University of Anbar
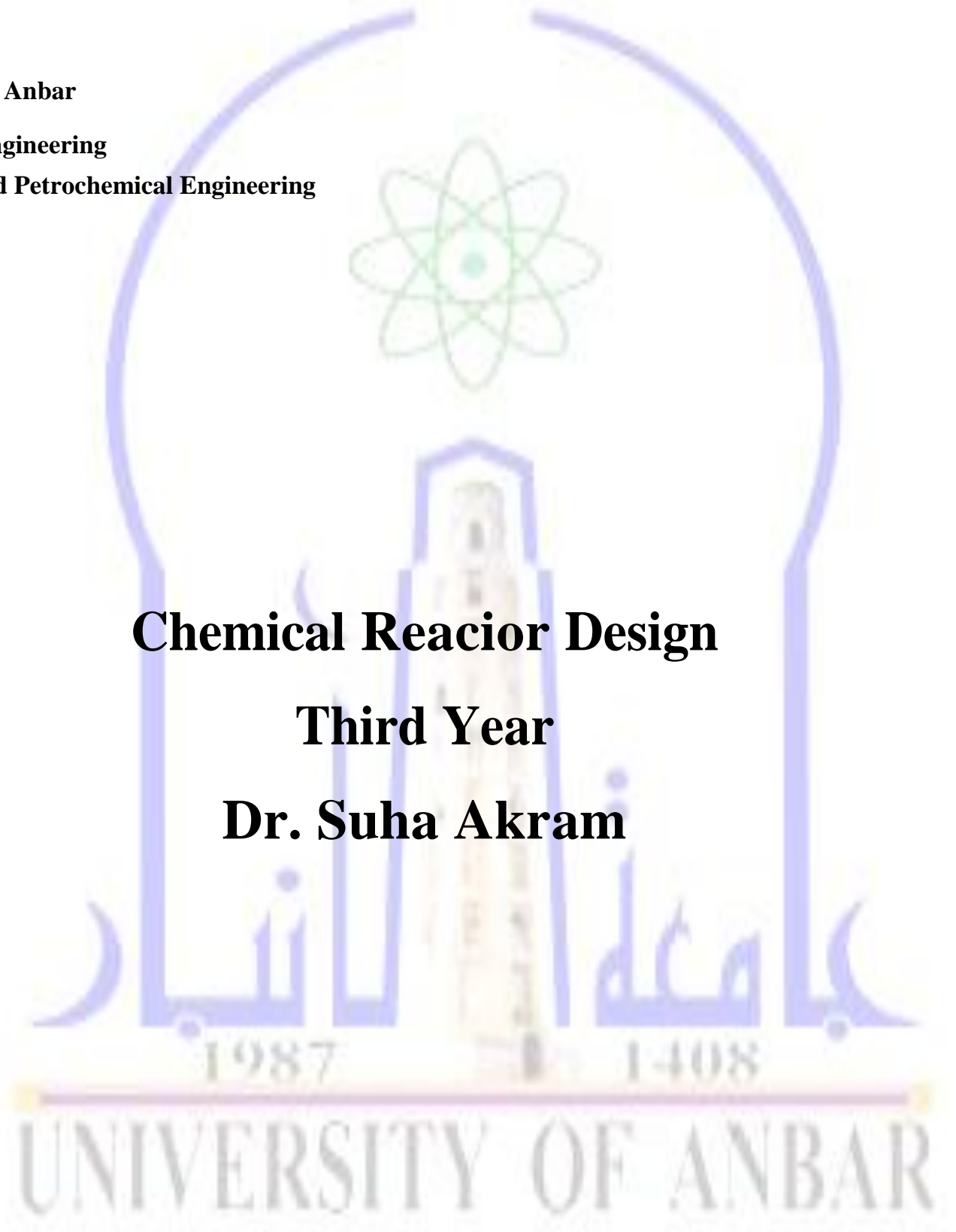
College of Engineering

Chemical and Petrochemical Engineering Department

Chemical Reacior Design

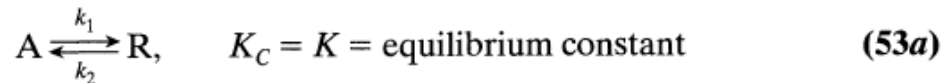# Third Year

Dr. Suha Akram

Lecture No.5:

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.. The simplest case is the opposed **unimolecular**-type reaction:

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

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

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = k_1 C_A - k_2 C_R$$

$$= k_1 (C_{A0} - C_{A0}X_A) - k_2 (MC_{A0} + C_{A0}X_A) \qquad (53b)$$
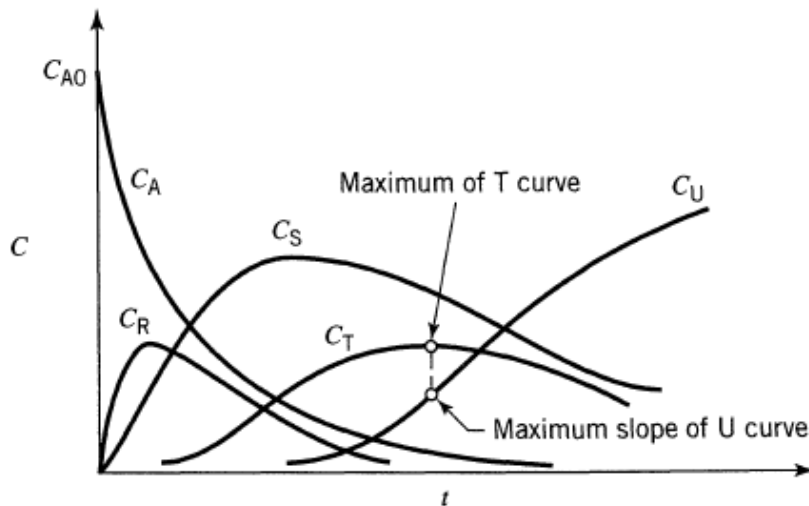
Figure 3.12 Concentration-time curves for a chain of successive first-order reactions. Only for the last two compounds do the maximum and the inflection points occur at the same time.

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

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}} \quad \longrightarrow \quad K_C = \frac{k_1}{k_2}$$

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

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = -\ln\frac{C_A - C_{Ae}}{C_{A0} - C_{Ae}} = \frac{M+1}{M + X_{Ae}}k_1 t \qquad (54)$$

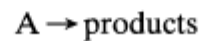A plot of $-\ln(1 - X_A/X_{Ae})$ vs. t, as shown in Fig. 3.13, gives a straight line.

Thus, the irreversible reaction is simply the special case of the reversible reaction in which $C_{Ae} = 0$, or $X_{Ae} = 1$, or $K_C = \infty$.
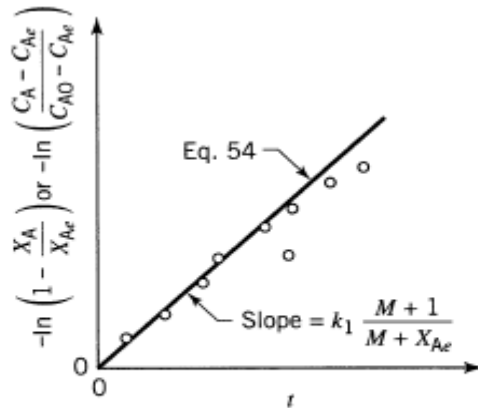
Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

EXAMPLE 3.1   *FIND A RATE EQUATION USING THE INTEGRAL METHOD*

Reactant A decomposes in a batch reactor
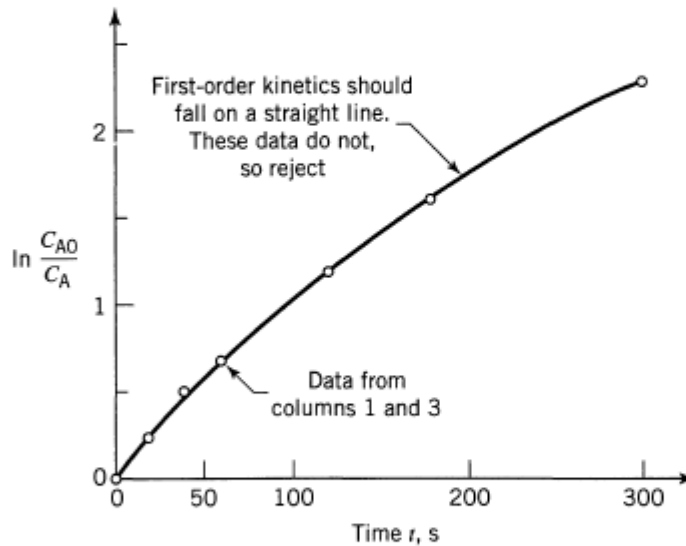
$$A \rightarrow products$$

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.

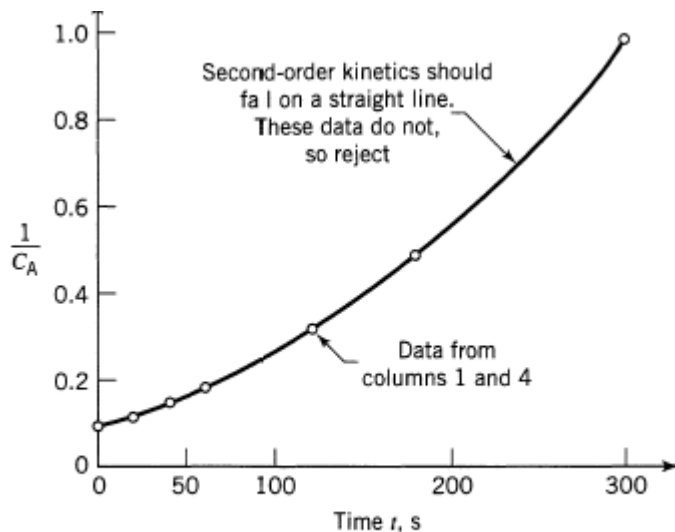| Column 1	Column 2	Column 3	Column 4
Time t, s	Concentration C_A, mol/liter	$\ln\dfrac{C_{A0}}{C_A}$	$\dfrac{1}{C_A}$
0	$C_{A0} = 10$	ln 10/10 = 0	0.1
20	8	ln 10/8 = 0.2231	0.125
40	6	0.511	0.167
60	5	0.6931	0.200
120	3	1.204	0.333
180	2	1.609	0.500
300	1	2.303	1.000
	Reported data		Calculated

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.

First-order kinetics should
fall on a straight line.
These data do not,
so reject

$\ln \dfrac{C_{AO}}{C_A}$

Data from
columns 1 and 3

Time t, s

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.

Second-order kinetics should
fa l on a straight line.
These data do not,
so reject

$\dfrac{1}{C_A}$

Data from
columns 1 and 4

Time t, s

Figure E3.1b

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

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

Next take logarithms

$$\underset{y}{\underline{\log t_F}} = \overbrace{\underset{a}{\underline{\log\left(\frac{0.8^{1-n}-1}{k(n-1)}\right)}}}^{\text{a constant}} + \underset{bx}{\underline{(1-n)\log C_{A0}}}$$ (ii)

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}	$C_{A\,end}$ $(= 0.8C_{A0})$	Time needed t_F, s	$\log t_F$	$\log C_{A0}$
10	8	$0 \to 18.5 = 18.5$	$\log 18.5 = 1.27$	1.00
5	4	$59 \to 82 = 23$	1.36	0.70
2	1.6	$180 \to 215 = 35$	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.
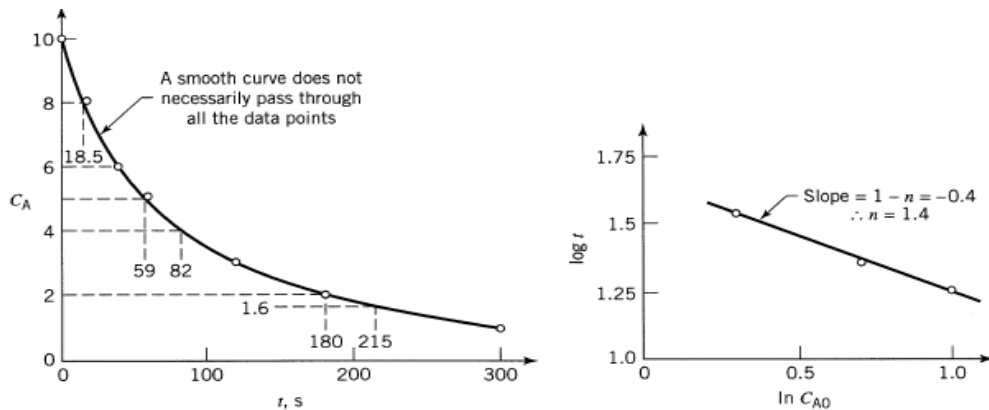
Figures E3.1c and E3.1d

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

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

■

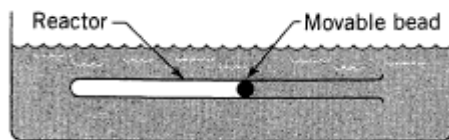## VARYING-VOLUME BATCH REACTOR

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

V_0 = initial volume of the reactor

V = the volume at time t.

microreactors.   Thus,

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

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

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

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

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

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

$$A \rightarrow 4R$$

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

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

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

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

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

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

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

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

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

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

Integrating gives

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

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

$$-r_A = \frac{C_{A0}}{\varepsilon_A}\frac{d(\ln V)}{dt} = kC_A = kC_{A0}\left(\frac{1 - X_A}{1 + \varepsilon_A X_A}\right) \qquad (71)$$
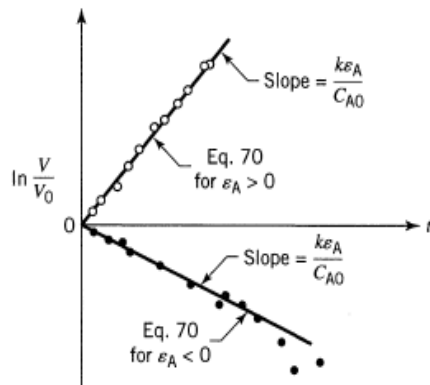
Replacing X_A by V from Eqs. 63 and integrating gives

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

A semilogarithmic plot of Eq. 72, as shown in Fig. 3.22, yields a straight line of slope k.
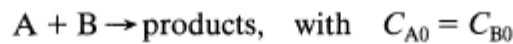
Second-Order Reactions. For a bimolecular-type second-order reaction

$$2A \longrightarrow products$$
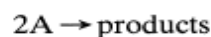
Figure 3.21 Test for a homogeneous zero-order reaction, Eq. 69, in a constant-pressure, varying volume reactor.

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

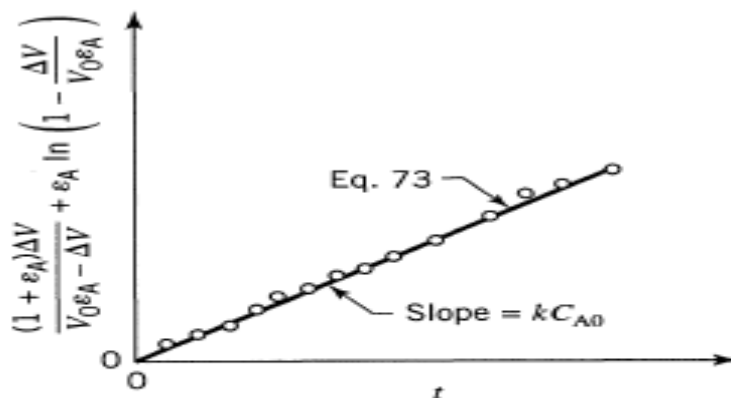$$A + B \rightarrow \text{products}, \quad \text{with} \quad C_{A0} = C_{B0}$$

the rate is given by

$$-r_A = \frac{C_{A0}}{\varepsilon_A} \frac{d \ln V}{dt} = kC_A^2 = kC_{A0}^2 \left(\frac{1 - X_A}{1 + \varepsilon_A X_A} \right)^2$$
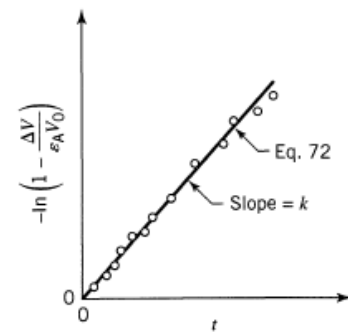
Replacing X_A by V from Eqs. 63 and then integrating gives, after much algebraic manipulation,

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

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.

EXAMPLE .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:

$$\text{at } 400 \text{ K} \quad -r_A = 2.3 \, p_A^2$$
$$\text{at } 500 \text{ K} \quad -r_A = 2.3 \, p_A^2$$

where

$$\begin{cases} -r_A = \left[\dfrac{mol}{m^3 \cdot s} \right] \\ p_A = [atm] \end{cases}$$

(a) Evaluate the activation using these units

(b) 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

(a) 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

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

(b) Transform p_A into C_A, then find E.   First write the rate equations with all units shown:

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

Next change p_A to C_A. From ideal gas law

$$p_A = \frac{n_A}{V} RT = C_A RT$$

Combining the two preceding equations

$$-r_A = 2.3 \, C_A^2 R^2 T^2$$

At 400 K

$$-r_{A1} = 2.3 \frac{mol}{m^3 \cdot s \cdot atm^2} \cdot C_A^2 \left(82.06 \times 10^{-6} \frac{m^3 \cdot atm}{mol \cdot K}\right)^2 (400 \text{ K})^2$$

$$= 0.0025 C_A^2 \quad \text{where} \quad k_1 = 0.0025 \frac{m^3}{mol \cdot s}$$

At 500 K, similarly

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

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

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

or

$$E = 7394 \frac{J}{mol}$$

This example shows that E values differ when either p or C used to measure concentrations of materials. ∎