BITS, PILANI – K. K. BIRLA GOA CAMPUS

COLLECTION AND ANALYSIS OF RATE DATA

Chapter 5

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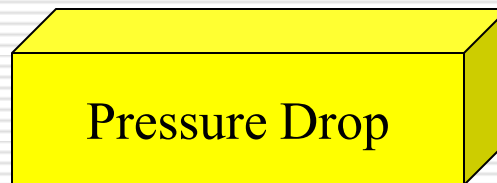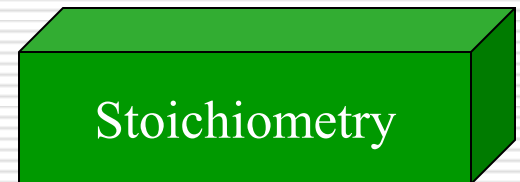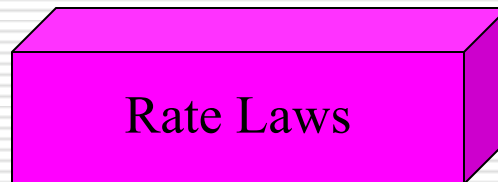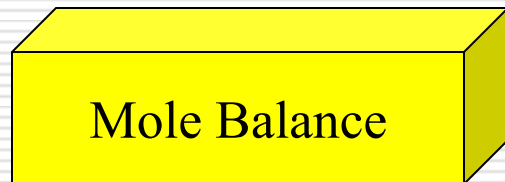# What now??

After this chapter you will be able to focus on ways of obtaining and analyzing reaction rate data to obtain the rate law for a specific reaction

Understand the Batch Reactor concept

Mole Balance

Rate Laws

Stoichiometry

Pressure Drop

Algorithm for Isothermal Reactor Design

1. **Mole Balance and Design Equation**
2. **Rate Law**
3. **Stoichiometry**
4. **Combine**
5. **Evaluate**

    A. Graphically (Chapter 2 plots)

    B. Numerical (Quadrature Formulas Chapter 2 and appendices)

    C. Analytical (Integral Tables in Appendix)

    D. Software Packages (Appendix- Polymath)

Evaluating the rate equation

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.

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.

Interpretation of Batch reactor data

Batch Reactor: Homogeneous data at constant volume and isothermally

Flow reactor for homogeneous systems

Integral and Differential Method of Analysis

THE DIFFERENTIAL METHOD OF ANALYSIS

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.

Requires large amount of accurate data

Develop or build a rate equation to fit 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 INTEGRAL METHOD OF ANALYSIS

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

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.

Differential vs Integral method

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.
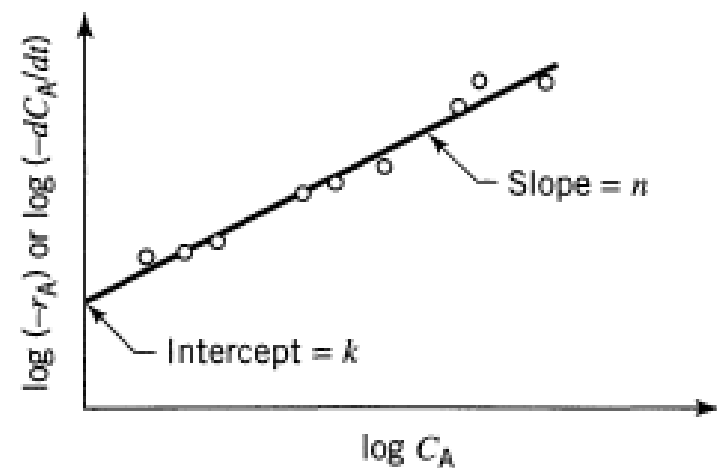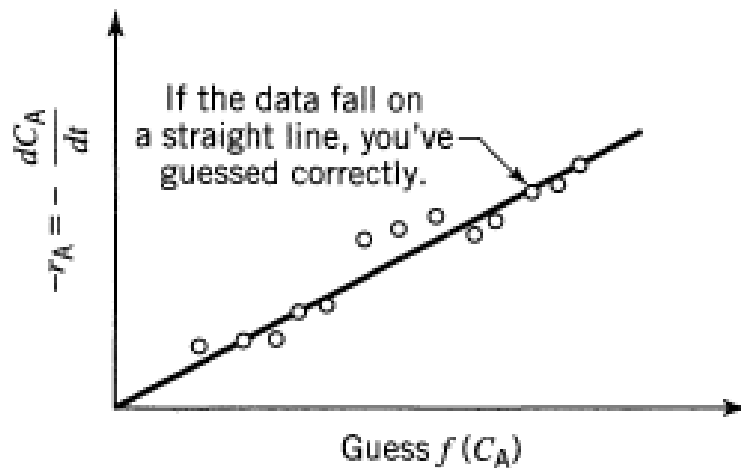
Batch reactor data

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.

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

Batch reactor data

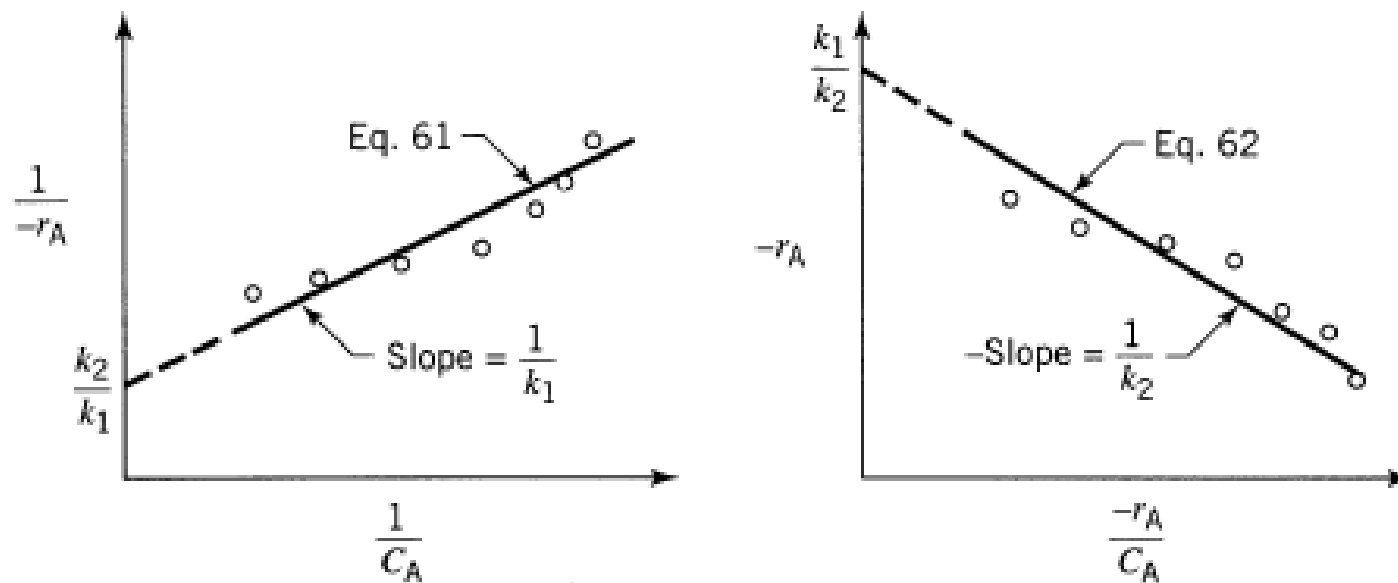$$-r_A = -\frac{dC_A}{dt} = \frac{k_1 C_A}{1 + k_2 C_A}$$

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

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

$1/(-r_A)$ vs. $1/C_A$ is linear. $-r_A$ vs. $(-r_A)/C_A$ is linear.

Batch reactor data

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

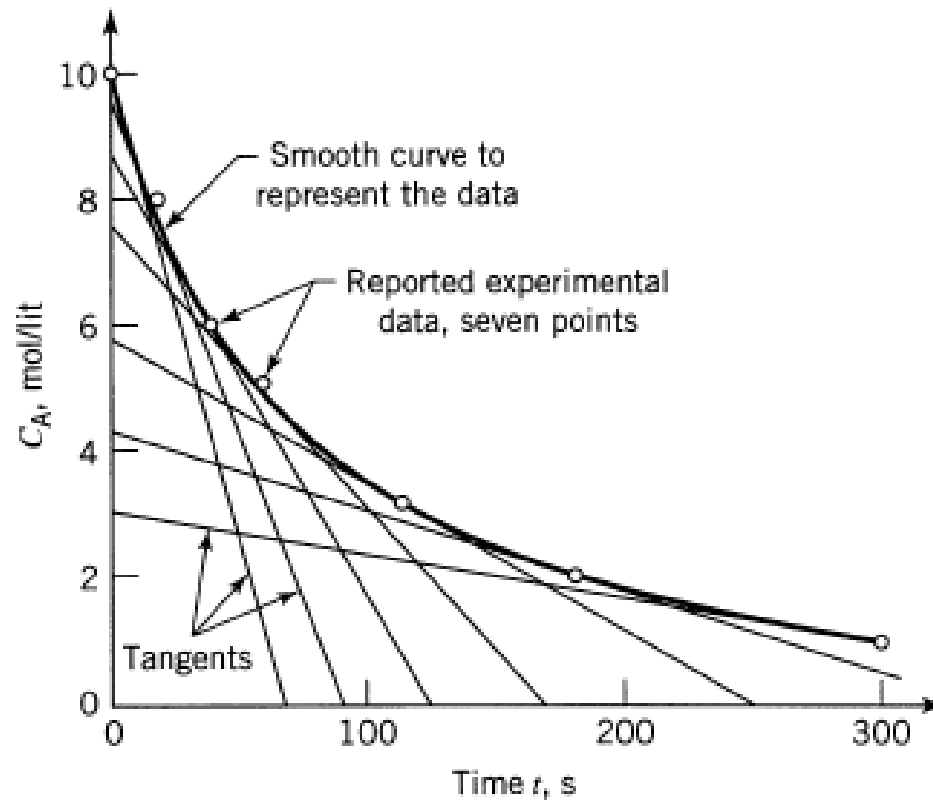# Batch reactor data

Reactant A decomposes in a batch reactor

$$A \rightarrow products$$

Column 1	Column 2
Time t, s	Concentration C_A, mol/liter
0	$C_{A0} = 10$
20	8
40	6
60	5
120	3
180	2
300	1

Reported data

Try to fit an nth-order rate equation to

the concentration vs. time data

Batch reactor data

Batch reactor data

Column 1	Column 2	Column 3	Column 4	Column 5
Time t, s	Concentration C_A, 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 nth-order rate equation to this data, or

Batch reactor data

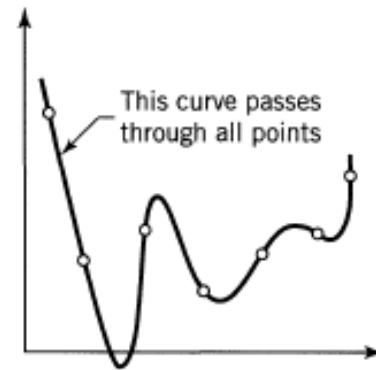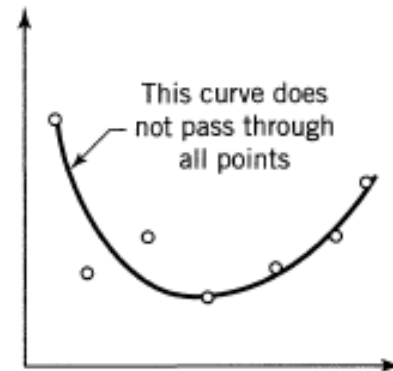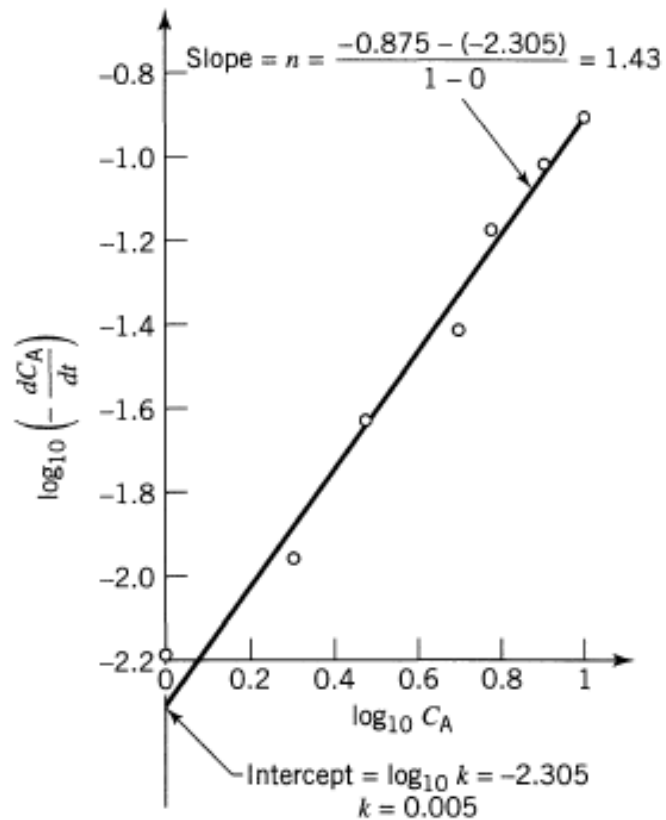$$-r_{A} = -\frac{dC_{A}}{dt} = kC_{A}^{n}$$

$$\underbrace{\log_{10}\left(-\frac{dC_{A}}{dt}\right)}_{y} = \underbrace{\log_{10}k}_{\text{intercept}} + \underbrace{n}_{\text{slope}}\underbrace{\log_{10}C_{A}}_{x}$$

$$-r_{A} = -\frac{dC_{A}}{dt} = \left(0.005\,\frac{\text{liter}^{0.43}}{\text{mol}^{0.43}\cdot\text{s}}\right) C_{A}^{1.43},\ \frac{\text{mol}}{\text{liter}\cdot\text{s}}$$

Batch reactor data

Batch reactor data

Consider the following reaction that occurs in a constant volume batch reactor: (We will withdraw samples and record the concentration of A as a function of time.)

Mole balance $\qquad \dfrac{dN_A}{dt} = r_A V$

Rate Law $\qquad -r_A = kC_A^{\alpha}$
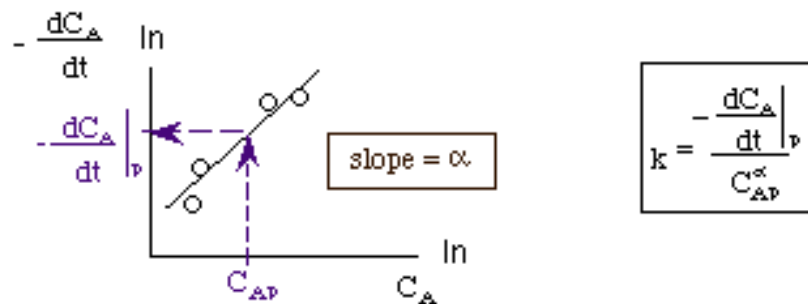
Stoichiometry $\qquad V = V_0$

$$-\dfrac{dC_A}{dt} = kC_A^{\alpha}$$

Batch reactor data
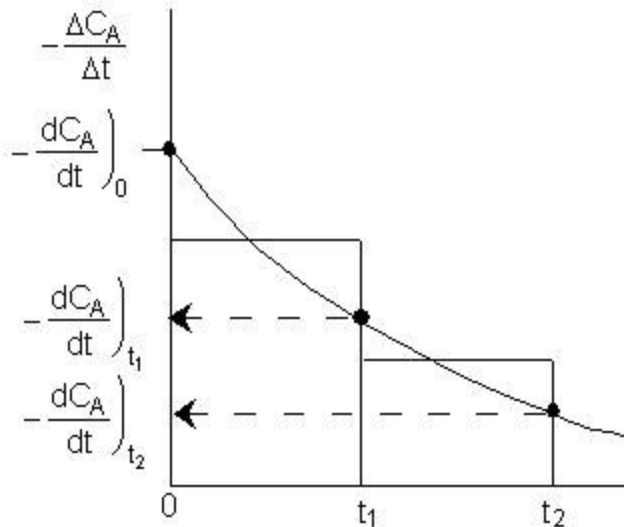
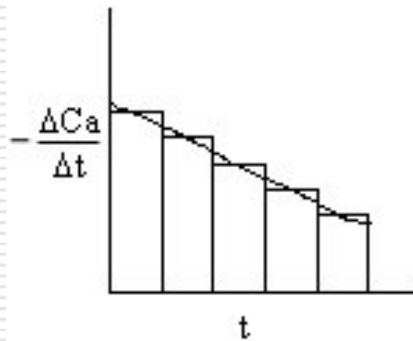$$\ln\left(-\frac{dC_A}{dt}\right) = \ln k + \alpha \ln C_A$$

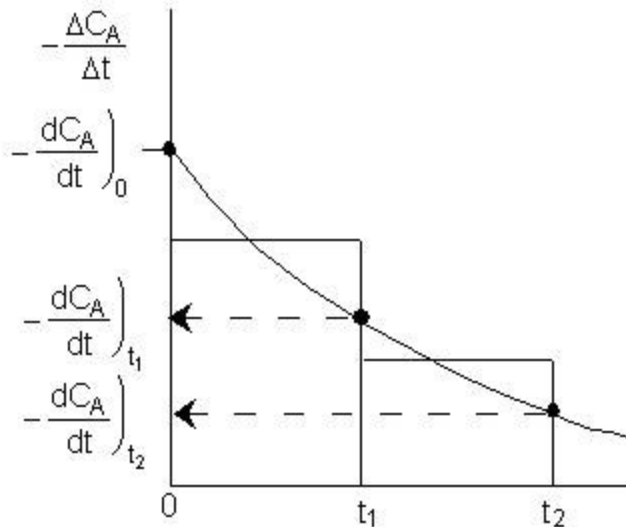$$\left(-\frac{dC_A}{dt}\right) \text{ vs } C_A \qquad \textbf{\textcolor{red}{PLOT}}$$

Batch reactor data (Graphical)

time (s)	0	t_1	t_2	t_3
concentration (mol/dm^3)	C_{Ao}	C_{A1}	C_{A2}	C_{A3}

Batch reactor data (Graphical)

time (s)	0	t_1	t_2	t_3
concentration (mol/dm^3)	C_{Ao}	C_{A1}	C_{A2}	C_{A3}

Batch reactor data (Finite Difference)

Initial Point: (dC_A/dt) at $t = t_o$

$$(-3C_{Ao} + 4C_{A1} - C_{A2})/ 2\Delta t$$

Interior points

$$\frac{dC}{dt}\Big)_i = \frac{C_{i+1} - C_{i-1}}{2\Delta t}$$

Re attempt problem on Slide 12 using this method

Final Point: (dC_A/dt) at $t = t_n$

$$(C_{A(n-2)} - 4C_{A(n-1)} + 3C_{An})/ 2\Delta t$$

Constant Volume Batch reactor

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

$$r_i = \frac{1}{\mathbf{R}T}\frac{dp_i}{dt}$$

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.

Analysis of Total Pressure data

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 π to the changing concentration or partial pressure of any of the reaction components.

$$aA \quad + \quad bB \quad + \cdots = \quad rR \quad + \quad sS \quad + \cdots$$

At time 0: N_{A0} N_{B0} N_{R0} N_{S0} N_{inert}

At time t: $N_A = N_{A0} - ax$ $N_B = N_{B0} - bx$ $N_R = N_{R0} + rx$ $N_S = N_{S0} + sx$ N_{inert}

Analysis of Total Pressure data

Initially the total number of moles present in the system is

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

but at time t it is

$$N = N_0 + x(r + s + \cdots - a - b - \cdots) = N_0 + x\,\Delta n$$

where

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

Analysis of Total Pressure data

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

$$C_A = \frac{p_A}{\mathbf{R}T} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} \qquad\qquad C_A = \frac{N_{A0}}{V} - \frac{a}{\Delta n}\frac{N - N_0}{V}$$

$$p_A = C_A\mathbf{R}T = p_{A0} - \frac{a}{\Delta n}(\pi - \pi_0)$$

Equation 5 gives the concentration or partial pressure of reactant A as a function of the total pressure π at time t, initial partial pressure of A, p_{A0}, and initial total pressure of the system, π_0.

$$p_R = C_R\mathbf{R}T = p_{R0} + \frac{r}{\Delta n}(\pi - \pi_0)$$

Integral Method

- ☐ Trial and error method to find reaction order
- ☐ Used normally when order is known and k needs to be evaluated (for activation energy)
- ☐ Linear plots of functions of C_A vs t for zero, first and second order reactions

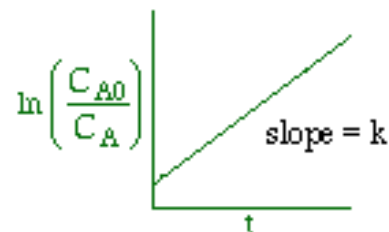| Mole Balance		$\frac{dN_A}{dt} = r_A V$	
Rate Law	First-order		Second-order
	$-r_A = kC_A$		$-r_A = kC_A^2$
Stoichiometry $(V=V_o)$		$C_A = \frac{N_A}{V} = \frac{N_A}{V_o}$	
Combine	$\frac{d(N_A/V_o)}{dt} = \frac{dC_A}{dt} = -kC_A$		$\frac{d(N_A/V_o)}{dt} = \frac{dC_A}{dt} = -kC_A^2$
Integrate	$t = \frac{1}{k}\ln\frac{C_{A0}}{C_A}$		$t = \frac{1}{k}\left[\frac{1}{C_A} - \frac{1}{C_{A0}}\right]$

Integral Method

Zero Order, $\alpha = 0$
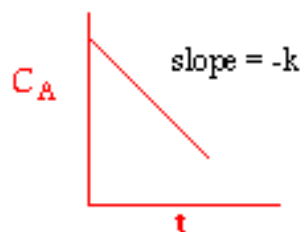
$$\frac{dC_A}{dt} = r_A = -k$$

at $t = 0$, $C_A = C_{A0}$

$$\Rightarrow C_A = C_{A0} - kt$$

First Order, $\alpha = 1$
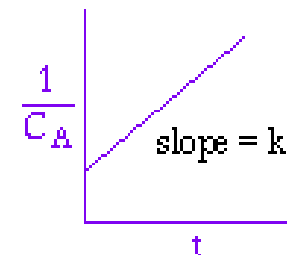
$$\frac{dC_A}{dt} = r_A = -kC_A$$

at $t = 0$, $C_A = C_{A0}$

$$\Rightarrow \ln\left(\frac{C_{A0}}{C_A}\right) = kt$$

Second Order, $\alpha = 2$
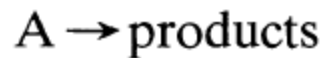
$$\frac{dC_A}{dt} = r_A = -kC_A^2$$

at $t = 0$, $C_A = C_{A0}$

$$\Rightarrow \frac{1}{C_A} - \frac{1}{C_{A0}} = kt$$

Irreversible Uni-molecular type First Order Reaction

$$A \rightarrow \text{products}$$

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

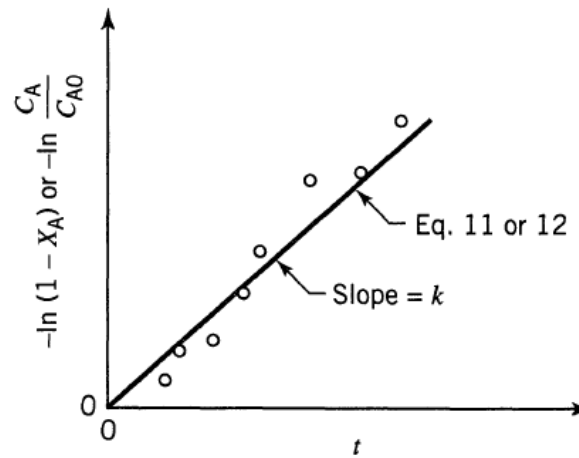$$\implies \int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

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

$$\boxed{-\ln(1 - X_A) = kt}$$

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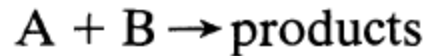
Caution

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

$$-\ln \frac{C_A}{C_{A0}} = kt$$

Graph: vertical axis labeled $-\ln(1 - X_A)$ or $-\ln \frac{C_A}{C_{A0}}$, horizontal axis labeled t. Line with Slope $= k$, labeled Eq. 11 or 12.

Irreversible Bi-molecular type Second Order Reaction

$$A + B \rightarrow products$$

$$-r_A = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B$$

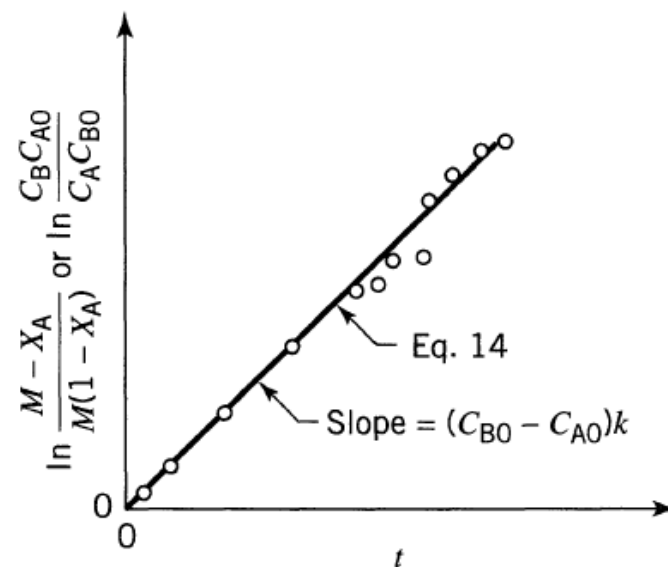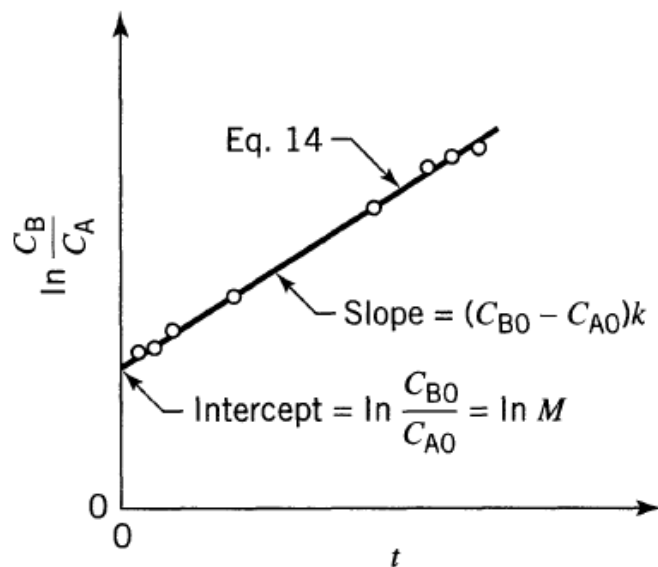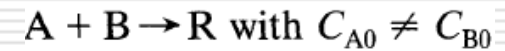$$-r_A = C_{A0}\frac{dX_A}{dt} = kC_{A0}^2(1 - X_A)(M - X_A) \qquad M = C_{B0}/C_{A0} \qquad = \Theta$$

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

Irreversible Bi-molecular type Second Order Reaction

$$\ln \frac{1 - X_B}{1 - X_A} = \ln \frac{M - X_A}{M(1 - X_A)} = \ln \frac{C_B C_{A0}}{C_{B0} C_A} = \ln \frac{C_B}{MC_A}$$

$$= C_{A0}(M - 1)kt = (C_{B0} - C_{A0})kt, \qquad M \neq 1$$

$$A + B \rightarrow R \text{ with } C_{A0} \neq C_{B0}$$

Left plot: $\ln \frac{C_B}{C_A}$ vs t — Eq. 14, Slope $= (C_{B0} - C_{A0})k$, Intercept $= \ln \frac{C_{B0}}{C_{A0}} = \ln M$

Right plot: $\ln \frac{M - X_A}{M(1 - X_A)}$ or $\ln \frac{C_B C_{A0}}{C_A C_{B0}}$ vs t — Eq. 14, Slope $= (C_{B0} - C_{A0})k$

Irreversible Bi-molecular type Second Order Reaction (Caution 1)

If C_{B0} is much larger than C_{A0}, C_B remains approximately constant at all times,

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

$$2A \rightarrow \text{products} \qquad (15a)$$

Irreversible Bi-molecular type Second Order Reaction (Caution 1)

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

$$\boxed{\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}}\frac{X_A}{1 - X_A} = kt}$$

$A + B \rightarrow R$ with $C_{A0} = C_{B0}$
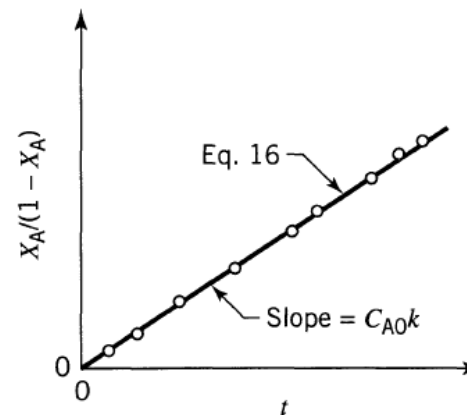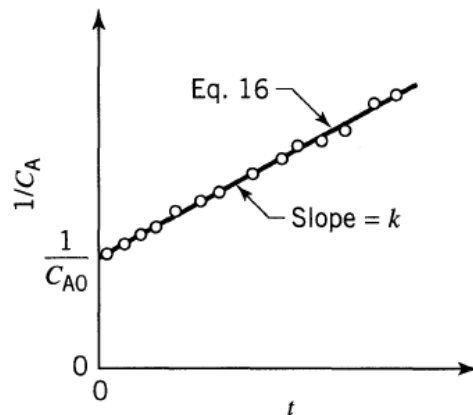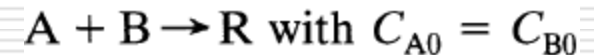
Irreversible Bi-molecular type Second Order Reaction (Caution 2)

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

$$A + 2B \rightarrow \text{products} \qquad (17a)$$

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

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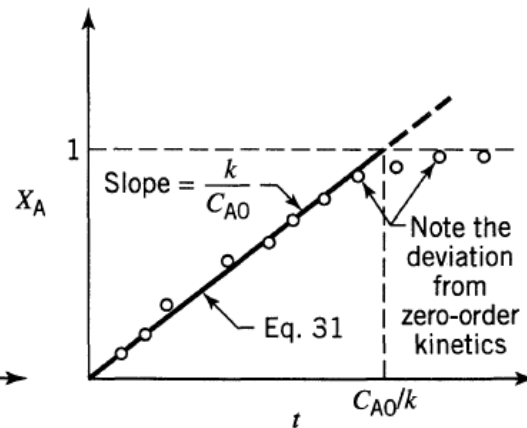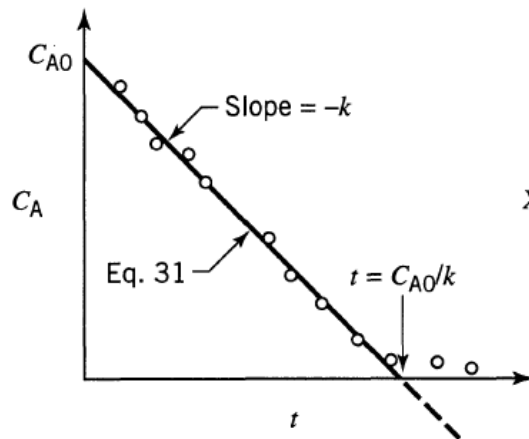
$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = 2kt, \qquad M = 2$$

Zero order reactions

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

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

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

Zero order reactions

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.

Empirical rate equations of nth order

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

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

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

Empirical rate equations of nth order

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.

Overall order of irreversible reactions from half life

$$\alpha A + \beta B + \cdots \rightarrow \text{products}$$
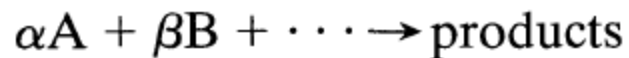
$$C_A^{1-n} - C_{A0}^{1-n} = \tilde{k}(n-1)t$$

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

n not equal to 1

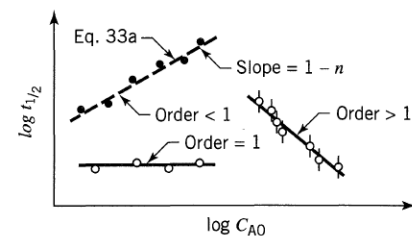$$-r_A = -\frac{dC_A}{dt} = kC_A^a C_B^b \cdots$$

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

$$C_B / C_A = \beta / \alpha$$

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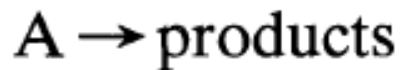

Figure 3.5 Overall order of reaction from a series of half-life experiments, each at a different initial concentration of reactant.

Problem Statement

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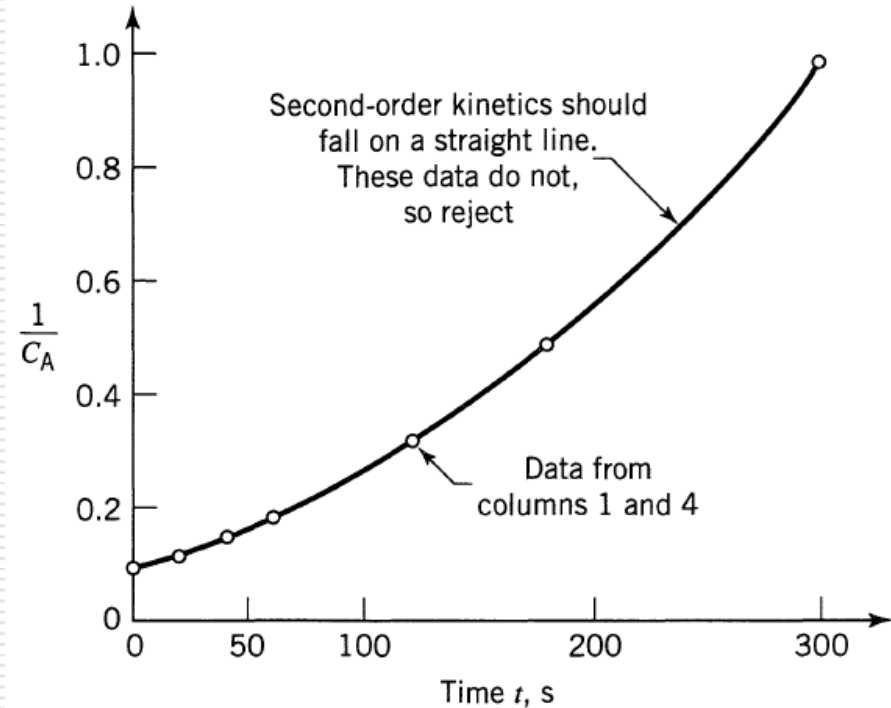
Column 1	Column 2	Column 3	Column 4
Time t, s	Concentration C_A, mol/liter	$\ln \dfrac{C_{A0}}{C_A}$	$\dfrac{1}{C_A}$
0	$C_{A0} = 10$	ln 10/10 = 0	0.1
20	8	ln 10/8 = 0.2231	0.125
40	6	0.511	0.167
60	5	0.6931	0.200
120	3	1.204	0.333
180	2	1.609	0.500
300	1	2.303	1.000
Reported data		Calculated	

Problem Solution
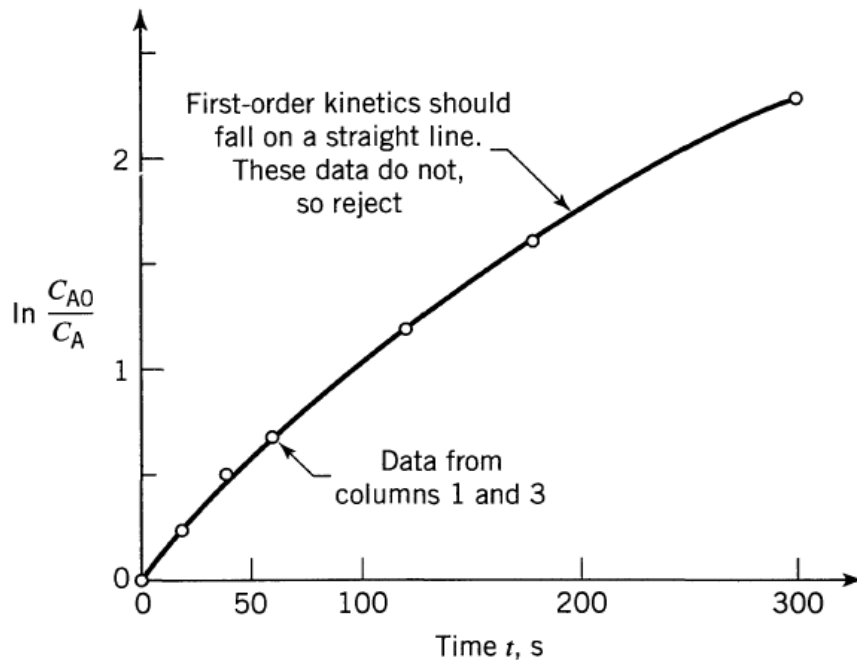
Guess: 1st order kinetics

Guess: 2nd order kinetics

Problem Solution

Guess nth order kinetics:

Fractional life method with F = 80%

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

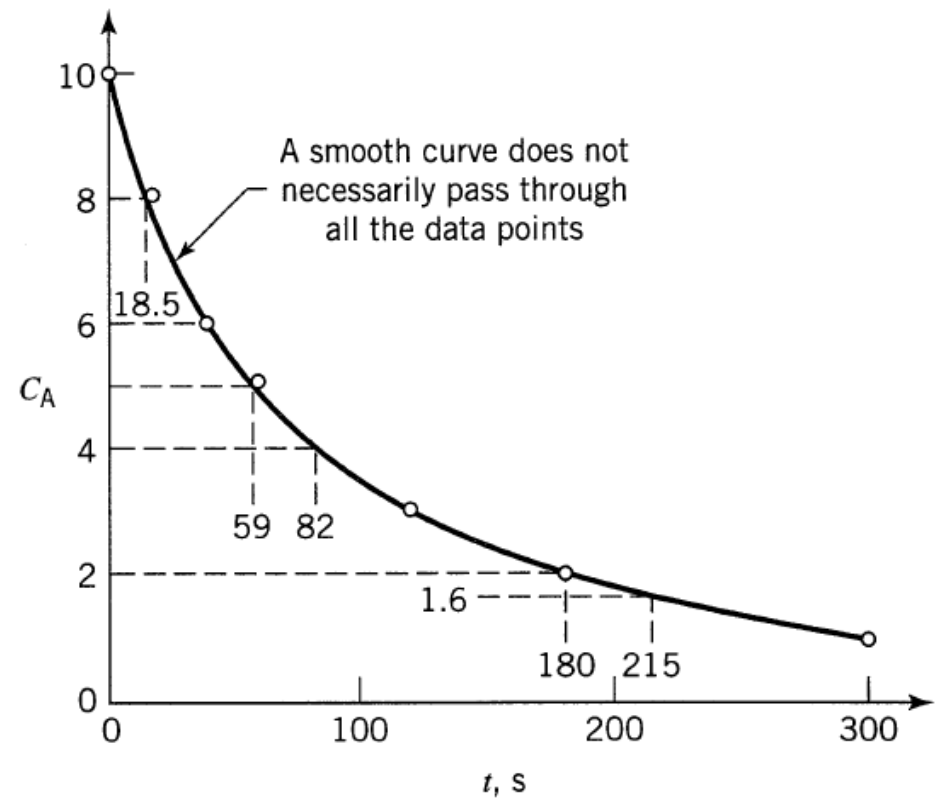Taking logarithms

$$\underbrace{\log t_F}_{y} = \underbrace{\log\left(\frac{0.8^{1-n}-1}{k(n-1)}\right)}_{a} + \underbrace{(1-n)\log C_{A0}}_{bx}$$

a constant

Problem Solution

- ☐ Accurately plot C_A Vs t data
- ☐ Draw smooth curve

Problem Solution

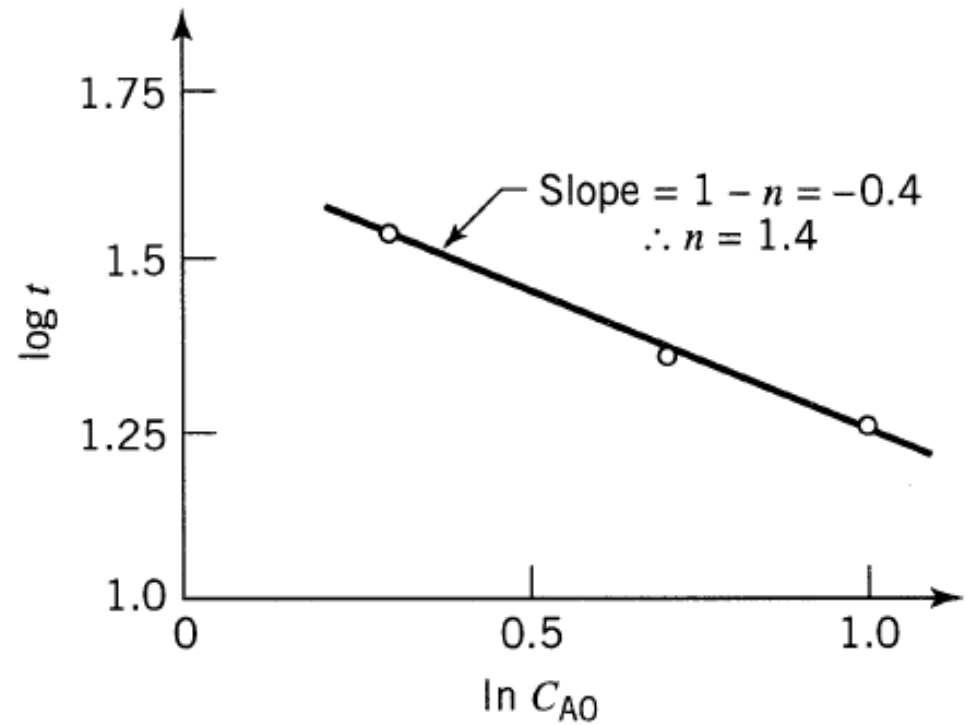□ Pick various concentrations and fill in the following table from the figure

C_{A0}	$C_{A\,end}$ $(= 0.8C_{A0})$	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

Problem Solution

Next, plot $\log t_F$ vs. $\log C_{A0}$,

Problem Solution

$$C_{A0} = 10 \qquad\qquad t_F = 18.5s$$

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

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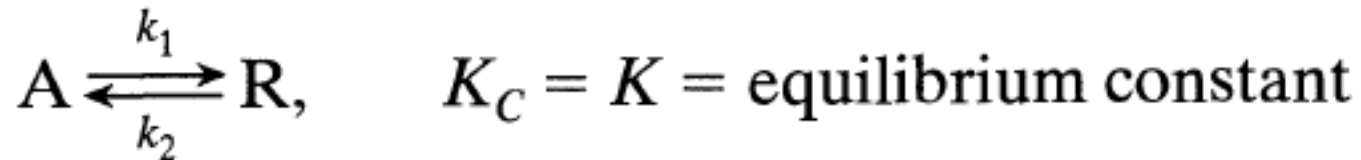
$$-r_A = \left(0.005 \, \frac{\text{liter}^{0.4}}{\text{mol}^{0.4} \cdot \text{s}}\right) C_A^{1.4}, \qquad \frac{\text{mol}}{\text{liter} \cdot \text{s}}$$

First-Order Reversible Reactions

☐ Reversible unimolecular-type reaction

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

Concentration ratio

$$\Theta = \frac{C_{R0}}{C_{A0}}$$

First-Order Reversible Reactions

- ☐ The rate equation is

$$\frac{dC_R}{dt} = -\frac{dC_A}{dt} = C_{A0}\frac{dX_A}{dt} = K_1 C_A - K_2 C_R$$

$$= K_1(C_{A0} - C_{A0}X_A) - K_2(\Theta C_{A0} + C_{A0}X_A)$$

At equilibrium, $\quad dC_A/dt = 0.$

Fractional conversion of A at equilibrium conditions,

$$K_C = \frac{C_{Re}}{C_{Ae}} = \frac{M + X_{Ae}}{1 - X_{Ae}}$$

First-Order Reversible Reactions

☐ Equilibrium constant

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

Combining the equations

On integration,

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

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

First-Order Reversible Reactions

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 $K_C = \infty$.
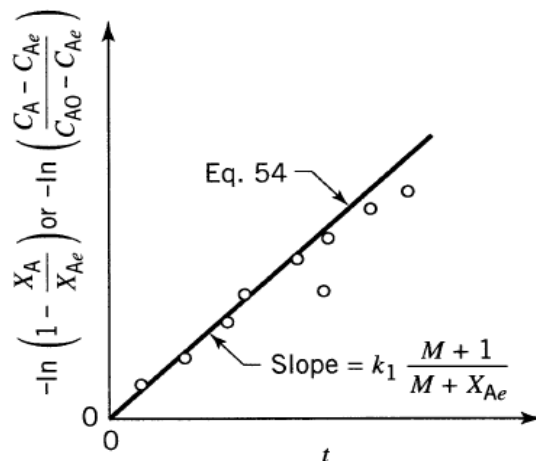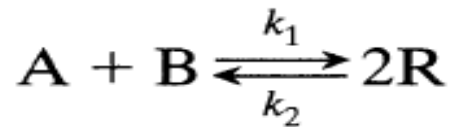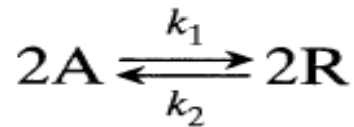

Figure 3.13 Test for the unimolecular type reversible reactions of Eq. 53.

Compare with 1ˢᵗ order irreversible

Second order Reversible Reaction

☐ Bimolecular type second order reactions

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R + S$$

$$2A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} 2R$$
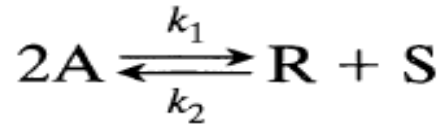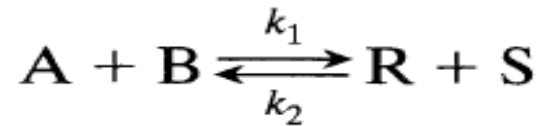
Second-Order Reversible Reactions

☐ Restrictions

$$C_{A0} = C_{B0} \qquad \text{and}$$

$$C_{R0} = C_{S0} = 0,$$

Integrated rate equation

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

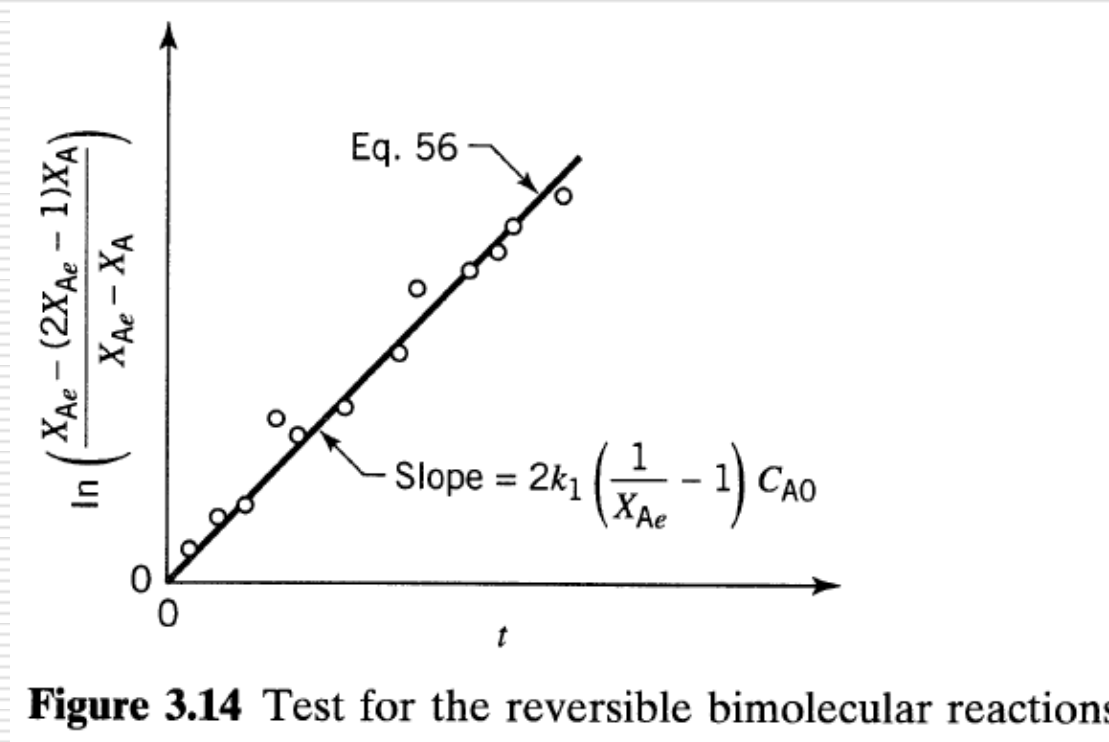# First-Order Reversible Reactions

☐ A plot is shown in the figure

Figure 3.14 Test for the reversible bimolecular reactions

Reactions of shifting order

Consider the reaction $A \rightarrow R$
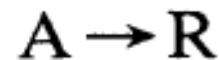
Rate equation $-r_A = -\dfrac{dC_A}{dt} = \dfrac{k_1 C_A}{1 + k_2 C_A}$

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 $k_2 C_A \ll 1$)

Reactions of shifting order
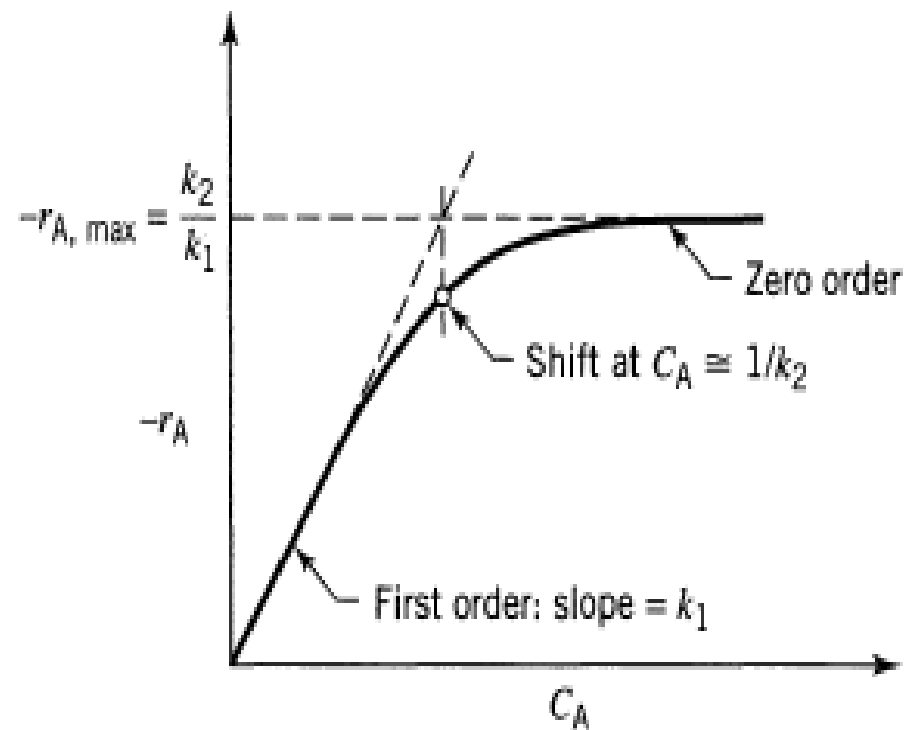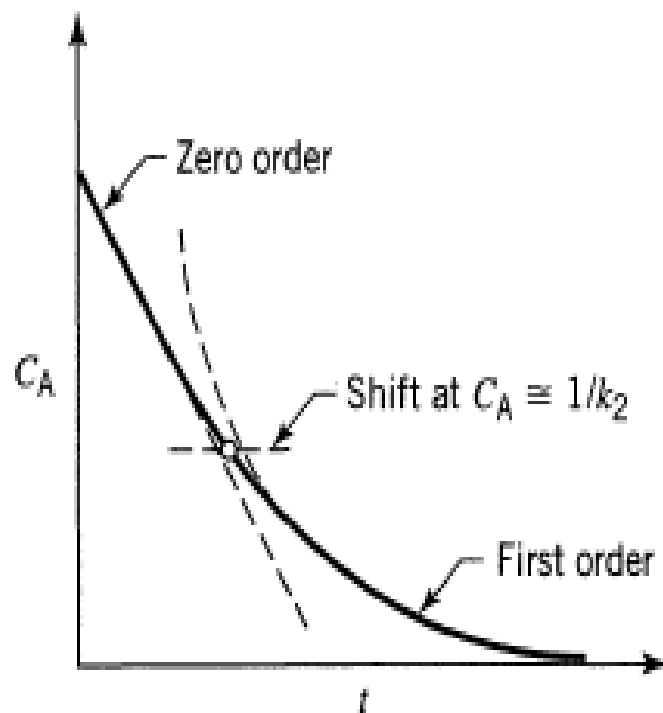
Reactions of shifting order

To apply the integral method, separate variables and integrate,

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

Linearize

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

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

Reactions of shifting order
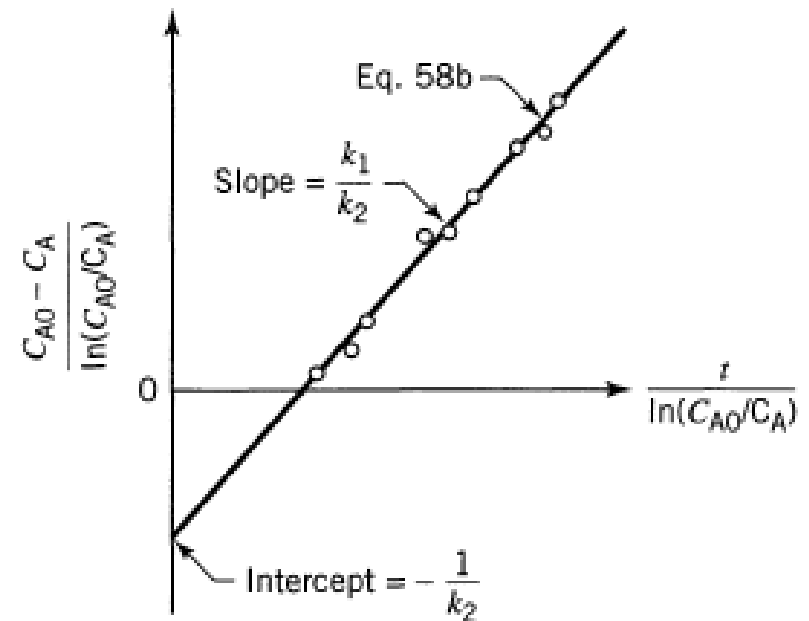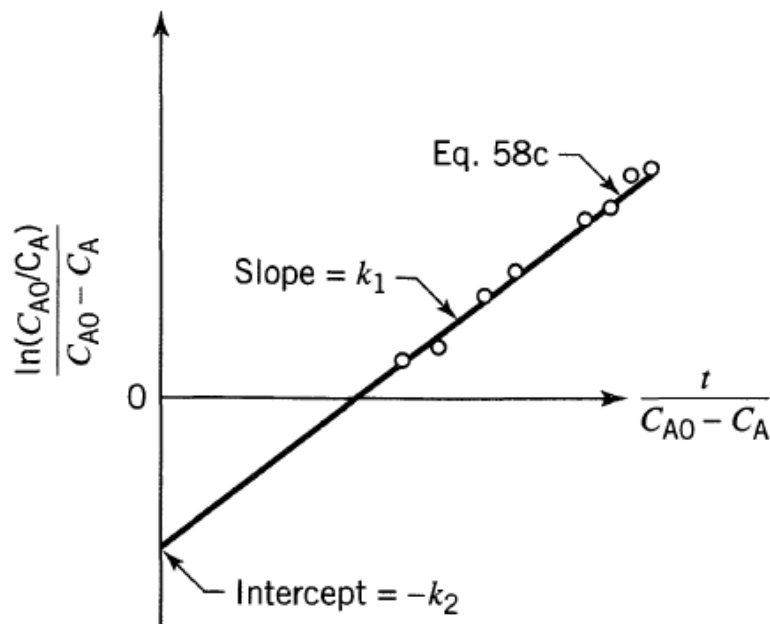
Autocatalytic Reactions

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

$$A + R \rightarrow R + R \qquad (41a)$$

for which the rate equation is

$$-r_A = -\frac{dC_A}{dt} = kC_A C_R \qquad (41b)$$

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

$$-r_A = -\frac{dC_A}{dt} = kC_A(C_0 - C_A)$$

Autocatalytic Reactions

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

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

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

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

Autocatalytic Reactions
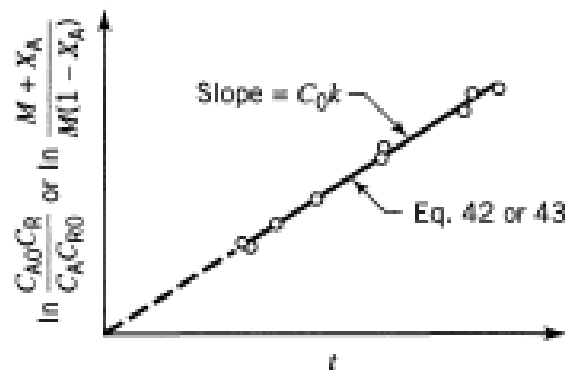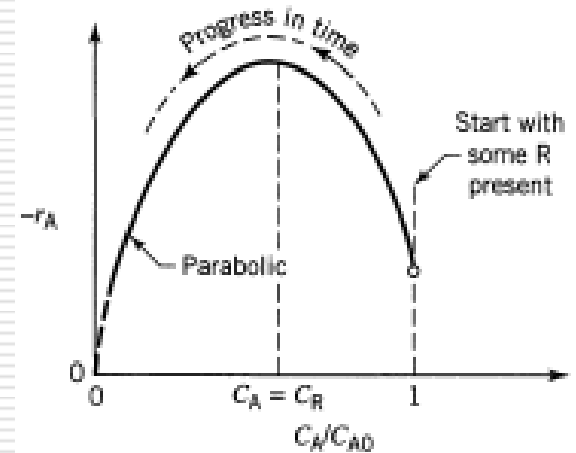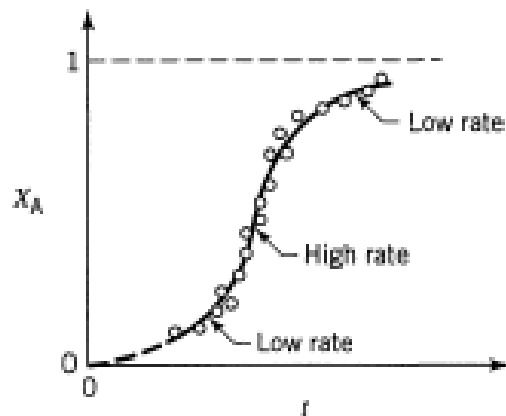
Practice Problems

1. The decomposition of acetaldehyde CH_3CHO to give CH_4 and CO is a second order reaction. The rate at a certain temperature is 0.18 mol/l.sec. when the acetaldehyde concentration is 0.1 mol/min

   a. What is the rate expression for this reaction?

   b . What is the value of rate constant?

   c. Calculate reaction rate when concentration of CH_3COOH is 0.2 mol/l?

   18 lit./mol.sec, 0.72 mol/lit.sec

Practice Problems

□ A certain reaction has a rate given by $-r_A =$ $0.007C_A^2$ If the concentration is to be expressed in mol/lit. and time is in hours, what would be the value and units of the rate constant? (1.167×10^{-7} lit./mol/hr). rate expression has units as mol/cm^3/min.

□ What is the formula for half life period of a first order reaction? The half life period of a certain first order reaction is 2.5×10^3 sec. How long will take for $1/4^{th}$ of the reactant the left behind?

$$n = 1 + \log [(t'_{1/2} / t''_{1/2}) / (C_A'' / C_A')]$$

Practice Problems

❑ Show analytically that the decomposition of N_2O_5 at 67 °C is a first order reaction. Calculate the value of the rate constant 0.3477 min^{-1}

Time / min	0	1	2	3	4
C_{N2O5} / mol/lit.	0.16	0.113	0.08	0.056	0.040

❑ In a gaseous reaction, time for half change for various partial pressures is given. What is the rate equation? 0.106 C_A

Time / min	0	4	8	12	16
PP / mm Hg	760	475	320	240	150

Practice Problems

☐ The half life for the conversion of ammonium cynate into urea at 303 K at initial concentrations of ammonium cynate of 0.1 and 0.2 mol/l are 1152 min and 568 min respectively. What is the order of the reaction? 2

☐ The half lives periods for decomposition of PH_3 for different initial pressures is given below: 1

P, Torr	707	79	37.5
$t_{1/2}$	84	84	84

Practice Problems

☐ Decomposition of a gas is of second order when the initial concentration of gas is 5×10^{-4} mol/lit. It is 40% decomposed in 50 min. what is the value of rate constant? 26.67 lit./mol.min

☐ At 25 °C the rate constant for the hydrolysis of ethyl acetate by NaOH is 6.5 lit per mol per min., starting with a concentration of base and ester of 0.03 mol/lit. of each. What proportion of ester will be hydrolyzed in 10 min? 66.1%

Practice Problems

☐ The partial pressure of azo-methane (A) was observed as a function of time at 600 K with the results given below. Confirm that the decomposition A → B + C is first order with respect to A and find the rate constant at this temperature 3.6×10^{-4} sec^{-1}

Time in min	0	1000	2000	3000	4000
Pressure (Torr)	820	572	399	278	194

Practice Problems

☐ The data for a chemical reaction A + B → P is given below

C_A	C_B	-dC_A/dt initial rate
0.5	0.5	0.02
1	0.5	0.08
1.0	1.0	0.16

What is the overall order of the reaction? 3

Practice Problems

The following data for the decomposition of azo-isopropane at 270 ^{o}C was obtained:

Time (s)	0	180	360	540	720	1020
Pressure / Torr	35.15	46.30	53.90	58.85	62.20	65.50

Treat decomposition reaction as A $\Longrightarrow$ B + C for calculation purpose, find order of reaction and the rate constant

$$K = 1/t \ln [(P_o / 2P_o - P)$$

Solution

but at time t it is

$$N = N_0 + x(r + s + \cdots - a - b - \cdots) = N_0 + x\,\Delta n$$

where

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

$P / P_o = (N_o + x) / N_o$

$x = [P / P_o - 1]N_o$

$$C_A = \frac{p_A}{\mathbf{R}T} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V}$$

Analysis of Total Pressure data

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V} \qquad C_A = \frac{N_{A0}}{V} - \frac{a}{\Delta n}\frac{N - N_0}{V}$$

$$C_A = (N_o/P_oV)(2P_o - P)$$

$$r_A = k\,(N_o/P_oV)(2P_o - P) = dP/dt$$

$$k = (1/t)\ln\,[P_o\,/\,2P_o - P]$$

1, 0.00206

Practice Problems

- ☐ The first order reversible liquid reaction A ⇔ R C_{Ao} = 0.5 mol/lit, C_{Ro} = 0 takes place in a batch reactor. After 8 minutes the conversion of A is 33.3%. While the equilibrium conversion is 66.7%, find the rate expression $dC_A/dt = 0.0577C_A - 0.0288C_R$

- ☐ Liquid B decomposes by first order kinetics and in a batch reactor. 50% of B is converted in a 5 min run. How much longer would it take to reach 75% conversion?

Varying Volume Batch Reactor
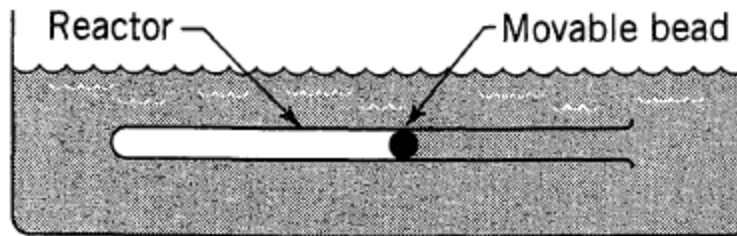
Figure 3.20 A varying-volume batch reactor.

V_0 = initial volume of the reactor

V = the volume at time t.

Varying Volume Batch Reactor

Volume is linearly related to conversion

$$V = V_0(1 + \varepsilon_A X_A) \quad \text{or} \quad X_A = \frac{V - V_0}{V_0 \varepsilon_A} \qquad dX_A = \frac{dV}{V_0 \varepsilon_A}$$
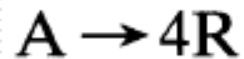
Where ε_A is the fractional change in the volume of the system

$$\varepsilon_A = \frac{V_{X_A=1} - V_{X_A=0}}{V_{X_A=0}}$$

Varying Volume Batch Reactor

Example $\qquad$ $A \rightarrow 4R$

Pure reactant $\qquad$ $\varepsilon_A = \dfrac{4-1}{1} = 3$

But with 50% inerts present at the start, two volumes of reactant mixture yield, on complete conversion, five volumes of product mixture

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

Varying Volume Batch Reactor

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

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

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

The general rate of reaction

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

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

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

Integral method of Analysis

Zero-order reactions:

$$-r_{A} = \frac{C_{A0}}{\varepsilon_{A}} \frac{d(\ln V)}{dt} = k$$
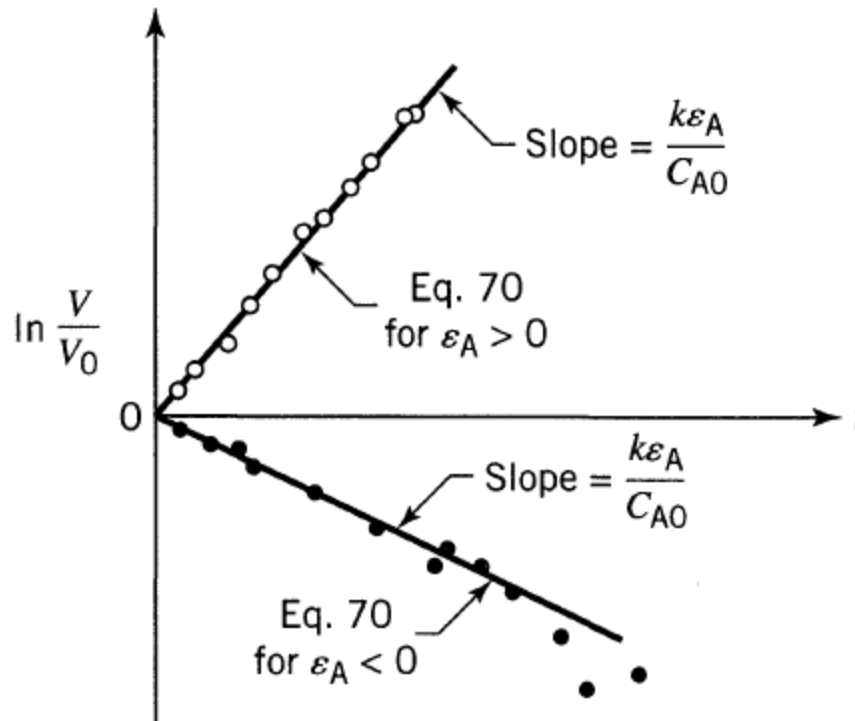
Integrating gives,

$$\boxed{\frac{C_{A0}}{\varepsilon_{A}} \ln \frac{V}{V_0} = kt}$$

As shown in the following figure, the log of fractional change in volume versus time yields a straight line with slope

$$k\varepsilon_{A}/C_{A0}.$$

Integral method of Analysis (Zero order)

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

Integral method of Analysis (First Order)

First order reaction

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

Replacing X_A by V

$$dX_A = \frac{dV}{V_0\varepsilon_A}$$

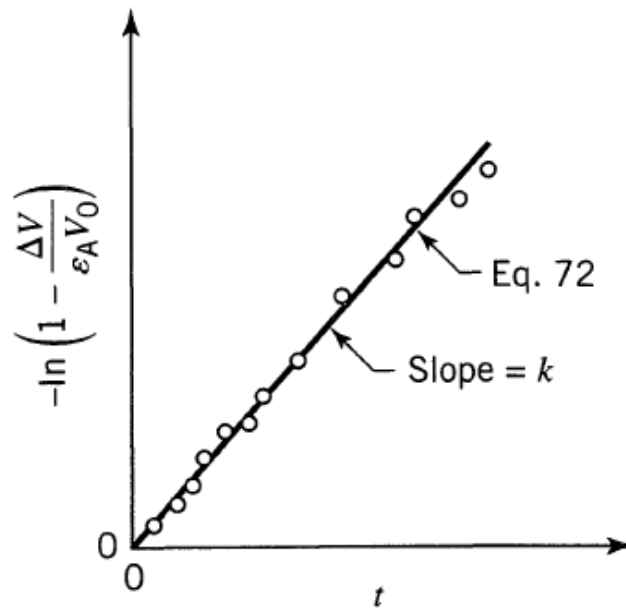$$\boxed{-\ln\left(1-\frac{\Delta V}{\varepsilon_A V_0}\right) = kt, \ \Delta V = V - V_0}$$

Semi logarithmic plot of this equation yields a straight line of slope k

Integral method of Analysis (First Order)
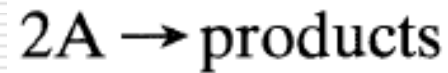

Figure 3.22 Test for a first-order reaction, Eq. in a constant-pressure, varying-volume reactor.

Integral method of Analysis (Second Order)

□ Second order reaction

$$2A \rightarrow \text{products}$$

Or

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

The rate is given by

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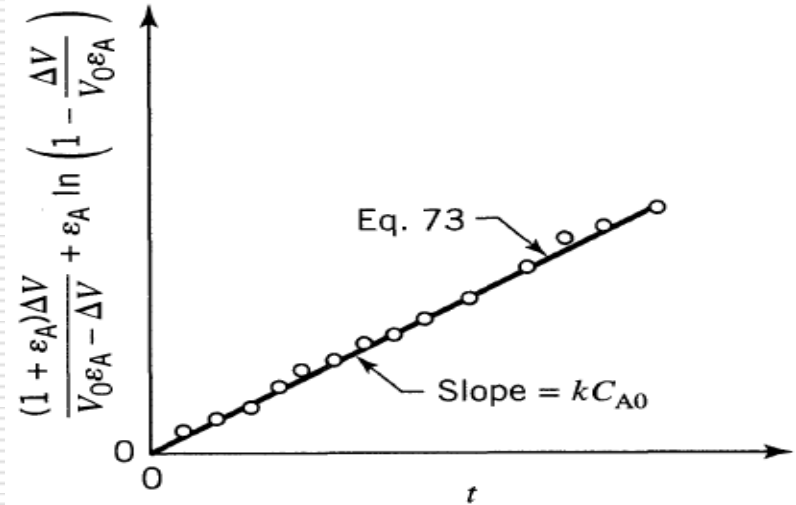
Integral method of Analysis (Second Order)

Replacing X_A by V and integrating

$$dX_A = \frac{dV}{V_0 \varepsilon_A}$$

$$\frac{(1 + \varepsilon_A)\,\Delta V}{V_0 \varepsilon_A - \Delta V} + \varepsilon_A \ln\left(1 - \frac{\Delta V}{V_0 \varepsilon_A}\right) = k C_{A0} t$$

The following figure 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.

Practice Problems

- ☐ Find the first order rate constant for the disappearance of A in a gas phase reaction

  $2A \rightarrow R$, if on holding the pressure, the volume of the reaction mixture starting with 80% A decreases by 20% in 3 mins 0.231 min^{-1}

- ❑ The gas reaction $2A = R + 2S$ is approximately 2nd order with respect to A. When pure A is introduced at 1 atm into a constant volume batch reactor the pressure rises by 40% in 3 mins. For a constant pressure batch reactor find the time required for the same conversion and fractional increase in volume at that time 3.906 min, increase in volume 40%

Final two

- A gas A decomposes irreversibly to form gas A = 2C. The decomposition is a first order reaction carried out in a constant pressure batch reactor. Derive an expression for the volume of the system as a function of time. Assume that the reacting gases behave ideally

- The decomposition of ammonia on a tungsten wire at 856 °C gave the following results

Total Pressure / Torr	228	250	273	318
Time / sec	200	400	600	1000

Determine order and rate constant: 0. 0.112

Objective Assessment of Chapter

- ☐ Determine the reaction order and specific reaction rate from experimental data obtained from either batch or flow reactors.

- ☐ Describe how to use equal-area differentiation, polynomial fitting, numerical difference formula

There are two ways of meeting difficulties: you alter the difficulties or you alter yourself meeting them