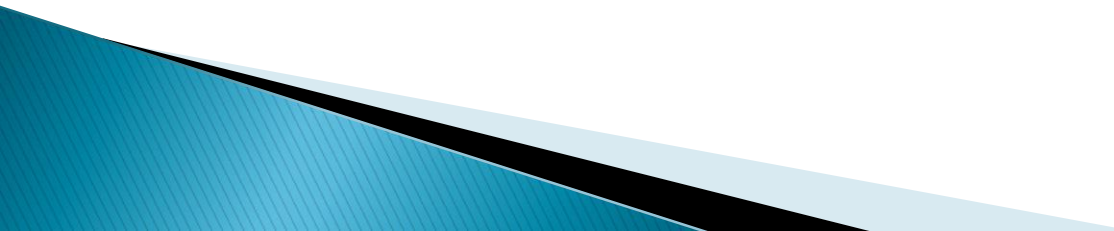


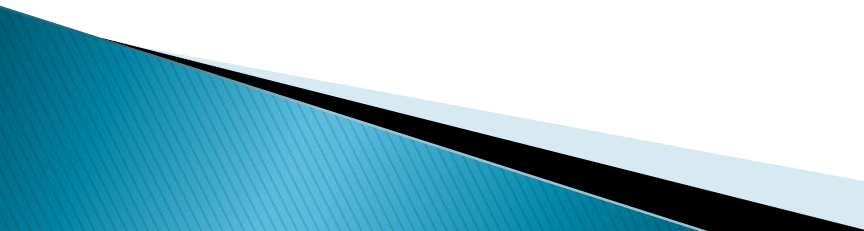
Chapter 3

Interpretation of Batch Reactor Data

Batch Reactor Data

- ▶ Determination of the rate equation is usually a two-step procedure
 - ▶ First the concentration dependency is found at fixed temperature
 - ▶ Temperature dependence of the rate constants is found
- 

Batch Reactor Data

- ▶ Empirical information is obtained can be divided into two types
 - ▶ Batch reactors
 - ▶ Flow reactors
 - ▶ Batch reactor is simply a container to hold the contents while they react
 - ▶ Extent of reaction at various times, and this can be followed in a number of ways
- 

Measure of extent of reaction at various time

- ▶ By following the concentration of a given component
- ▶ By following the change in some physical property of the fluid
e.g. electrical conductivity or refractive index
- By following the change in total pressure of a constant-volume system
- By following the change in volume of a constant-pressure system

experimental batch reactor is usually operated isothermally and at constant volume

Batch Reactor Data

Relatively simple device adaptable to small-scale laboratory set-ups

- ▶ need little auxiliary equipment or instrumentation
- ▶ used whenever possible for obtaining homogeneous kinetic data

Flow reactors


- flow reactor is used primarily in the study of the kinetics of heterogeneous reactions

Analyzing kinetic data

Two procedures for analyzing kinetic data

- ▶ Integral methods
- ▶ differential methods

Integral methods:

- ▶ In the integral method of analysis we guess a particular form of rate equation
 - ▶ Appropriate integration and mathematical manipulation,
 - ▶ Predict the plot of a certain concentration function versus time
 - ▶ Yield a straight line
- 

Integral methods Analysis

- ▶ The integral method can only test this or that particular mechanism or rate form
- ▶ Integral method is easy to use
- ▶ Recommended when testing specific mechanisms
- ▶ Relatively simple rate expressions
- ▶ When the data are so scattered that we cannot reliably find the derivatives needed in the differential method

suggested that **integral analysis** be attempted **first**, and, if not successful, that the differential method be tried.

Differential methods

Differential method of analysis

- ▶ First find $(1/V)(dN/dt)$ from the data
- ▶ Test the fit of the rate expression to the data directly and without any integration
- ▶ Attempting the fitting procedure.
- ▶ The differential method is useful in more complicated situations
- ▶ **requires more accurate or larger amounts of data**
- ▶ used to develop or build up a rate equation to fit the data

CONSTANT-VOLUME BATCH REACTOR

- ▶ Actually means a *constant-density reaction system*

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

- ▶ For ideal gases, where $C = p/RT$

- ▶ Rate of reaction of any component is given by the rate of change of its concentration or partial pressure

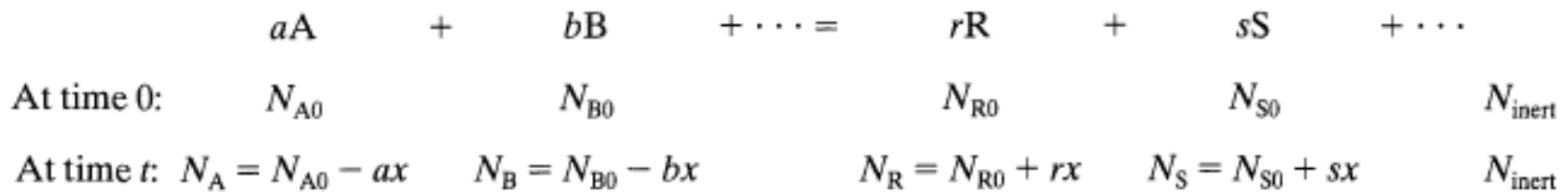
$$r_i = \frac{1}{RT} \frac{dp_i}{dt}$$

- ▶ Develop the general expression which relates the changing total pressure of the system P to the changing concentration or partial pressure of any of the reaction components.

Total Pressure Data Obtained in a Constant-Volume System

General stoichiometric equation

- ▶ Each term indicate the number of moles of that component



- ▶ Total number of moles present in the system is

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

- ▶ At time t it is

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

where

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

Total Pressure Data

$$C_A = \frac{p_A}{RT} = \frac{N_A}{V} = \frac{N_{A0} - ax}{V}$$

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

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

total pressure π at time t , initial partial pressure of A, p_{A0} , and initial total pressure of the system, π_0

Similarly, for any product R

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

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.

Conversion

- ▶ Suppose that N_{A0} is the initial amount of A in the reactor at time $t = 0$,
- ▶ that N_A is the amount present at time t .

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

$$dX_A = -\frac{dC_A}{C_{A0}}$$

Integral Method of Analysis of Data

- ▶ Integral method is especially useful for fitting simple reaction

Irreversible Unimolecular-Type First-Order Reactions



- ▶ Test the first-order rate equation

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

- ▶ Separating and integrating we obtain

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

- ▶ In terms of conversion

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

Integral method

- ▶ Rearranging and integrating gives

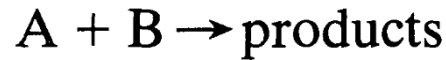
$$\int_0^{X_A} \frac{dX_A}{1 - X_A} = k \int_0^t dt$$

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

- ▶ Plot of $\ln(1 - X_A)$ or $\ln(C_A/C_{A0})$ vs. t
- ▶ Straight line through the origin for this form of rate of equation
- ▶ First order but are not amenable to this kind of analysis

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

Irreversible Bi-molecular type Second-Order Reactions



Corresponding rate equation

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

Amounts of A and B that have reacted at any time t are equal and given by $C_{A0}X$

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

Letting $M = C_{B0}/C_{A0}$

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

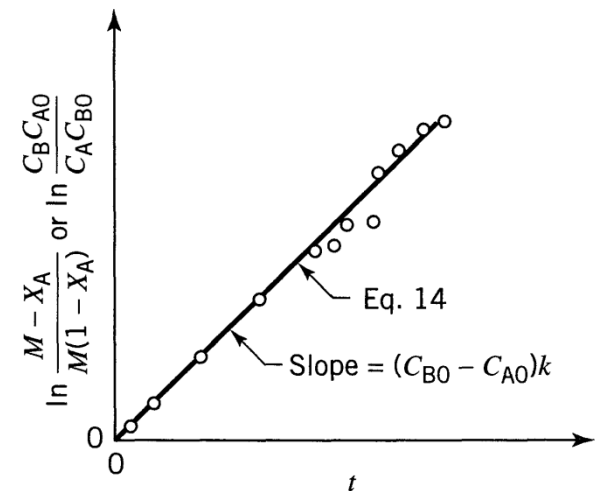
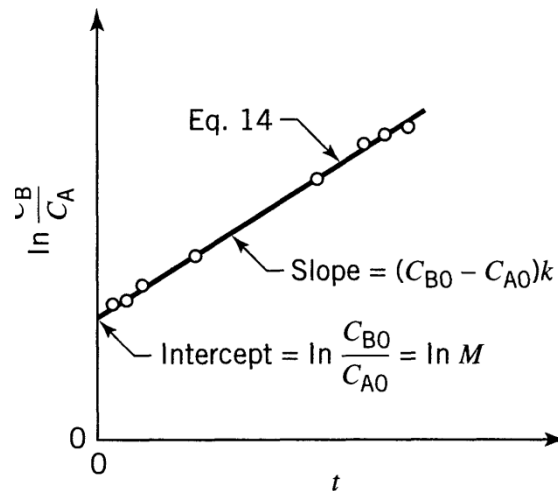
On separation and formal integration becomes

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

- ▶ Test for the bimolecular mechanism $A + B \rightarrow R$ with $C_{A0} \neq C_{B0}$
- ▶ Breakdown into partial fractions, integration, and rearrangement, the final result in a number of different forms

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

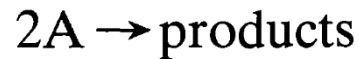
- ▶ Linear plot between the concentration function and time for this second-order rate law



Special case

- ▶ If C_{B_0} is much larger than C_{A_0} remains approximately constant at all times, and approaches for the first-order reaction
- ▶ Second order reaction becomes a pseudo first-order reaction

For the reaction

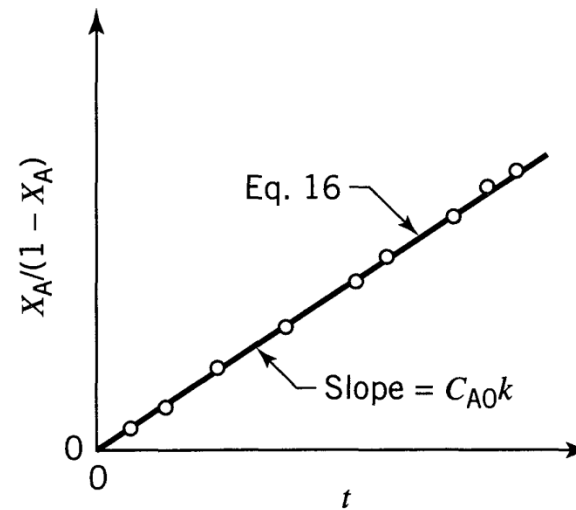
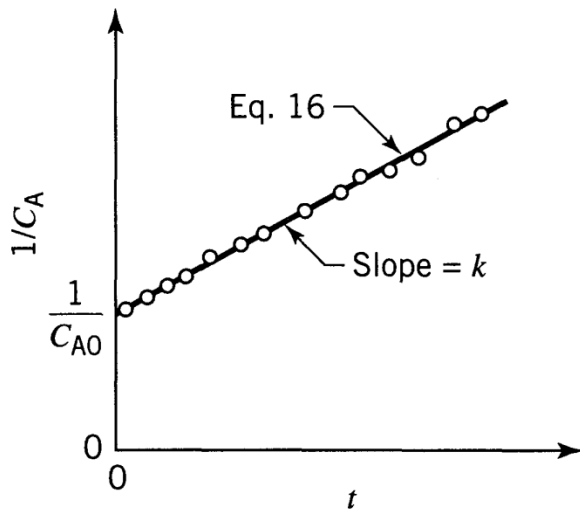


$$-r_A = -\frac{dC_A}{dt} = kC_A^2 = kC_{A0}^2(1 - X_A)^2$$

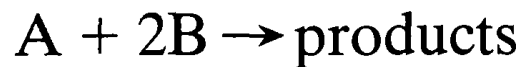
$$\frac{1}{C_A} - \frac{1}{C_{A0}} = \frac{1}{C_{A0}} \frac{X_A}{1 - X_A} = kt$$

Special case

- ▶ Test for the bimolecular mechanisms, $A + B \rightarrow R$ with $C_{A0} = C_{B0}$ for



The integrated expression depends on the stoichiometry as well as the kinetics



Second-order reaction

- ▶ Second order overall, first order with respect to both A and B

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

- ▶ Integrated form

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

- ▶ Stoichiometric reactant ratio is used the integrated form

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

Third-Order Reactions

Irreversible Trimolecular-Type

Irreversible Trimolecular-Type



Rate equation be

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

In terms of X_A

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

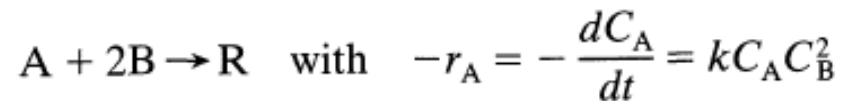
On integration, after manipulation

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

Third-Order Reactions

Special case

- ▶ If C_{D_0} is much larger than both C_{A_0} and C_{B_0} reaction becomes second order Trimolecular reactions



- ▶ In terms of conversions the rate of reaction

$$\frac{dX_A}{dt} = kC_{A0}^2 (1 - X_A)(M - 2X_A)^2 \quad \text{where } M = C_{B0}/C_{A0}$$

- ▶ *On* integration this gives

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

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

Third-Order Reactions

Special case

- ▶ for the reaction $A + B \rightarrow R$

$$-r_A = -\frac{dC_A}{dt} = kC_A C_B^2$$

- ▶ *On integration*

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

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

Empirical Rate Equations of n^{th} Order

When the mechanism of reaction is not known

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

- ▶ On separation and integration yields

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

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

- ▶ Reactions with order $n > 1$ can never go to completion in finite time
- ▶ $n < 1$, reactant concentration will fall to zero and then become negative at some finite time

Zero-Order Reactions

- ▶ Rate of reaction is independent of the concentration of materials
- ▶ Integrating and noting that C_A can never become negative

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

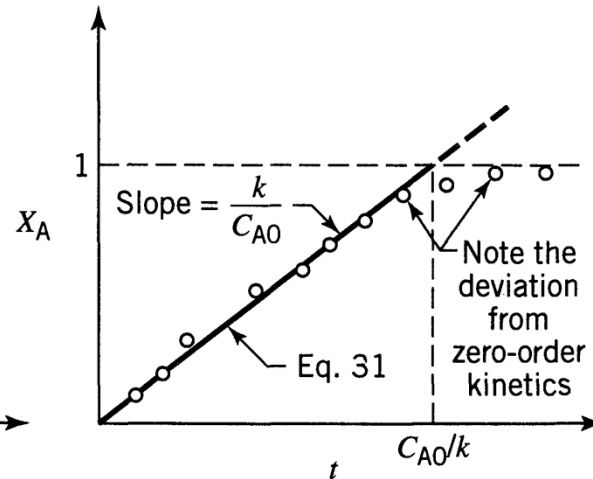
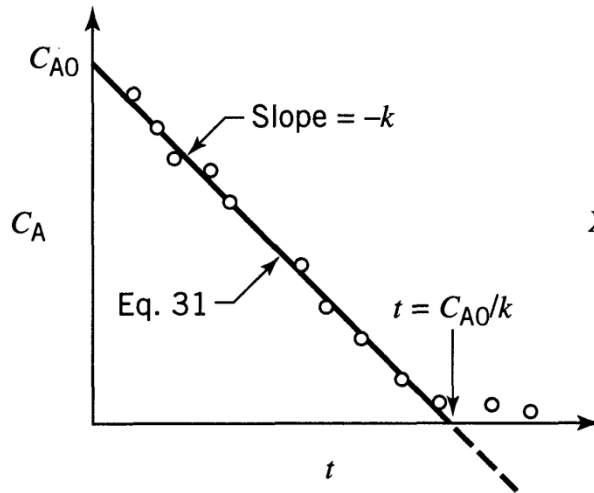
$$C_{A0} - C_A = C_{A0}X_A = kt \quad \text{for } t < \frac{C_{A0}}{k}$$

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

- ▶ Means that the conversion is proportional to time
- ▶ As a rule, reactions are of zero order only in certain concentration ranges—**higher concentrations**

Zero-order reaction

▶ Test for a zero-order reaction



Overall Order of Irreversible Reactions from the Half-Life $t_{1/2}$

- ▶ Irreversible reaction



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

- ▶ Reactants are present in their stoichiometric ratios
- ▶ Thus, for reactants A and B at any time

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

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

$$-\frac{dC_A}{dt} = \tilde{k}C_A^n$$

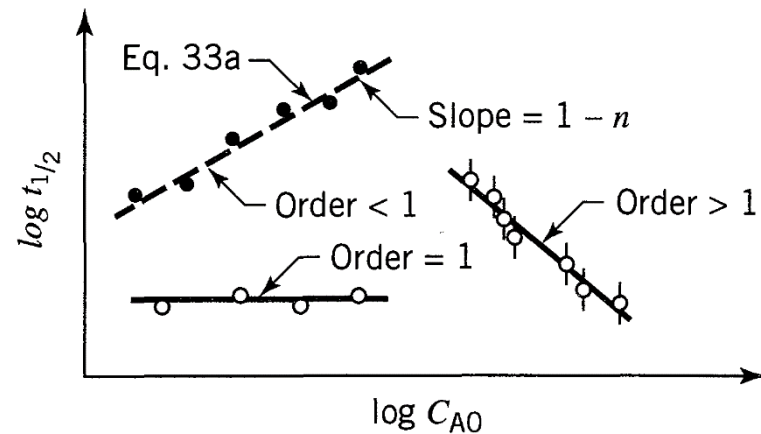
Half-Life of the reaction

- ▶ Integrating for $n \neq 1$

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

- ▶ 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
- ▶ Plot of $\log t_{1/2}$ vs. $\log C_{A0}$ gives a straight line of slope $(1 - n)$

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



Fractional Life Method, t_F

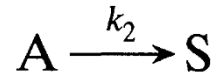
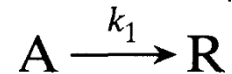
- ▶ Concentration of reactant drops to any fractional value $F = C_A/C_{A0}$ in time, t_F
- ▶ Derivation is a direct extension of the half-life method

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

- ▶ Plot of $\log t_F$ versus $\log C_{A0}$ *show straight line*

Multiple reactions

- ▶ Irreversible Reactions in Parallel
- ▶ Decomposition of A by two competing paths,
- ▶ Both elementary reactions



- ▶ rates of change of the three components

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

$$r_R = \frac{dC_R}{dt} = k_1 C_A \quad r_S = \frac{dC_S}{dt} = k_2 C_A$$

Evaluation of the rate constants for two competing elementary reaction

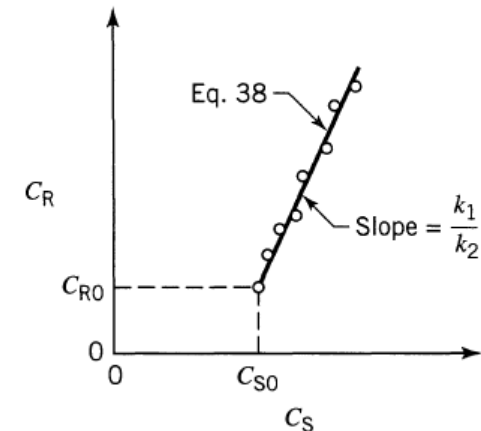
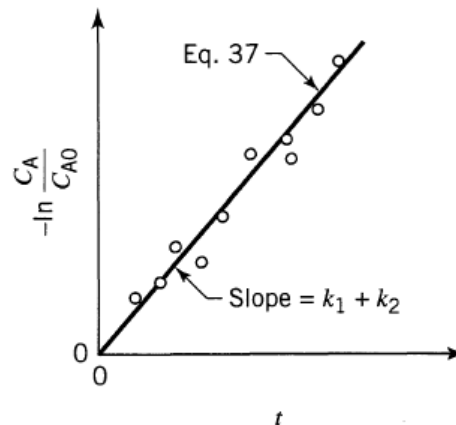
- From the stoichiometry, $C_A + C_R + C_S$ is constant
- k values are found using all three differential rate equations

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

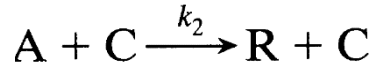
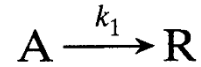
- Plotted as the slope is $k_1 + k_2$
- Further equation on when integrated gives

$$\frac{r_R}{r_S} = \frac{dC_R}{dC_S} = \frac{k_1}{k_2}$$

$$\frac{C_R - C_{R0}}{C_S - C_{S0}} = \frac{k_1}{k_2}$$



Homogeneous Catalyzed Reaction



- ▶ Corresponding reaction rates

$$-\left(\frac{dC_A}{dt}\right)_1 = k_1 C_A \quad -\left(\frac{dC_A}{dt}\right)_2 = k_2 C_A C_C$$

- ▶ Overall rate of disappearance of reactant A is

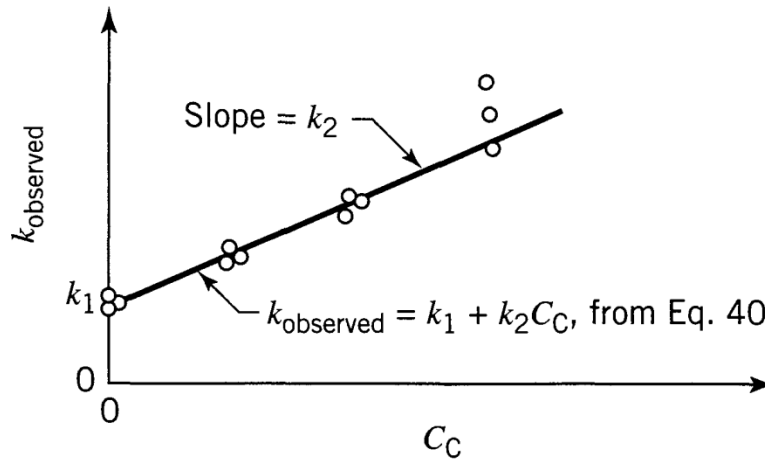
$$-\frac{dC_A}{dt} = k_1 C_A + k_2 C_A C_C = (k_1 + k_2 C_C) C_A$$

- ▶ On integration

$$-\ln \frac{C_A}{C_{A0}} = -\ln(1 - X_A) = (k_1 + k_2 C_C)t = k_{\text{observed}} t$$

Homogeneous Catalyzed Reaction

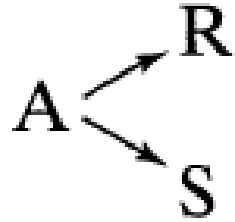
$$-\ln \frac{C_A}{C_{A0}} = -\ln(1 - X_A) = (k_1 + k_2 C_C)t = k_{\text{observed}} t$$



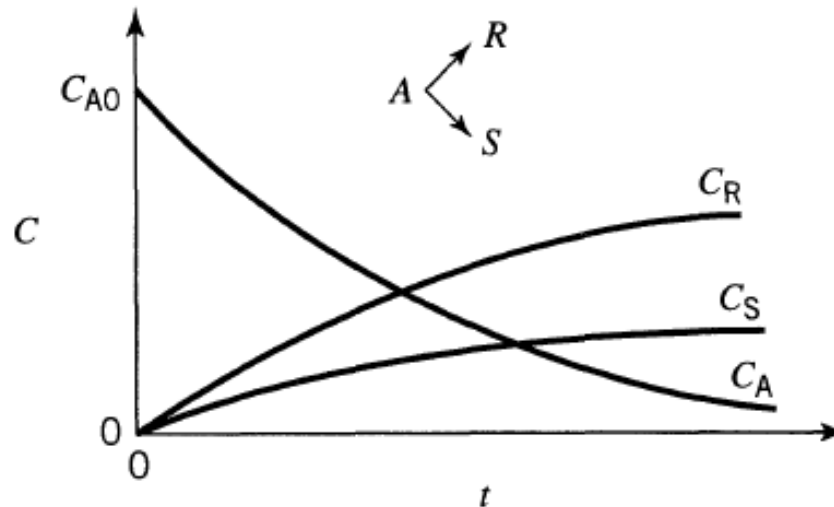
- ▶ Plot the k_{observed} value against the C_C
- ▶ Making a series of runs with different catalyst concentrations to find k_1 and k_2

Special case competing reactions

- ▶ First-order reactions of the type

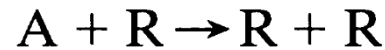


- ▶ concentration-time curves



Autocatalytic Reactions

- ▶ Products of reaction acts as a catalyst



- ▶ Rate equation

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

- ▶ Total number of moles of A and R remain unchanged

$$C_0 = C_A + C_R = C_{A0} + C_{R0} = \text{constant}$$

- ▶ Rate equation becomes

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

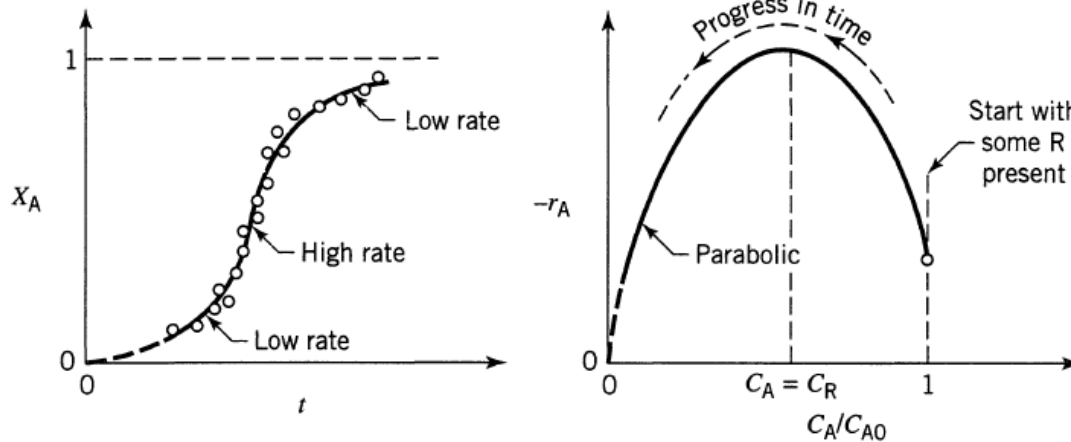
- ▶ Rearranging and breaking into partial fractions

$$-\frac{dC_A}{C_A(C_0 - C_A)} = -\frac{1}{C_0} \left(\frac{dC_A}{C_A} + \frac{dC_A}{C_0 - C_A} \right) = k dt$$

On integration

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

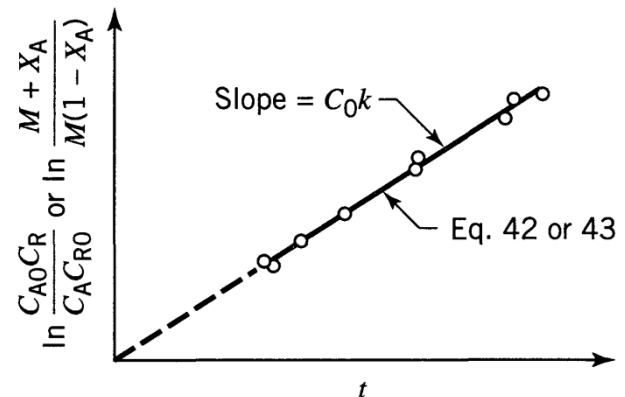
Conversion-time and rate-concentration



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

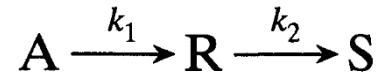
Test for an autocatalytic reaction

Plot the time and concentration a straight line passing through zero is obtained



Irreversible Reactions in Series

- ▶ Consecutive unimolecular type first-order reactions



- ▶ Rate equations for the three components

$$r_A = \frac{dC_A}{dt} = -k_1 C_A \qquad -\ln \frac{C_A}{C_{A0}} = k_1 t \quad \text{or} \quad C_A = C_{A0} e^{-k_1 t}$$

$$r_R = \frac{dC_R}{dt} = k_1 C_A - k_2 C_R \qquad \frac{dC_R}{dt} + k_2 C_R = k_1 C_{A0} e^{-k_1 t}$$

$$r_S = \frac{dC_S}{dt} = k_2 C_R \qquad C_R = C_{A0} k_1 \left(\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2} \right)$$

$$C_{A0} = C_A + C_R + C_S$$

$$C_S = C_{A0} \left(1 + \frac{k_2}{k_1 - k_2} e^{-k_1 t} + \frac{k_1}{k_2 - k_1} e^{-k_2 t} \right)$$

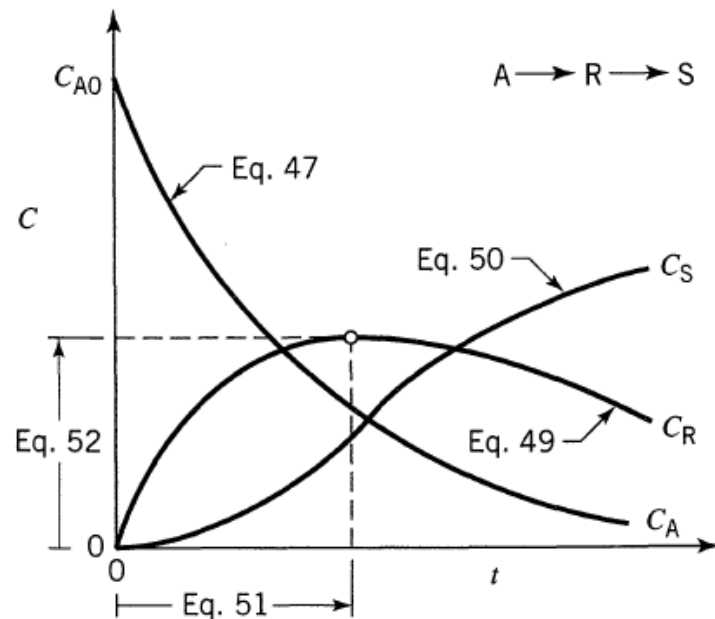
- ▶ If k_2 is much larger than k_1 $C_S = C_{A0} (1 - e^{-k_1 t}), \quad k_2 \gg k_1$
- ▶ If k_1 is much larger than k_2 $C_S = C_{A0} (1 - e^{-k_2 t}), \quad k_1 \gg k_2$

Reactions in Series

- ▶ Values of k_1 and k_2 also govern the location and maximum concentration of R
- ▶ Setting $dC_R/dt = 0$

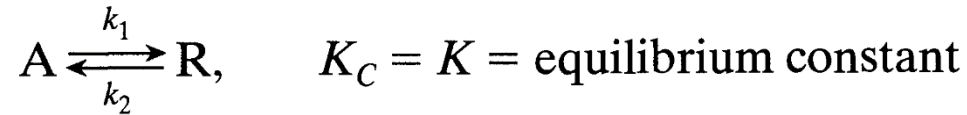
$$t_{\max} = \frac{1}{k_{\log \text{ mean}}} = \frac{\ln(k_2/k_1)}{k_2 - k_1}$$
- ▶ Maximum concentration of R is found by

$$\frac{C_{R,\max}}{C_{A0}} = \left(\frac{k_1}{k_2}\right)^{k_2/(k_2-k_1)}$$



First-Order Reversible Reactions

- ▶ Unimolecular-type reaction



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

- ▶ Concentration ratio $M = C_{R0}/C_{A0}$
$$= k_1 (C_{A0} - C_{A0} X_A) - k_2 (M C_{A0} + C_{A0} X_A)$$
- ▶ At equilibrium $dC_A/dt = 0$

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

- ▶ The equilibrium constant

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

- ▶ Combining equations, in terms of the equilibrium conversion

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

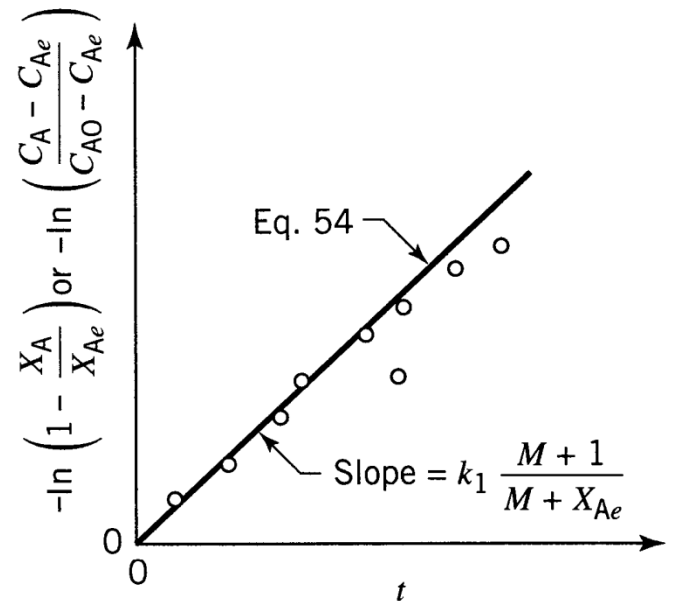
- ▶ As a pseudo first-order irreversible reaction

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

- ▶ A plot of $-\ln(1 - X_A/X_{Ae})$ vs . T

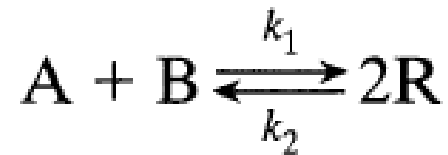
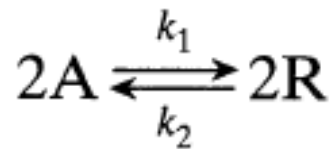
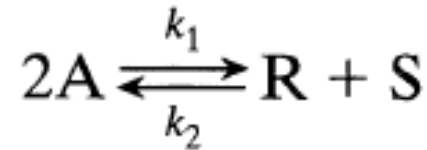
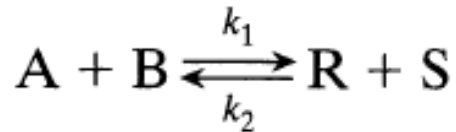
- ▶ Special case of the reversible reaction in which

$C_{A,} = 0$, or $X_{Ae} = 1$, or $Kc = \infty$.



Second-Order Reversible Reactions

- ▶ Bimolecular-type second-order reactions

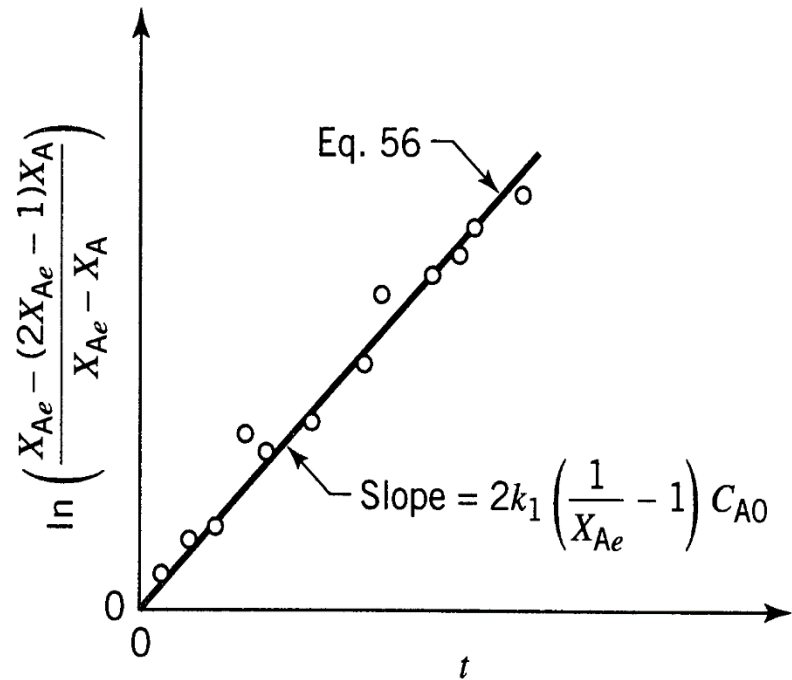


- ▶ Restrictions that $C_{A0} = C_{B0}$, and $C_{R0} = C_{S0} = 0$
- ▶ Integrated rate equations for A and B are all identical

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

Reversible Reactions

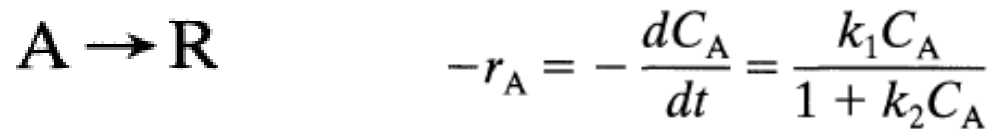
- ▶ A plot can then be used to test the adequacy of these kinetic
- ▶ orders other than one or two, integration of the rate equation becomes cumbersome



- ▶ Rate equation is best done by the **differential method**

Reactions of Shifting Order

- ▶ Data are well fitted by one reaction order at high concentrations but another order at low concentrations



- ▶ 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 $k_2 C_A \ll 1$)
- ▶ Integral method, separate variables and integrate

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

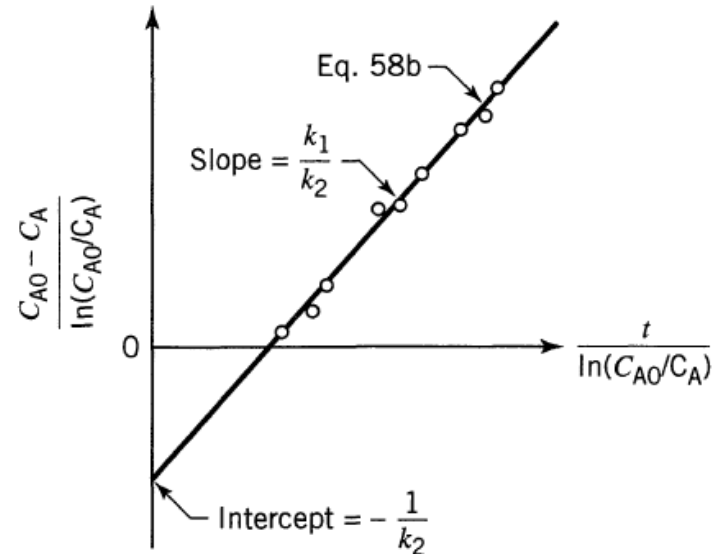
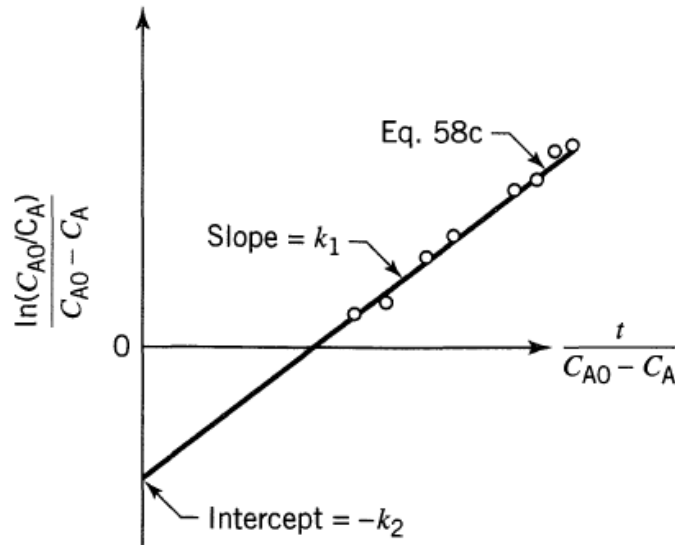
Reactions of Shifting Order

To linearize, rearrange

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

Two ways to test this rate

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



Find A Rate Equation Using The Integral Method



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

Reported data

Calculated

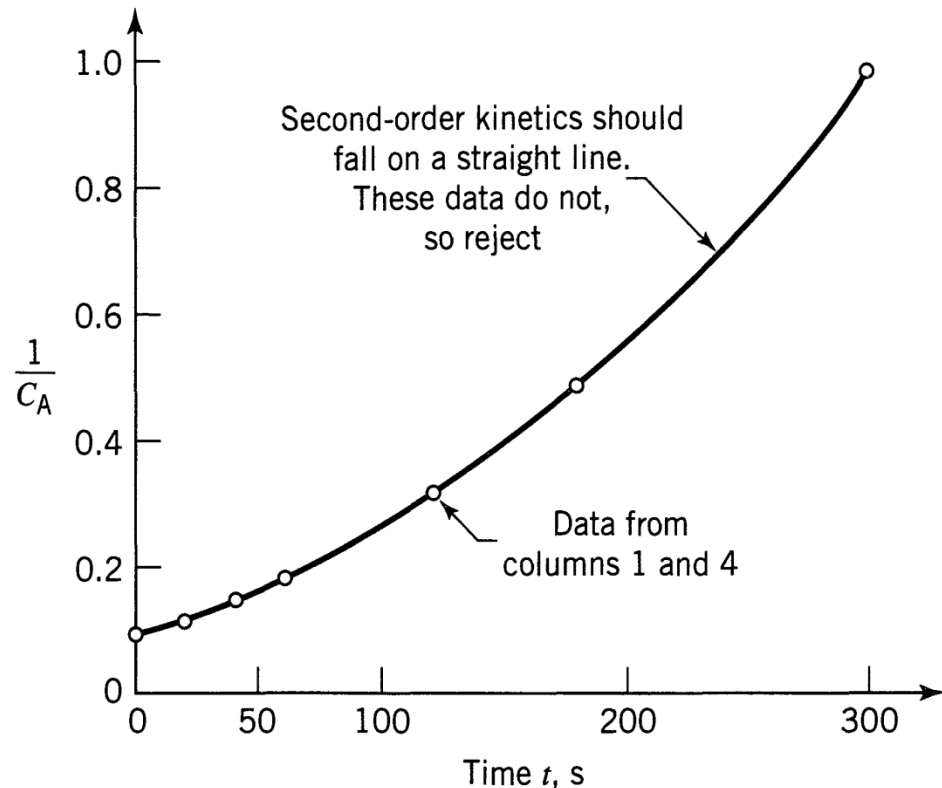
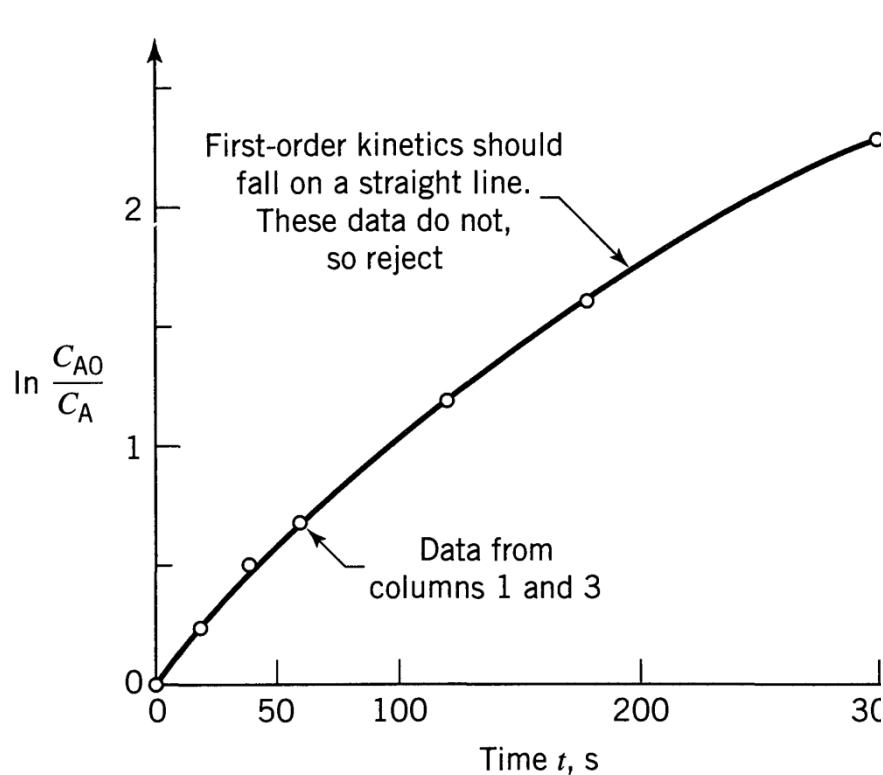
Solution

▶ **Guess First-Order Kinetics**

This means that $\ln C_{A0}/C_A$ vs t should give a straight line

▶ **Guess Second-Order Kinetics**

$1/C_A$ vs. t should give a straight line

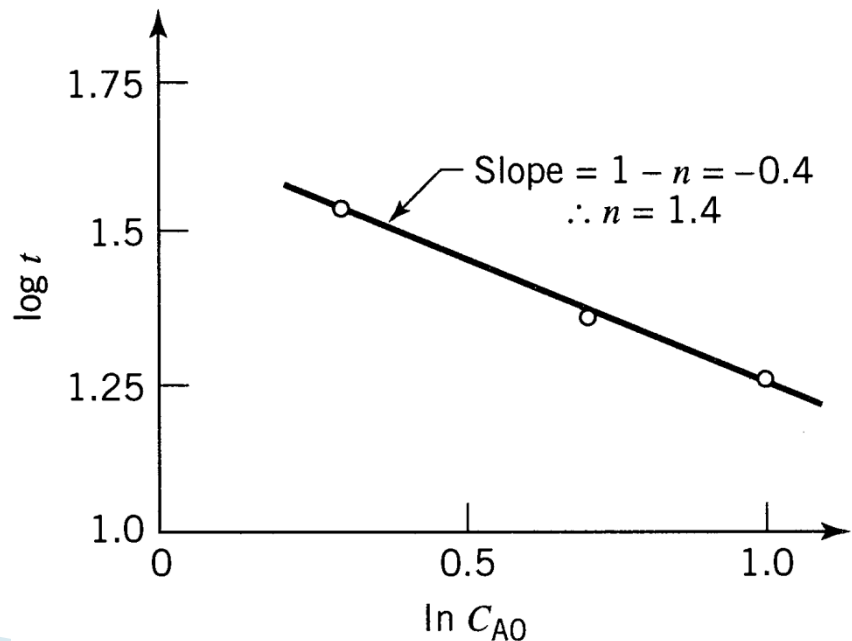
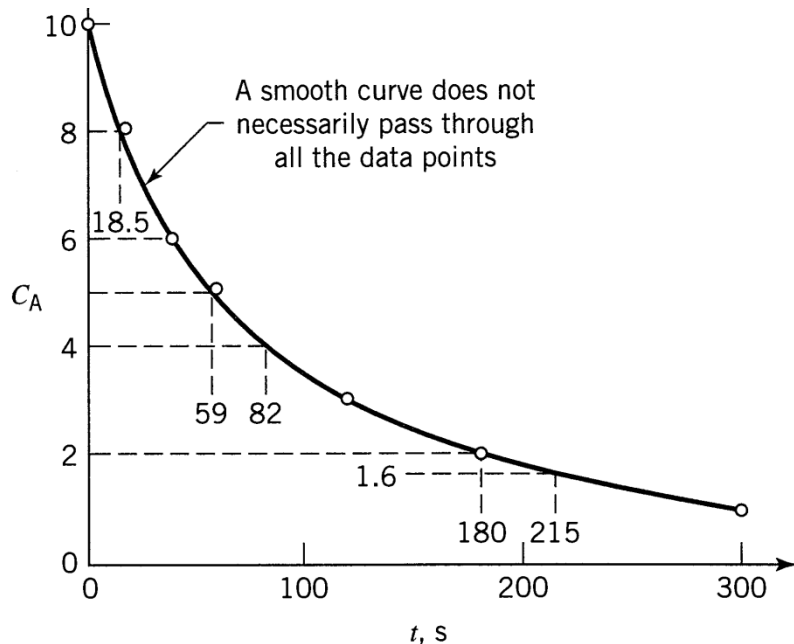


Find A Rate Equation

Choose $C_{A0} = 10, 5, \text{ and } 2$ From the curve

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

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



Find A Rate Equation

- ▶ Pick $C_{A0} = 10$, for which $t_F = 18.5$ s

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

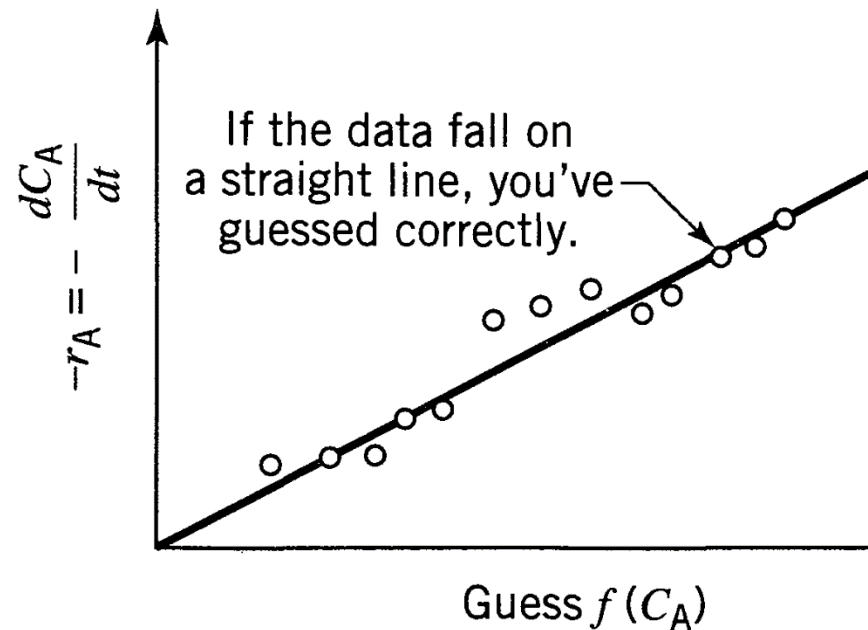
$$k = 0.005$$

Rate equation that represents this reaction is

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

Differential Method of Analysis

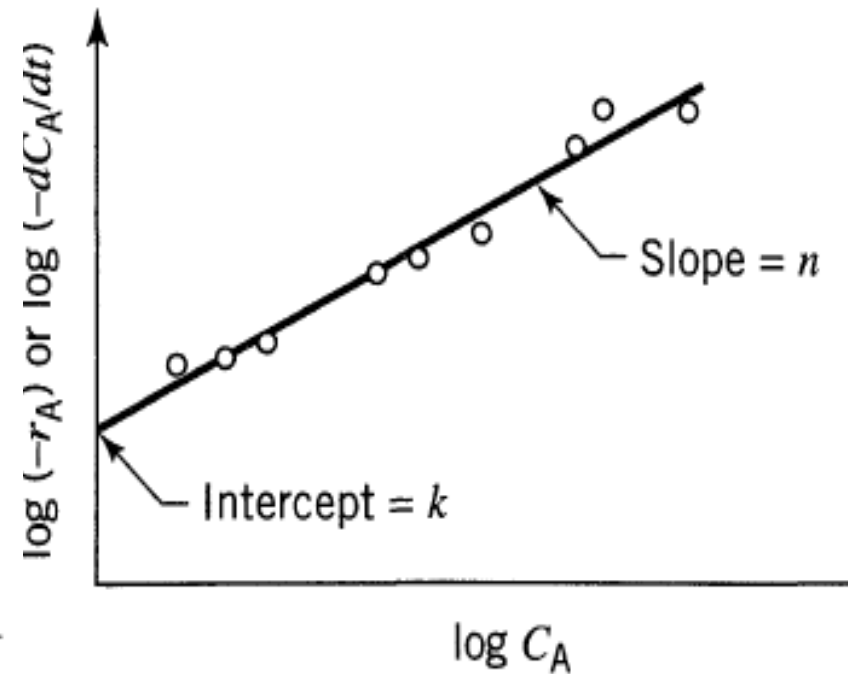
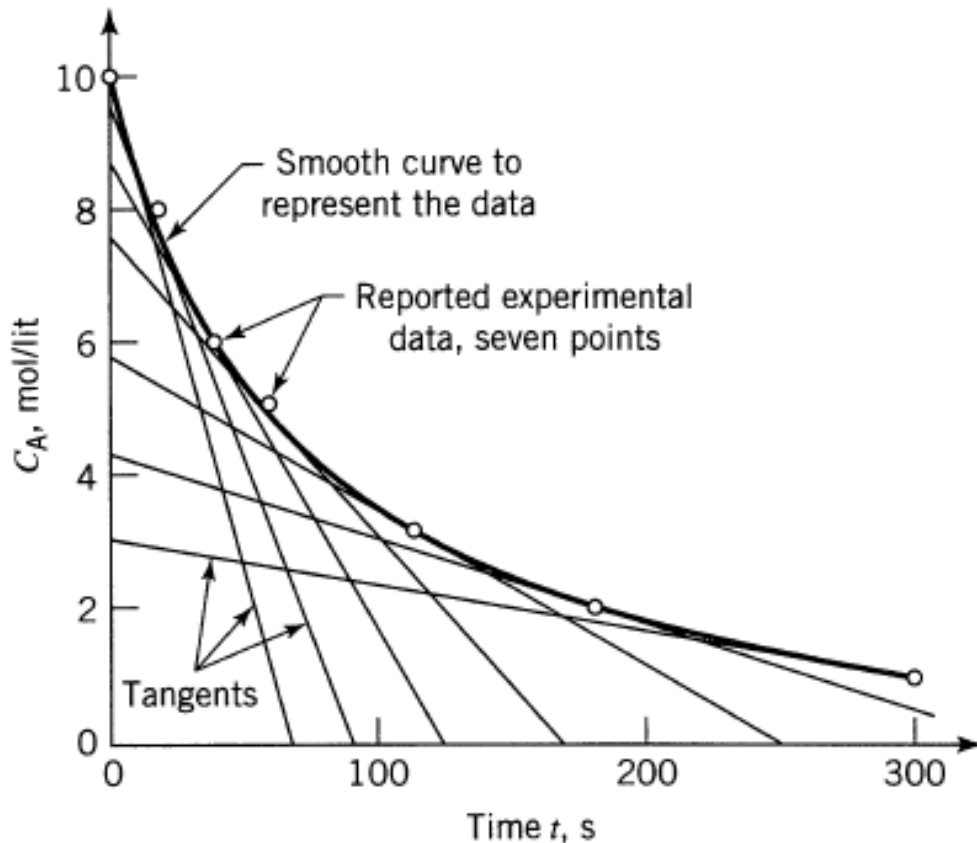
- ▶ Plot the C_A vs. t data
- ▶ Draw a smooth curve
- ▶ Determine the slope of this curve
- ▶ Slopes $dC_A/dt = r_A$ are the rates of reaction



Differential Method of Analysis

- ▶ Testing n^{th} order form
- ▶ Taking logarithms

$$-r_A = kC_A^n$$



Fit the M-M equation

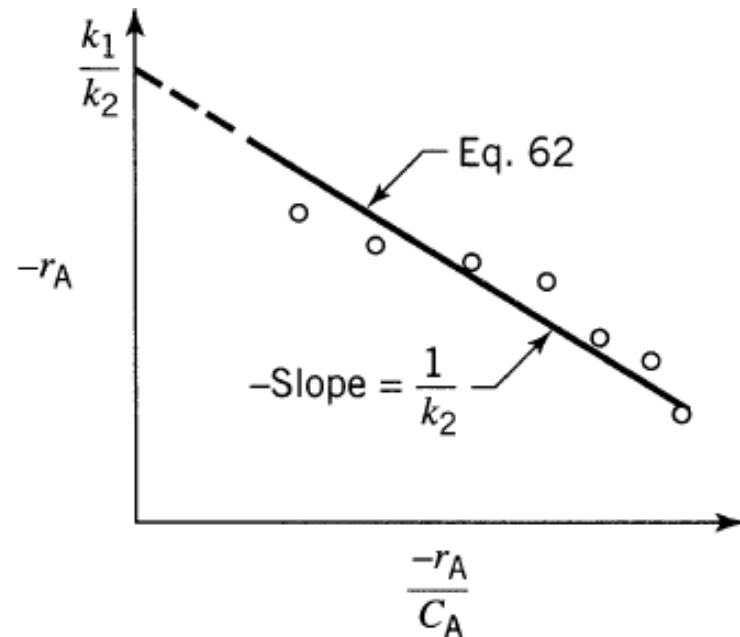
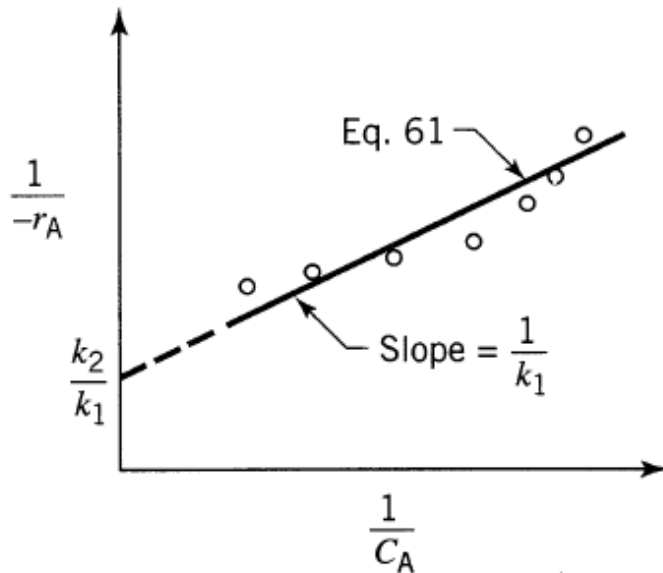
- ▶ Set of C_A vs t data to which we want to fit the M-M equation

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

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

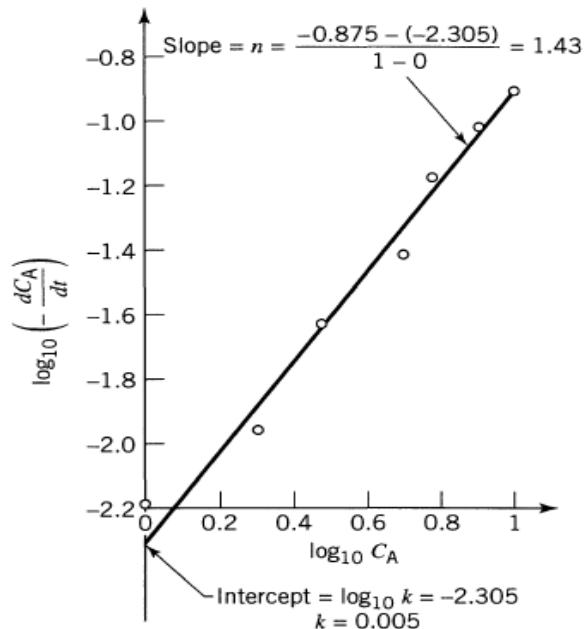
- ▶ $1/(-r_A)$ vs. $1/C_A$ **or**

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



Rate Equation To Fit The Differential Method

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



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

y
intercept
x

slope

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

VARYING-VOLUME BATCH REACTOR

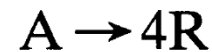
- ▶ This kind of reactor can be used for isothermal constant pressure operations
- ▶ V_0 = initial volume of the reactor
- ▶ V = the volume at time t .

$$V = V_0(1 + \varepsilon_A X_A)$$

$$X_A = \frac{V - V_0}{V_0 \varepsilon_A} \quad dX_A = \frac{dV}{V_0 \varepsilon_A}$$

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

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



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

- ▶ With 50% inerts present at the start, $\varepsilon_A = \frac{5 - 2}{2} = 1.5$

Volume Change with Reaction

- Increase in the total number of moles per mole of A reacted

$$\delta = \frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1$$

$$N_T = N_{T0} + \delta N_{A0} X$$

$$\frac{N_T}{N_{T0}} = 1 + \frac{N_{A0}}{N_{T0}} \delta X = 1 + \delta y_{A0} X$$

$\epsilon = \frac{\text{change in total number of moles for complete conversion}}{\text{total number of moles fed to the reactor}}$

$$\epsilon = \left(\frac{d}{a} + \frac{c}{a} - \frac{b}{a} - 1 \right) \frac{N_{A0}}{N_{T0}} = y_{A0} \delta$$

$$\boxed{\epsilon = y_{A0} \delta}$$

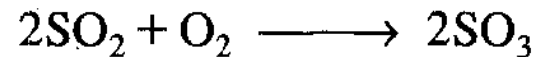
$$V = V_0 \left(\frac{P_0}{P} \right) \frac{T}{T_0} \left(\frac{Z}{Z_0} \right) (1 + \epsilon X)$$

compressibility factor will not change

$$V = V_0 \left(\frac{P_0}{P} \right) (1 + \epsilon X) \frac{T}{T_0}$$

Volume Change with Reaction

- A mixture of 28% SO₂ and 72% air is charged to a flow reactor in which SO₂ is oxidized.



$$\varepsilon = y_{A0} \delta = (0.28)(1 - 1 - \frac{1}{2}) = -0.14$$

VARYING-VOLUME BATCH REACTOR

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

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

$$\frac{C_A}{C_{A0}} = \frac{1 - X_A}{1 + \varepsilon_A X_A}$$

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

The rate of reaction

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

$$-r_A = \frac{C_{A0}}{(1 + \varepsilon_A X_A)} \frac{dX_A}{dt} \quad \longrightarrow \quad -r_A = \frac{C_{A0}}{V\varepsilon_A} \cdot \frac{dV}{dt} = \frac{C_{A0}}{\varepsilon_A} \cdot \frac{d(\ln V)}{dt}$$

Differential Method of Analysis

Replace

$$\frac{dC_A}{dt} \quad \text{with} \quad \frac{C_{A0}}{V\varepsilon_A} \frac{dV}{dt}$$

or

$$\frac{C_{A0}}{\varepsilon_A} \frac{d(\ln V)}{dt}$$

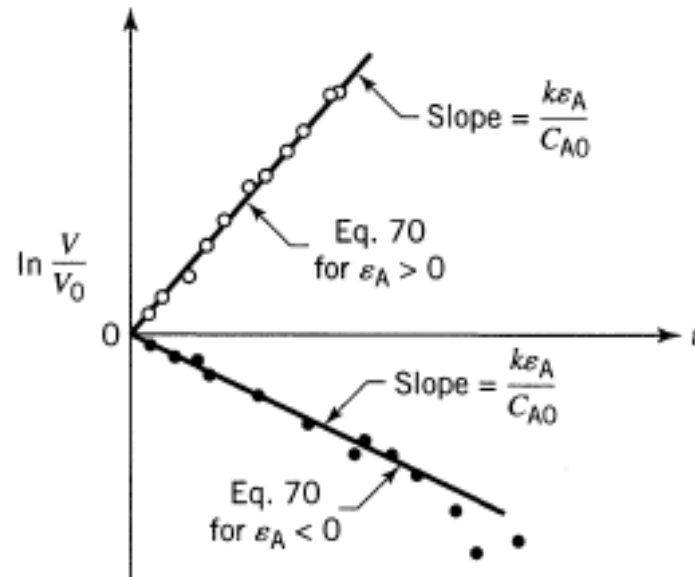
This means plot $(\ln V)$ vs. t and take slopes

Integral Method of Analysis

▶ Zero-Order Reactions

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

$$\frac{C_{A0}}{\varepsilon_A} \ln \frac{V}{V_0} = kt$$



- logarithm of the fractional change in volume versus time yields a straight line of slope $k\varepsilon_A/C_{A0}$

Integral Method of Analysis varying-volume reactor

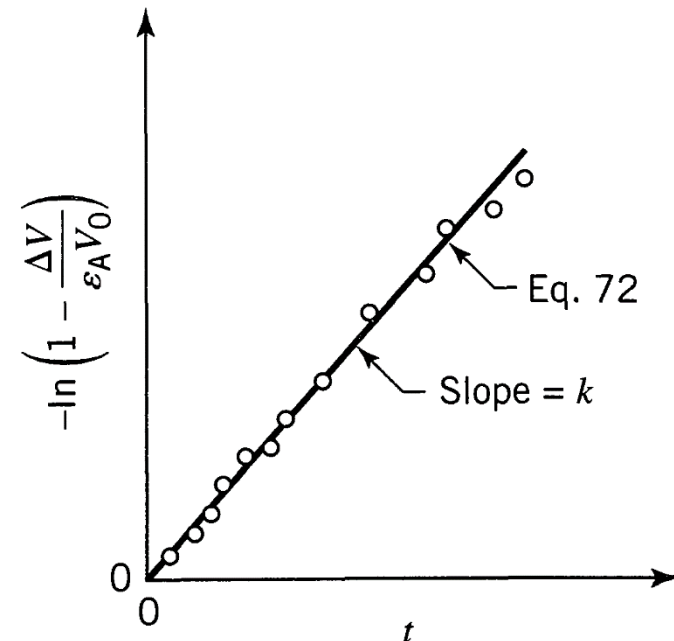
First-Order Reactions

- ▶ Replacing X_A by V after integrating gives

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

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

- ▶ Yields a straight line of slope k .



Integral Method of Analysis varying-volume reactor

▶ Second-Order Reactions

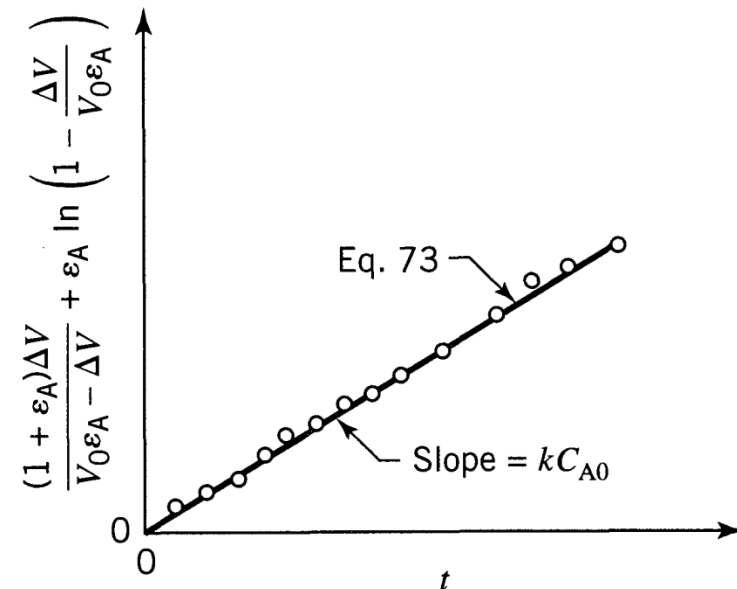


▶ Rate is given by

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

▶ Replacing X_A by V

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



CORRECT AND INCORRECT E VALUES

- ▶ Batch reactor using pressure units show exactly the same rate at two different temperatures

Evaluate the activation using these units

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

- ▶ **Using Pressure Units**

Change in temperature does not affect the rate of reaction

This means that $E = 0$

- ▶ **Transform p_A into C_A , then find E**

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

Change p_A to C_A .

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

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

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

At 500 K

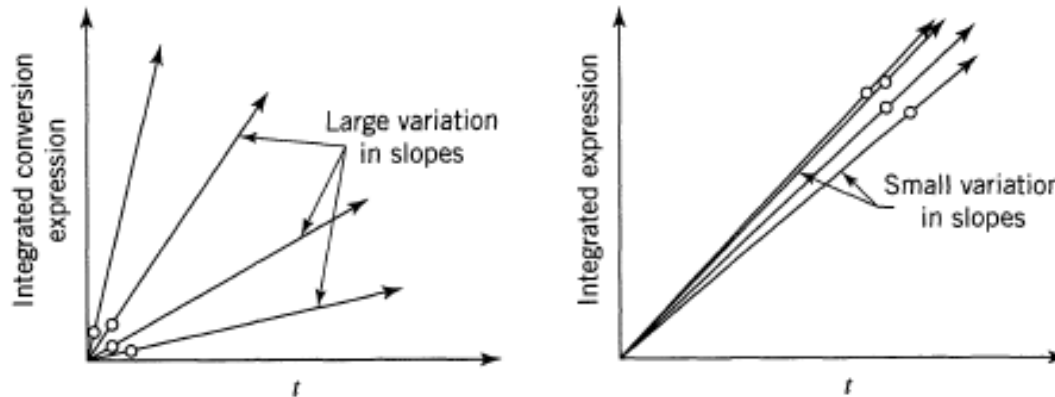
$$-r_{A2} = 0.0039 C_A^2 \quad \text{where} \quad k_2 = 0.0039 \frac{\text{m}^3}{\text{mol} \cdot \text{s}}$$

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

Calculation of k

k from Individual Data Points

- ▶ k values calculated for points near the origin (low conversion) will vary widely
- ▶ far from the origin will show little variation

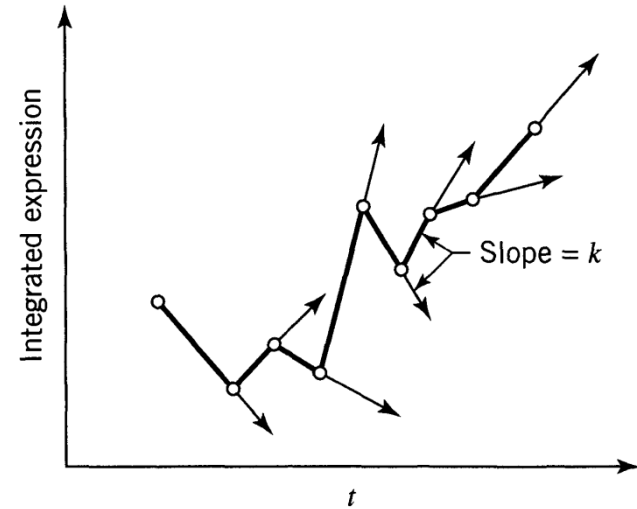


k from Pairs of Data Points.

- ▶ k values can be calculated from successive pairs of experimental points
- ▶ this procedure will give widely different k values from which k_{true} will be difficult to determine

Calculation of k

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



Graphical Method of Fitting Data

- ▶ This method the data are plotted and then examined for deviations from linearity
- ▶ When in doubt we should take more data
- ▶ probably the safest, soundest, and most reliable method for evaluating the fit of rate equations