{\text{mol}}{\text{liter} \cdot \text{s}}}}$$

Warning. In step 1, if you use a computer to fit a polynomial to the data it could lead to disaster. For example, consider fitting a sixth-degree polynomial to the seven data points, or an $(n - 1)$ degree polynomial to n points.

Fitting by eye you'd get a smooth curve, as shown in Fig. E3.2c. But if a computer is used to obtain a polynomial that would pass through all the points the result would very well be as shown in Fig. E3.2d.

Now, which of these curves makes more sense and which would you use? This is why we say "draw a smooth curve by eye to represent the data." But beware, to draw such a curve is not that simple. Take care.

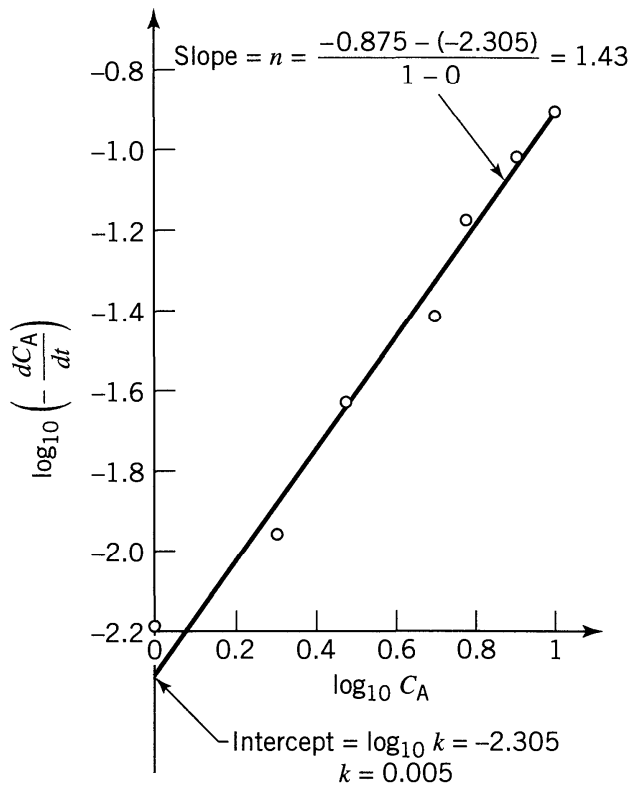


Figure E3.2b

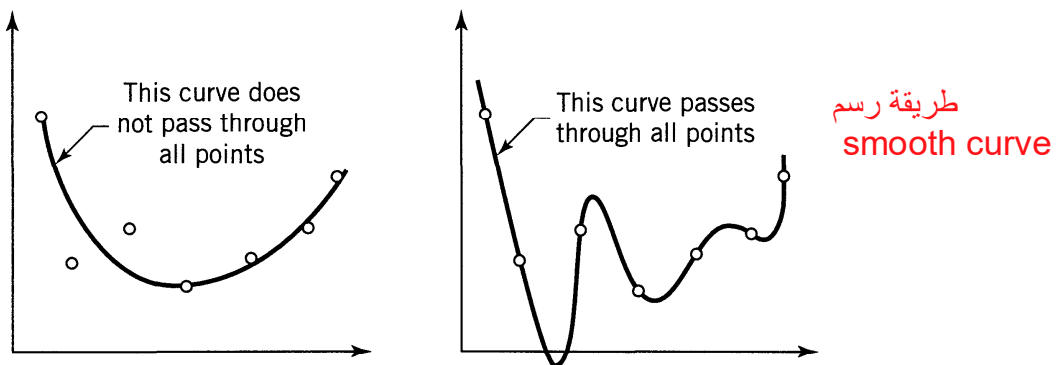


Figure E3.2c, d The same seven points fitted by curves two different ways.

3.2 VARYING-VOLUME BATCH REACTOR

These reactors are much more complex than the simple constant-volume batch reactor. Their main use would be in the microprocessing field where a capillary tube with a movable bead would represent the reactor (see Fig. 3.20).

The progress of the reaction is followed by noting the movement of the bead with time, a much simpler procedure than trying to measure the composition of the mixture, especially for microreactors. Thus,

V_0 = initial volume of the reactor

V = the volume at time t .