

# Chapter 3

## Interpretation of Batch Reactor Data

طريقة ايجاد وتمييز معادلة التفاعل عن طريق التجارب العملية

حساب ثابت التفاعل ومعرفة ومعرفة رتبة المعادلة عند حرارة ثابتة

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A rate equation characterizes the rate of reaction, and its form may either be suggested by theoretical considerations or simply be the result of an empirical curve-fitting procedure. In any case, the value of the constants of the equation can only be found by experiment; predictive methods are inadequate at present.

The determination of the rate equation is usually a two-step procedure; first the concentration dependency is found at fixed temperature and then the temperature dependence of the rate constants is found, yielding the complete rate equation.

المعلومات التجريبية

Equipment by which empirical information is obtained can be divided into two types, the *batch* and *flow* reactors. The batch reactor is simply a container to hold the contents while they react. All that has to be determined is the extent of reaction at various times, and this can be followed in a number of ways, for example:

1. By following the concentration of a given component.
2. By following the change in some physical property of the fluid, such as the electrical conductivity or refractive index.
3. By following the change in total pressure of a constant-volume system.
4. By following the change in volume of a constant-pressure system.

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The experimental batch reactor is usually operated isothermally and at constant volume because it is easy to interpret the results of such runs. This reactor is a relatively simple device adaptable to small-scale laboratory set-ups, and it needs but little auxiliary equipment or instrumentation. Thus, it is used whenever possible for obtaining homogeneous kinetic data. This chapter deals with the batch reactor.

The flow reactor is used primarily in the study of the kinetics of heterogeneous reactions. Planning of experiments and interpretation of data obtained in flow reactors are considered in later chapters.

There are two procedures for analyzing kinetic data, the *integral* and the *differential* methods. In the integral method of analysis we guess a particular form of rate equation and, after appropriate integration and mathematical manipulation, predict that the plot of a certain concentration function versus time

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should yield a straight line. The data are plotted, and if a reasonably good straight line is obtained, then the rate equation is said to satisfactorily fit the data.

In the differential method of analysis we test the fit of the rate expression to the data directly and without any integration. However, since the rate expression is a differential equation, we must first find  $(1/V)(dN/dt)$  from the data before attempting the fitting procedure.

There are advantages and disadvantages to each method. The integral method is easy to use and is recommended when testing specific mechanisms, or relatively simple rate expressions, or when the data are so scattered that we cannot reliably find the derivatives needed in the differential method. The differential method is useful in more complicated situations but requires more accurate or larger amounts of data. The integral method can only test this or that particular mechanism or rate form; the differential method can be used to develop or build up a rate equation to fit the data.

In general, it is suggested that integral analysis be attempted first, and, if not successful, that the differential method be tried.

### 3.1 CONSTANT-VOLUME BATCH REACTOR

When we mention the constant-volume batch reactor we are really referring to the volume of reaction mixture, and not the volume of reactor. Thus, this term actually means a *constant-density reaction system*. Most liquid-phase reactions as well as all gas-phase reactions occurring in a constant-volume bomb fall in this class.

In a constant-volume system the measure of reaction rate of component  $i$  becomes

$$r_i = \frac{1}{V} \frac{dN_i}{dt} = \frac{d(N_i/V)}{dt} = \frac{dC_i}{dt} \quad (1)$$

or for ideal gases, where  $C = p/RT$ ,

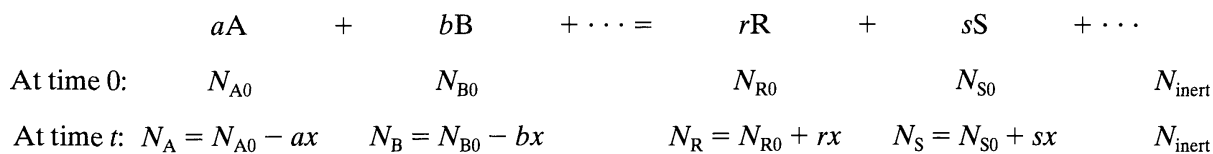
$$r_i = \frac{1}{RT} \frac{dp_i}{dt} \quad (2)$$

Thus, the rate of reaction of any component is given by the rate of change of its concentration or partial pressure; so no matter how we choose to follow the progress of the reaction, we must eventually relate this measure to the concentration or partial pressure if we are to follow the rate of reaction.

For gas reactions with changing numbers of moles, a simple way of finding the reaction rate is to follow the change in total pressure  $\pi$  of the system. Let us see how this is done.

**Analysis of Total Pressure Data Obtained in a Constant-Volume System.** For isothermal gas reactions where the number of moles of material changes during reaction, let us develop the general expression which relates the changing total pressure of the system  $\pi$  to the changing concentration or partial pressure of any of the reaction components.

Write the **general stoichiometric equation**, and under each term indicate the **number of moles of that component**:



**Initially the total number** of moles present in the system is

$$N_0 = N_{A0} + N_{B0} + \dots + N_{R0} + N_{S0} + \dots + N_{\text{inert}}$$

but at time  $t$  it is

$$N = N_0 + x(r + s + \dots - a - b - \dots) = N_0 + x \Delta n \quad (3)$$

where

$$\Delta n = r + s + \dots - a - b - \dots$$

Assuming that the ideal gas law holds, we may write for any reactant, say A in the system of volume  $V$

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} \quad (4)$$

Combining Eqs. 3 and 4 we obtain

$$C_A = \frac{N_{A0}}{V} - \frac{a}{\Delta n} \frac{N - N_0}{V}$$

or

$$p_A = C_A RT = p_{A0} - \frac{a}{\Delta n} (\pi - \pi_0) \quad (5)$$

Equation 5 gives the **concentration** or **partial pressure of reactant A** as a function of the **total pressure  $\pi$**  at time  $t$ , **initial partial pressure of A,  $p_{A0}$** , and **initial total pressure of the system,  $\pi_0$** .

Similarly, for any product R we can find

$$p_R = C_R RT = p_{R0} + \frac{r}{\Delta n} (\pi - \pi_0) \quad (6)$$

Equations 5 and 6 are the desired relationships between total pressure of the system and the partial pressure of reacting materials.

It should be emphasized that if the precise stoichiometry is not known, or if more than one stoichiometric equation is needed to represent the reaction, then the "total pressure" procedure cannot be used.

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 $\pi$   
 هو ضغط النظام الكلي في اي زمن

مقدار التحول للمادة بعد نهاية التفاعل او خلال اي زمن منه

**The Conversion.** Let us introduce one other useful term, the fractional conversion, or the fraction of any reactant, say A, converted to something else, or the fraction of A reacted away. We call this, simply, the conversion of A, with symbol  $X_A$ .

Suppose that  $N_{A0}$  is the initial amount of A in the reactor at time  $t = 0$ , and that  $N_A$  is the amount present at time  $t$ . Then the conversion of A in the constant volume system is given by

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$$X_A = \frac{N_{A0} - N_A}{N_{A0}} = 1 - \frac{N_A/V}{N_{A0}/V} = 1 - \frac{C_A}{C_{A0}} \quad (7)$$

and

$$dX_A = -\frac{dC_A}{C_{A0}} \quad (8)$$

We will develop the equations in this chapter in terms of concentration of reaction components and also in terms of conversions.

Later we will relate  $X_A$  and  $C_A$  for the more general case where the volume of the system does not stay constant.

### Integral Method of Analysis of Data

**General Procedure.** The integral method of analysis always puts a particular rate equation to the test by integrating and comparing the predicted  $C$  versus  $t$  curve with the experimental  $C$  versus  $t$  data. If the fit is unsatisfactory, another rate equation is guessed and tested. This procedure is shown and used in the cases next treated. It should be noted that the integral method is especially useful for fitting simple reaction types corresponding to elementary reactions. Let us take up these kinetic forms.

**Irreversible Unimolecular-Type First-Order Reactions.** Consider the reaction

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Suppose we wish to test the first-order rate equation of the following type,

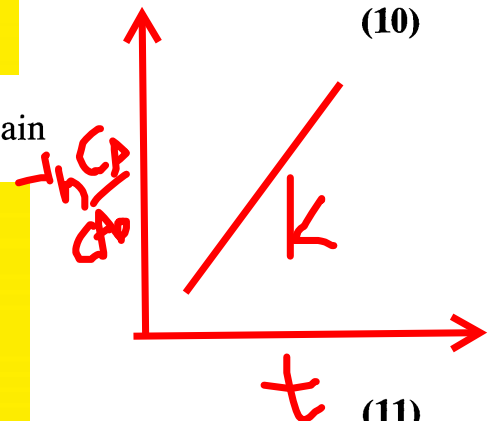
$$-r_A = -\frac{dC_A}{dt} = kC_A \quad (10)$$

for this reaction. Separating and integrating we obtain

$$-\int_{C_{A0}}^{C_A} \frac{dC_A}{C_A} = k \int_0^t dt$$

or

$$-\ln \frac{C_A}{C_{A0}} = kt \quad (11)$$



In terms of conversion (see Eqs. 7 and 8), the rate equation, Eq. 10, becomes

$$\frac{dX_A}{dt} = k(1 - X_A)$$

which on rearranging and integrating gives

$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

or

$$-\ln(1 - X_A) = kt \quad (12)$$

A plot of  $-\ln(1 - X_A)$  or  $\ln(C_A/C_{A0})$  vs.  $t$ , as shown in Fig. 3.1, gives a straight line through the origin for this form of rate of equation. If the experimental data seems to be better fitted by a curve than by a straight line, try another rate form because the first-order reaction does not satisfactorily fit the data.

**Caution.** We should point out that equations such as

$$-\frac{dC_A}{dt} = kC_A^{0.6}C_B^{0.4}$$

are first order but are not amenable to this kind of analysis; hence, not all first-order reactions can be treated as shown above.

**Irreversible Bimolecular-Type Second-Order Reactions.** Consider the reaction

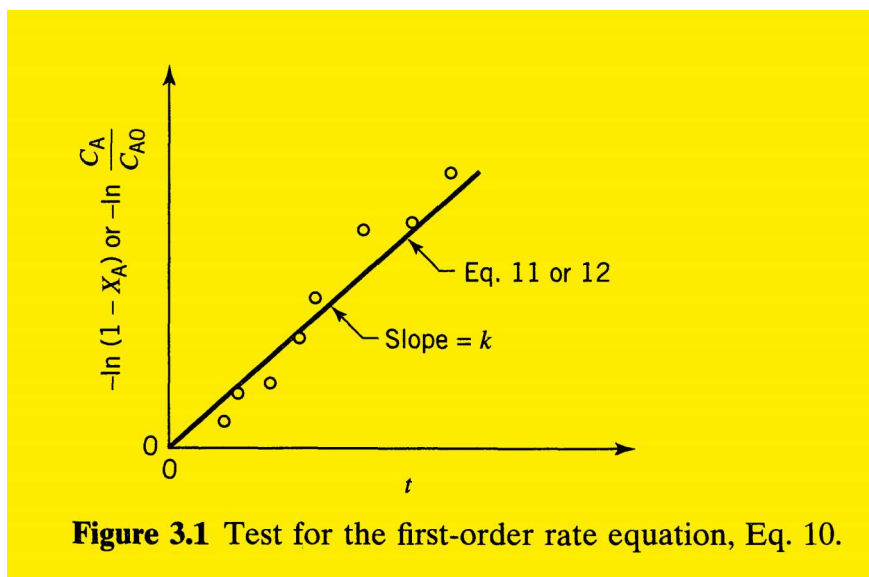
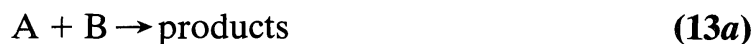


Figure 3.1 Test for the first-order rate equation, Eq. 10.

with corresponding rate equation

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \quad (13b)$$

Noting that the amounts of A and B that have reacted at any time  $t$  are equal and given by  $C_{A0}X_A$ , we may write Eqs. 13a and b in terms of  $X_A$  as

$$-r_A = C_{A0} \frac{dX_A}{dt} = k \underbrace{(C_{A0} - C_{A0}X_A)}_{C_A} \underbrace{(C_{B0} - C_{A0}X_A)}_{C_B}$$

Letting  $M = C_{B0}/C_{A0}$  be the initial molar ratio of reactants, we obtain

$$-r_A = C_{A0} \frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A)$$

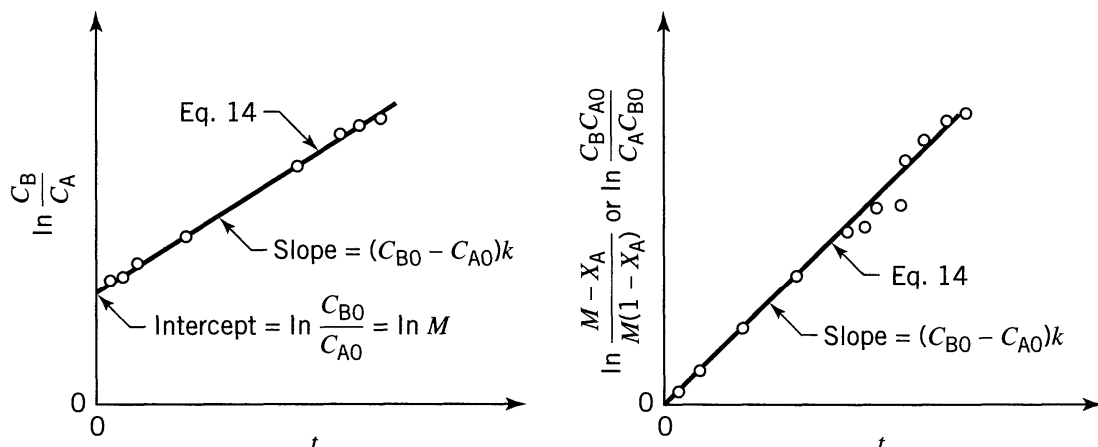
which on separation and formal integration becomes

$$\int_0^{X_A} \frac{dX_A}{(1 - X_A)(M - X_A)} = C_{A0}k \int_0^t dt$$

After breakdown into partial fractions, integration, and rearrangement, the final result in a number of different forms is

$$\begin{aligned} \ln \frac{1 - X_B}{1 - X_A} &= \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{C_B}{M C_A} \\ &= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \quad M \neq 1 \end{aligned} \quad (14)$$

Figure 3.2 shows two equivalent ways of obtaining a linear plot between the concentration function and time for this second-order rate law.



**Figure 3.2** Test for the bimolecular mechanism  $A + B \rightarrow R$  with  $C_{A0} \neq C_{B0}$ , or for the second-order reaction, Eq. 13.

If  $C_{B0}$  is much larger than  $C_{A0}$ ,  $C_B$  remains approximately constant at all times, and Eq. 14 approaches Eq. 11 or 12 for the first-order reaction. Thus, the second-order reaction becomes a pseudo first-order reaction.

**Caution 1.** In the special case where reactants are introduced in their stoichiometric ratio, the integrated rate expression becomes indeterminate and this requires taking limits of quotients for evaluation. This difficulty is avoided if we go back to the original differential rate expression and solve it for this particular reactant ratio. Thus, for the second-order reaction with equal initial concentrations of A and B, or for the reaction



the defining second-order differential equation becomes

$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2 \quad (15b)$$

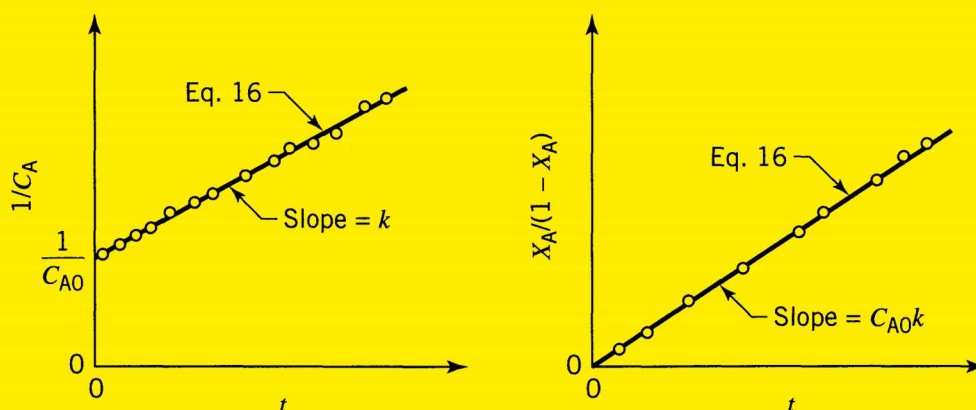
which on integration yields

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = kt \quad (16)$$

Plotting the variables as shown in Fig. 3.3 provides a test for this rate expression.

In practice we should choose reactant ratios either equal to or widely different from the stoichiometric ratio.

**Caution 2.** The integrated expression depends on the stoichiometry as well as the kinetics. To illustrate, if the reaction



**Figure 3.3** Test for the bimolecular mechanisms,  $A + B \rightarrow R$  with  $C_{A0} = C_{B0}$ , or for the second-order reaction of Eq. 15.

is first order with respect to both A and B, hence second order overall, or

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B = kC_{A0}^2 (1 - X_A)(M - 2X_A) \quad (17b)$$

The integrated form is

$$\ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{M - 2X_A}{M(1 - X_A)} = C_{A0}(M - 2)kt, \quad M \neq 2 \quad (18)$$

When a stoichiometric reactant ratio is used the integrated form is

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt, \quad M = 2 \quad (19)$$

These two cautions apply to all reaction types. Thus, special forms for the integrated expressions appear whenever reactants are used in stoichiometric ratios, or when the reaction is not elementary.

**Irreversible Trimolecular-Type Third-Order Reactions.** For the reaction



let the rate equation be

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B C_D \quad (20b)$$

or in terms of  $X_A$

$$C_{A0} \frac{dX_A}{dt} = kC_{A0}^3 (1 - X_A) \left( \frac{C_{B0}}{C_{A0}} - X_A \right) \left( \frac{C_{D0}}{C_{A0}} - X_A \right)$$

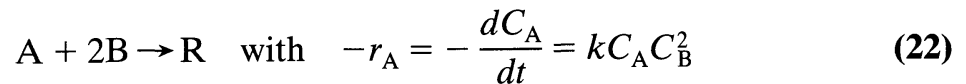
On separation of variables, breakdown into partial fractions, and integration, we obtain after manipulation

$$\begin{aligned} \frac{1}{(C_{A0} - C_{B0})(C_{A0} - C_{D0})} \ln \frac{C_{A0}}{C_A} + \frac{1}{(C_{B0} - C_{D0})(C_{B0} - C_{A0})} \ln \frac{C_{B0}}{C_B} \\ + \frac{1}{(C_{D0} - C_{A0})(C_{D0} - C_{B0})} \ln \frac{C_{D0}}{C_D} = kt \end{aligned} \quad (21)$$

Now if  $C_{D0}$  is much larger than both  $C_{A0}$  and  $C_{B0}$ , the reaction becomes second order and Eq. 21 reduces to Eq. 14.



All trimolecular reactions found so far are of the form of Eq. 22 or 25. Thus



In terms of conversions the rate of reaction becomes

$$\frac{dX_A}{dt} = kC_{A0}^2 (1 - X_A)(M - 2X_A)^2$$

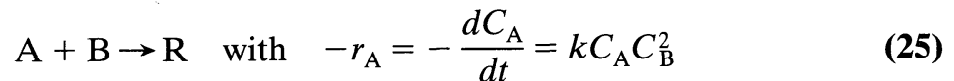
where  $M = C_{B0}/C_{A0}$ . On integration this gives

$$\frac{(2C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_A C_{B0}} = (2C_{A0} - C_{B0})^2 kt, \quad M \neq 2 \quad (23)$$

or

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 8kt, \quad M = 2 \quad (24)$$

Similarly, for the reaction



integration gives

$$\frac{(C_{A0} - C_{B0})(C_{B0} - C_B)}{C_{B0}C_B} + \ln \frac{C_{A0}C_B}{C_{B0}C_A} = (C_{A0} - C_{B0})^2 kt, \quad M \neq 1 \quad (26)$$

or

$$\frac{1}{C_A^2} - \frac{1}{C_{A0}^2} = 2kt, \quad M = 1 \quad (27)$$

**Empirical Rate Equations of  $n$ th Order.** When the mechanism of reaction is not known, we often attempt to fit the data with an  $n$ th-order rate equation of the form

$$-r_A = -\frac{dC_A}{dt} = kC_A^n \quad (28)$$

which on separation and integration yields

$$C_A^{1-n} - C_{A0}^{1-n} = (n-1)kt, \quad n \neq 1 \quad (29)$$

The order  $n$  cannot be found explicitly from Eq. 29, so a trial-and-error solution must be made. This is not too difficult, however. Just select a value for  $n$  and calculate  $k$ . The value of  $n$  which minimizes the variation in  $k$  is the desired value of  $n$ .

One curious feature of this rate form is that reactions with order  $n > 1$  can never go to completion in finite time. On the other hand, for orders  $n < 1$  this rate form predicts that the reactant concentration will fall to zero and then become negative at some finite time, found from Eq. 29, so

$$C_A = 0 \quad \text{at} \quad t \geq \frac{C_{A0}^{1-n}}{(1-n)k}$$

Since the real concentration cannot fall below zero we should not carry out the integration beyond this time for  $n < 1$ . Also, as a consequence of this feature, in real systems the observed fractional order will shift upward to unity as reactant is depleted.

**Zero-Order Reactions.** A reaction is of zero order when **the rate of reaction is independent of the concentration of materials**; thus

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$$-r_A = -\frac{dC_A}{dt} = k$$

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دالة للحرارة  
فقط لان الثابت  
يعتمد على  
الحرارة

(30)

Integrating and noting that  $C_A$  can never become negative, we obtain directly

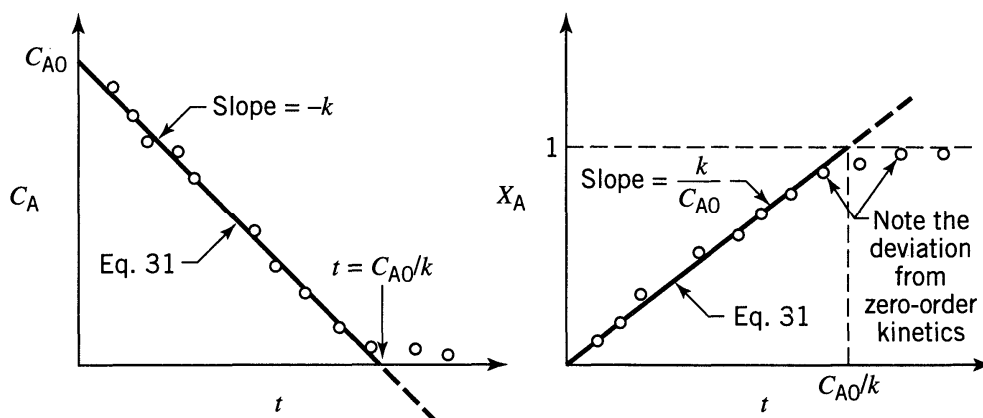
$$C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for} \quad t < \frac{C_{A0}}{k}$$

$$C_A = 0 \quad \text{for} \quad t \geq \frac{C_{A0}}{k}$$

(31)

which means that the conversion is proportional to time, as shown in Fig. 3.4.

As a rule, reactions are of zero order only in certain concentration ranges—the higher concentrations. If the concentration is lowered far enough, we usually



**Figure 3.4** Test for a zero-order reaction, or rate equation, Eq. 30.

find that the reaction becomes concentration-dependent, in which case the order rises from zero.

In general, zero-order reactions are those whose rates are determined by some factor other than the concentration of the reacting materials, e.g., the intensity of radiation within the vat for photochemical reactions, or the surface available in certain solid catalyzed gas reactions. It is important, then, to define the rate of zero-order reactions so that this other factor is included and properly accounted for.

**Overall Order of Irreversible Reactions from the Half-Life  $t_{1/2}$ .** Sometimes, for the irreversible reaction



we may write

$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \dots$$

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

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

or

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n \quad (32)$$

Integrating for  $n \neq 1$  gives

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

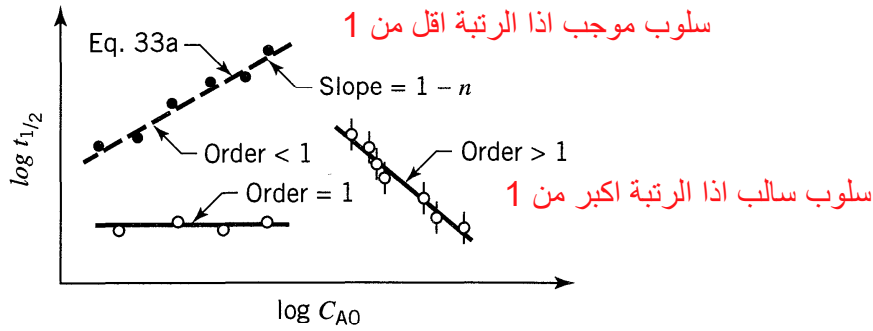
Defining the **half-life of the reaction,  $t_{1/2}$** , as the time needed for the concentration of reactants to drop to one-half the original value, we obtain

$$C_A = \frac{1}{2} C_{A0}$$

$$t_{1/2} = \frac{(0.5)^{1-n} - 1}{\tilde{k}(n-1)} C_{A0}^{1-n} \quad (33a)$$

This expression shows that a **plot of  $\log t_{1/2}$  vs.  $\log C_{A0}$**  gives a straight line of slope  **$1 - n$** , as shown in Fig. 3.5.

The half-life method requires making a series of runs, each at a different initial concentration, and shows that the fractional conversion in a given time rises with increased concentration for orders greater than one, drops with increased



**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

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

في بعض التفاعل من الصعوبة الوصول الى زمن النصف بسهولة لذلك يمكن استبداله بقيمة ثانية (33b)

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:

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