

Figure E3.2b

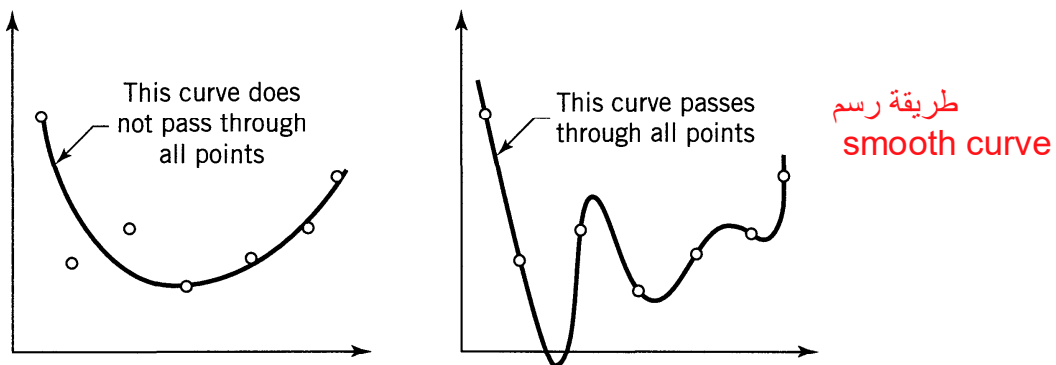


Figure E3.2c, d The same seven points fitted by curves two different ways.

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 .

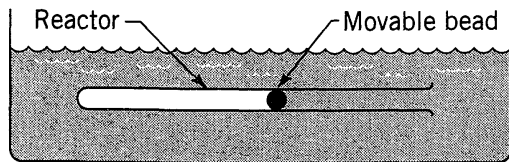


Figure 3.20 A varying-volume batch reactor.

This kind of reactor can be used for isothermal constant pressure operations, of reactions having a single stoichiometry. For such systems the volume is linearly related to the conversion, or

الحجم يتناسب طرديا
مع التحول
عكس التركيز

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A} \quad (63a)$$

or

$$dX_A = \frac{dV}{V_0 \varepsilon_A} \quad (63b)$$

where ε_A is the fractional change in volume of the system between no conversion and complete conversion of reactant A. Thus

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}} \quad (64)$$

As an example of the use of ε_A , consider the isothermal gas-phase reaction



By starting with pure reactant A,

$$\varepsilon_A = \frac{4 - 1}{1} = 3$$

but with 50% inerts present at the start, two volumes of reactant mixture yield, on complete conversion, five volumes of product mixture. In this case

$$\varepsilon_A = \frac{5 - 2}{2} = 1.5$$

كل مول من A يقابله مول واحد من ال inerts
في حالة ال 50 %

We see, then, that ε_A accounts for both the reaction stoichiometry and the presence of inerts. Noting that

$$N_A = N_{A0}(1 - X_A) \quad (65)$$

we have, on combining with Eq. 63,

$$C_A = \frac{N_A}{V} = \frac{N_{A0}(1 - X_A)}{V_0(1 + \varepsilon_A X_A)} = C_{A0} \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

Thus

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A} \quad \text{or} \quad X_A = \frac{1 - C_A/C_{A0}}{1 + \varepsilon_A C_A/C_{A0}} \quad (66)$$

which is the relationship between conversion and concentration for isothermal varying-volume (or varying-density) systems satisfying the linearity assumption of Eq. 63.

The rate of reaction (disappearance of component A), is, in general

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt}$$

Replacing V from Eq. 63a and N_A from Eq. 65 we end up with the rate in terms of the conversion

$$-r_A = \frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{dX_A}{dt}$$

or in terms of volume, from Eqs. 63

$$-r_A = \frac{C_{A0}}{V\varepsilon_A} \cdot \frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A} \cdot \frac{d(\ln V)}{dt} \quad (67)$$

Differential Method of Analysis

The procedure for differential analysis of isothermal varying volume data is the same as for the constant-volume situation except that we replace

$$\frac{dC_A}{dt} \quad \text{with} \quad \frac{C_{A0}}{V\varepsilon_A} \frac{dV}{dt} \quad \text{or} \quad \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} \quad (68)$$

This means plot $\ln V$ vs. t and take slopes.

Integral Method of Analysis

Unfortunately, only a few of the simpler rate forms integrate to give manageable V vs. t expressions. Let us look at these.

Zero-Order Reactions For a homogeneous zero-order reaction the rate of change of any reactant A is independent of the concentration of materials, or

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = k \quad (69)$$

Integrating gives

$$\boxed{\frac{C_{A0}}{\varepsilon_A} \ln \frac{V}{V_0} = kt} \quad (70)$$

As shown in Fig. 3.21, the logarithm of the fractional change in volume versus time yields a straight line of slope $k\varepsilon_A/C_{A0}$.

First-Order Reactions. For a unimolecular-type first-order reaction the rate of change of reactant A is

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt} = kC_A = kC_{A0} \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right) \quad (71)$$

Replacing X_A by V from Eqs. 63 and integrating gives

$$\boxed{-\ln \left(1 - \frac{\Delta V}{\varepsilon_A V_0} \right) = kt, \Delta V = V - V_0} \quad (72)$$

A semilogarithmic plot of Eq. 72, as shown in Fig. 3.22, yields a straight line of slope k .

Second-Order Reactions. For a bimolecular-type second-order reaction

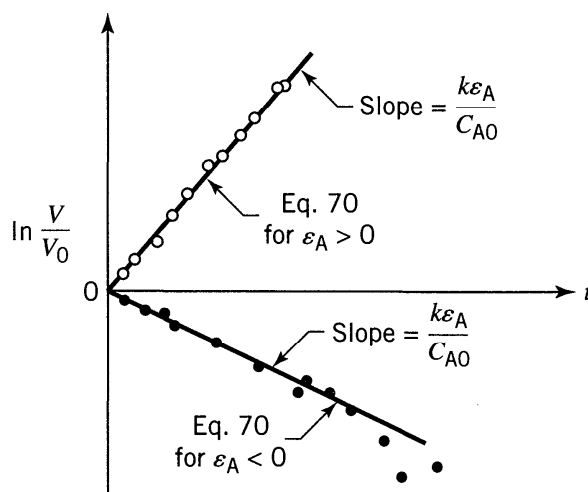
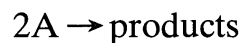


Figure 3.21 Test for a homogeneous zero-order reaction, Eq. 69, in a constant-pressure, varying volume reactor.

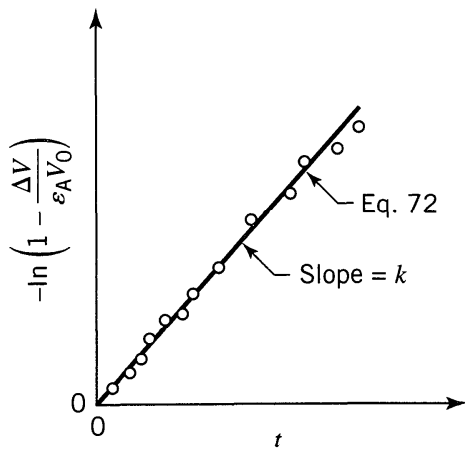
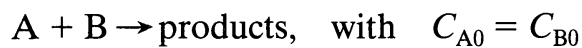


Figure 3.22 Test for a first-order reaction, Eq. 71, in a constant-pressure, varying-volume reactor.

or



the rate is given by

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d \ln V}{dt} = kC_A^2 = kC_{A0}^2 \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)^2$$

Replacing X_A by V from Eqs. 63 and then integrating gives, after much algebraic manipulation,

$$\boxed{\frac{(1 + \varepsilon_A) \Delta V}{V_0 \varepsilon_A - \Delta V} + \varepsilon_A \ln \left(1 - \frac{\Delta V}{V_0 \varepsilon_A} \right) = kC_{A0}t} \quad (73)$$

Figure 3.23 shows how to test for those kinetics.

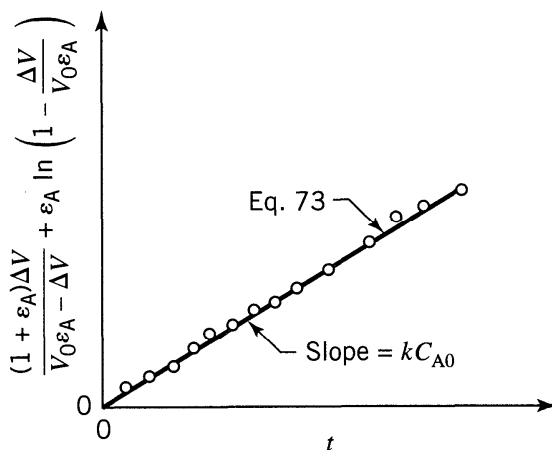


Figure 3.23 Test for the second-order reaction, Eq. 73, in a constant-pressure, varying-volume reactor.

***n*th-Order and Other Reactions.** For all rate forms other than zero-, first-, and second-order the integral method of analysis is not useful.

3.3 TEMPERATURE AND REACTION RATE

So far we have examined the effect of concentration of reactants and products on the rate of reaction, all at a given temperature level. To obtain the complete rate equation, we also need to know the role of temperature on reaction rate. Now in a typical rate equation we have

$$-r_A = -\frac{1}{V} \frac{dN_A}{dt} = kf(C)$$

and it is the reaction rate constant, the concentration-independent term, which is affected by the temperature, whereas the concentration-dependent terms $f(C)$ usually remain unchanged at different temperatures.

Chemical theory predicts that the rate constant should be temperature-dependent in the following manner:

$$k \propto T^m e^{-E/RT}$$

However, since the exponential term is much more temperature-sensitive than the power term, we can reasonably consider the rate constants to vary approximately as $e^{-E/RT}$.

Thus, after finding the concentration dependency of the reaction rate, we can then examine for the variation of the rate constant with temperature by an Arrhenius-type relationship

$$k = k_0 e^{-E/RT}, \quad E = \left[\frac{\text{J}}{\text{mol}} \right] \quad (2.34) \text{ or } (74)$$

This is conveniently determined by plotting $\ln k$ versus $1/T$, as shown in Fig. 3.24.

If the rate constant is found at two different temperatures we have from Chap. 2,

$$\ln \frac{k_2}{k_1} = \frac{E}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad \text{or} \quad E = \frac{RT_1 T_2}{T_2 - T_1} \ln \frac{k_2}{k_1} \quad (2.35) \text{ or } (75)$$

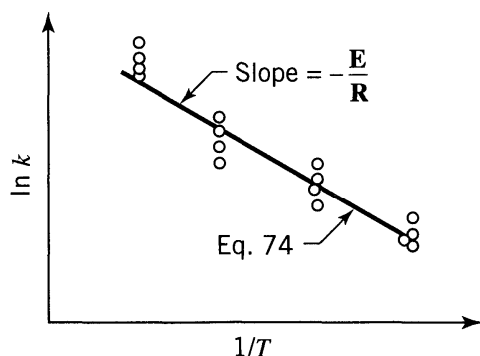


Figure 3.24 Temperature dependency of a reaction according to Arrhenius' law.

Finally, as mentioned in Chap. 2, a shift in E with temperature reflects a change in controlling mechanism of reaction. Since this is likely to be accompanied by a change in concentration dependency, this possibility should also be examined.

Warning on Using Pressure Measures. When dealing with gases, engineers and chemists often measure compositions in terms of partial and total pressures, and then develop their rate equations in terms of pressures, without realizing that this can lead to problems. The reason is that the activation energy calculated when using these units is incorrect. Let us illustrate.

EXAMPLE 3.4 CORRECT AND INCORRECT E VALUES

Experimental studies of a specific decomposition of A in a batch reactor using pressure units show exactly the same rate at two different temperatures:

$$\begin{array}{l} \text{at 400 K} \\ \text{at 500 K} \end{array} \quad \begin{array}{l} -r_A = 2.3 p_A^2 \\ -r_A = 2.3 p_A^2 \end{array} \quad \text{where} \quad \begin{cases} -r_A = \left[\frac{\text{mol}}{\text{m}^3 \cdot \text{s}} \right] \\ p_A = [\text{atm}] \end{cases}$$

- Evaluate the activation using these units
- Transform the rate expressions into concentration units and then evaluate the activation energy.

The pressure is not excessive, so the ideal gas law can be used.

SOLUTION

- Using Pressure Units.** We see right away that a change in temperature does not affect the rate of reaction. This means that

$$\underline{\underline{E = 0}}$$

Alternatively, we can find E by going through the calculations. Thus

$$\ln \frac{k_2}{k_1} = \ln \frac{2.3}{2.3} = 0$$

hence replacing in Eq. 75 shows that

$$\underline{\underline{E = 0}}$$

- Transform p_A into C_A , then find E .** First write the rate equations with all units shown:

$$-r_A, \frac{\text{mol}}{\text{m}^3 \cdot \text{s}} = \left(2.3, \frac{\text{mol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}^2} \right) (p_A^2, \text{atm}^2)$$

Next change p_A to C_A . From ideal gas law

$$p_A = \frac{n_A}{V} \mathbf{R}T = C_A \mathbf{R}T$$

Combining the two preceding equations

$$-r_A = 2.3 C_A^2 \mathbf{R}^2 T^2$$

At 400 K

$$\begin{aligned} -r_{A1} &= 2.3 \frac{\text{mol}}{\text{m}^3 \cdot \text{s} \cdot \text{atm}^2} \cdot C_A^2 \left(82.06 \times 10^{-6} \frac{\text{m}^3 \cdot \text{atm}}{\text{mol} \cdot \text{K}} \right)^2 (400 \text{ K})^2 \\ &= 0.0025 C_A^2 \quad \text{where} \quad k_1 = 0.0025 \frac{\text{m}^3}{\text{mol} \cdot \text{s}} \end{aligned}$$

At 500 K, similarly

$$-r_{A2} = 0.0039 C_A^2 \quad \text{where} \quad k_2 = 0.0039 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

Here we see that in concentration units the rate constants are not independent of temperature. Evaluating the activation energy from Eq. 75, and replacing numbers gives

$$\mathbf{E} = \frac{(8.314)(400)(500)}{500 - 400} \ln \frac{0.0039}{0.0025}$$

or

$$\underline{\underline{\mathbf{E} = 7394 \frac{\text{J}}{\text{mol}}}}$$

This example shows that \mathbf{E} values differ when either p or C used to measure concentrations of materials. ■

Final Notes

1. Chemistry (collision theory or transition state theory) has developed the equations for reaction rates and activation energies in terms of concentration.
2. Literature tabulations for \mathbf{E} and $-r_A$ for homogeneous reactions are normally based on concentrations. The clue to this is that the units for the rate constant are often s^{-1} , liter/mol·s, etc., without pressure appearing in the units.

3. It is a good idea when making runs at different temperatures first to change all p values to C values by using the relationships

$$p_A = C_A \mathbf{RT} \quad \text{for ideal gases}$$

$$p_A = z C_A \mathbf{RT} \quad \text{for nonideal gases, where } z = \text{compressibility factor}$$

and then proceed to solve the problem. This will avoid confusion on units later on, especially if the reaction is reversible or involves liquids and/or solids as well as gases.

3.4 THE SEARCH FOR A RATE EQUATION

In searching for a rate equation and mechanism to fit a set of experimental data, we would like answers to two questions:

1. Have we the correct mechanism and corresponding type of rate equation?
2. Once we have the right form of rate equation, do we have the best values for the rate constants in the equation?

The difficult question to answer is the first of the preceding two questions. Let us see why this is so.

Suppose we have a set of data and we wish to find out whether any one of the families of curves—parabolas, cubics, hyperbolas, exponentials, etc., each representing a different rate family—really fits these data better than any other. This question cannot be answered simply; neither can high-powered mathematical or statistical methods help in deciding for us. The one exception to this conclusion occurs when one of the families being compared is a straight line. For this situation we can simply, consistently, and fairly reliably tell whether the straight line does not reasonably fit the data. Thus, we have what is essentially a negative test, one that allows us to reject a straight line family when there is sufficient evidence against it.

All the rate equations in this chapter were manipulated mathematically into a linearized form because of this particular property of the family of straight lines that allows it to be tested and rejected.

Three methods are commonly used to test for the linearity of a set of points. These are as follows:

Calculation of k from Individual Data Points. With a rate equation at hand, the rate constant can be found for each experimental point by either the integral or differential method. If no trend in k values is discernible, the rate equation is considered to be satisfactory and the k values are averaged.

Now the k values calculated this way are the slopes of lines joining the individual points to the origin. So for the same magnitude of scatter on the graph the k values calculated for points near the origin (low conversion) will vary widely, whereas those calculated for points far from the origin will show little variation (Fig. 3.25). This fact can make it difficult to decide whether k is constant and, if so, what is its best mean value.

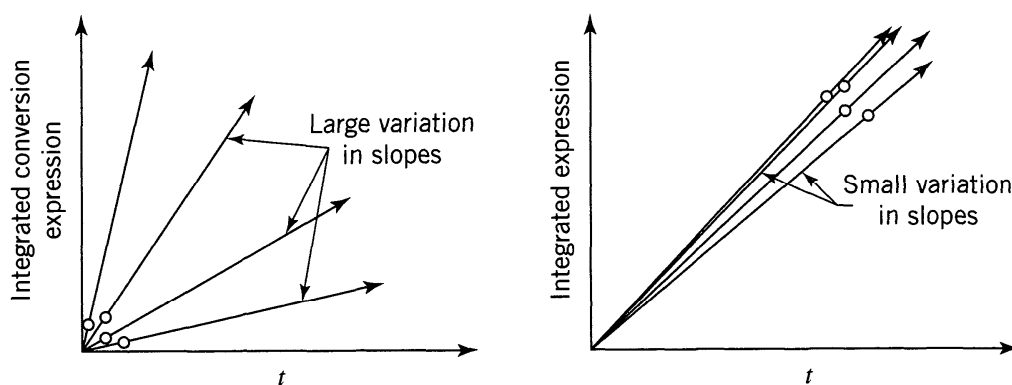


Figure 3.25 How the location of the experimental points influences the scatter in calculated k values.

Calculation of k from Pairs of Data Points. k values can be calculated from successive pairs of experimental points. For large data scatter, however, or for points close together, this procedure will give widely different k values from which k_{mean} will be difficult to determine. In fact, finding k_{mean} by this procedure for points located at equal intervals on the x -axis is equivalent to considering only the two extreme data points while ignoring all the data points in between. This fact can easily be verified. Figure 3.26 illustrates this procedure.

This is a poor method in all respects and is not recommended for testing the linearity of data or for finding mean values of rate constants.

Graphical Method of Fitting Data. Actually, the preceding methods do not require making a plot of the data to obtain k values. With the graphical method the data are plotted and then examined for deviations from linearity. The decision whether a straight line gives a satisfactory fit is usually made intuitively by using good judgment when looking at the data. When in doubt we should take more data.

The graphical procedure is probably the safest, soundest, and most reliable method for evaluating the fit of rate equations to the data, and should be used whenever possible. For this reason we stress this method here.

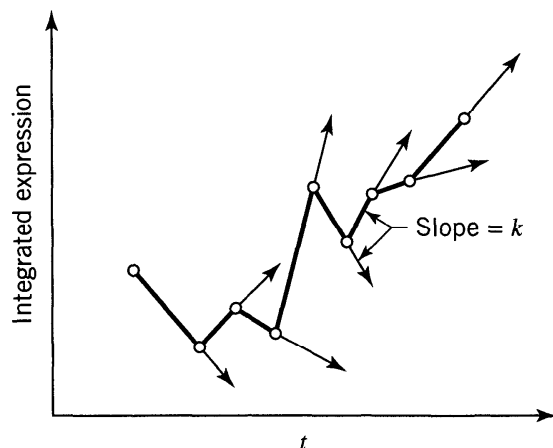


Figure 3.26 Calculated k values from successive experimental points are likely to fluctuate widely.