

ENVE 301

Environmental Engineering Unit Operations

CHAPTER: 2

Reaction kinetics

Material balances

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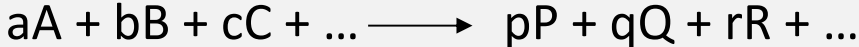
Department of Environmental Engineering

Istanbul, Turkey

Stoichiometry Reaction Kinetics

Material Balances

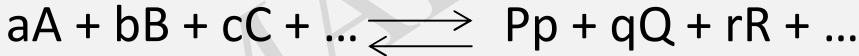
Stoichiometry:



- A, B, C \longrightarrow Reactant species
- P, Q, R \longrightarrow Product species
- a, b, c, p, q, r \longrightarrow Stoichiometric coefficients

Reactant stoichiometric coeff. = (-) sign \longrightarrow for irreversible reactions

Product stoichiometric coeff. = (+) sign



Signs of both reactants and products (+) \longrightarrow for reversible reactions

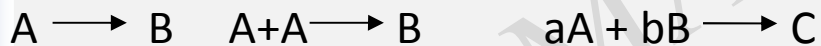
Classes of Reactions That Occur In Nature

Homogenous Reactions

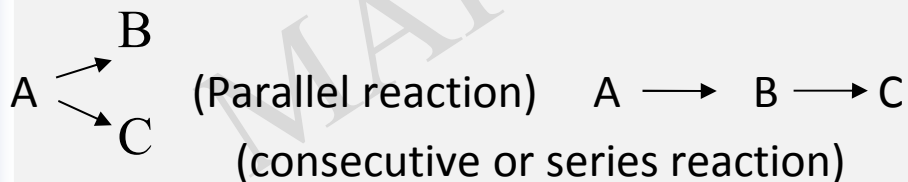
Reactions that occur within a single phase (i.e., liquid, solid or gas)

Reactants are distributed continuously (but not necessarily uniformly) throughout the fluid.

1a. Single irreversible reaction:



1b. Multiple irreversible reaction:



1c. Reversible reaction:



Heterogenous Reactions

Reactions that occur at surfaces between phases.

Examples:

Reactions on the surface of ion exchange resin

Reactions that require the presence of a solid phase catalyst

Rate and Order of Reaction

Rate of reaction \longrightarrow The rate at which reactant disappears or a product is formed in any given stoichiometric reaction.

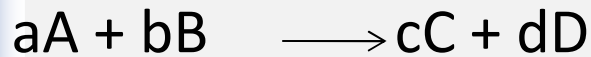
Rate of reaction (r) $\begin{cases} \longrightarrow \text{For homogeneous rxn} & r = \frac{\text{mol}}{\text{Lt}} \\ \longrightarrow \text{For heterogeneous rxn} & r = \frac{\text{mol}}{\text{m}^2\text{t}} \end{cases}$

Reactants \longrightarrow have negative (-) rates of rxn.

Products \longrightarrow have positive (+) rates of rxn.

@ constant temperature,

the rate of rxn. (disappearance of a reactant or formation of a product) is some function of the concentration of the reactants



order of the rxn. respect to individual reactants A and B
(0, 1, 2 may be fractional)

Overall rate of rxn = $r =$

$$k [A]^{\alpha} [B]^{\beta}$$

(mol/Lt)

molar concentrations of reactants (mol/ L)

reaction rate constant

Overall order of rxn = $\alpha + \beta$

Order of rxn with respect to reactant A = α

Order of rxn with respect to reactant B = β

Unit of k (reaction rate constant)

For 0 order rxn. \longrightarrow $k = \frac{\text{mol}}{\text{Lt}}$
 $r = k[A]^0 \longrightarrow r = k$

For 1st order rxn. \longrightarrow $k = \frac{\frac{\text{mol}}{\text{Lt}}}{\frac{\text{mol}}{\text{L}}} = \frac{1}{\text{t}}$
 $r = k [A]$

For 2nd order rxn. \longrightarrow $k = \frac{\frac{\text{mol}}{\text{Lt}}}{(\text{mol} / \text{L})^2} = \frac{\text{L}}{\text{mol.t}}$
 $r = k [A]^2$

Example :

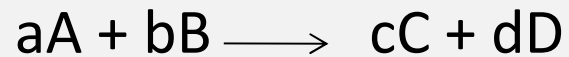
$$r = k [A]^2 [B]$$

Order of overall rxn. = 2 + 1 = 3

Order of rxn. with respect to reactant A = 2

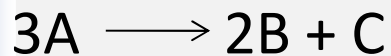
Order of rxn. with respect to reactant B = 1

Stoichiometric Relationships Between Rates of Reactions



$$\frac{r_a}{-a} = \frac{r_b}{-b} = \frac{r_c}{c} = \frac{r_d}{d}$$

Example :



If the overall rate of rxn is 1st order wrt to A , then $r = k [A]$

$$r = \frac{r_a}{-3} = \frac{r_b}{2} = \frac{r_c}{1}$$

$$r_a = \text{rxn. rate wrt to A} = -3 k [A]$$

$$r_b = \text{rxn. rate wrt to B} = 2 k [A]$$

$$r_c = \text{rxn. rate wrt to C} = k [A]$$

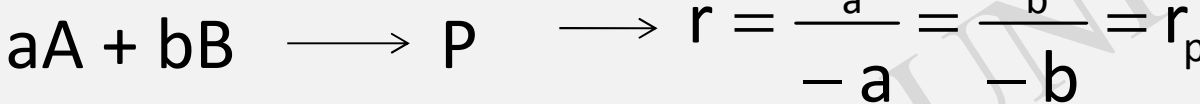
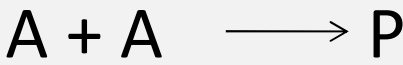
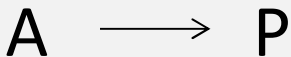
The one limits the overall rxn rate \longrightarrow slowest one \longrightarrow C

Types of Reactions and Reaction Rates

- irreversible rxns
- reversible rxns
- saturation rxns
- autocatalytic rxns

Irreversible Reactions

a)Single Irreversible Rxns:



Example:



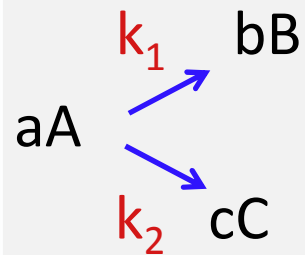
$$r = k [A]$$

$$r_a = -a k [A]$$

$$r_p = p k [A]$$

b) Multiple Irreversible Rxns:

b-1) Parallel rxns:



$$r_1 = \frac{r_a}{-a} = \frac{r_b}{b}$$

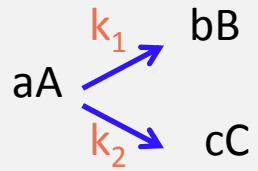
$$r_2 = \frac{r_a}{-a} = \frac{r_c}{c}$$

Overall rate of rxn: $r_1 + r_2 = -\frac{r_a}{a} = \frac{r_b}{b} + \frac{r_c}{c}$

Rate of rxn with respect to A = $r_a = -ar_1 - ar_2$

Rate of rxn with respect to B = $r_b = b r_1$

Rate of rxn with respect to C = $r_c = cr_2$



If both of the rates of rxn \rightarrow 1st order

$$r_1 = k_1[A]$$

$$r_2 = k_2[A]$$

$$r_A = -ak_1[A] - ak_2[A]$$

$$r_B = bk_1[A]$$

$$r_C = ck_2[A]$$

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b-2) Consecutive rxns

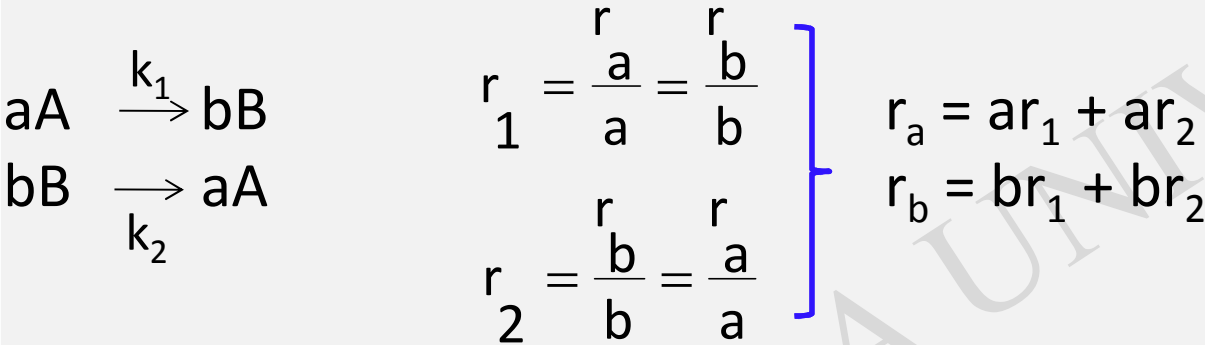
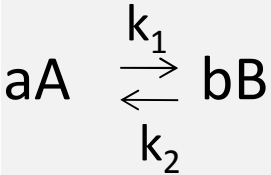


$aA \xrightarrow{k_1} bB$	}	$r_1 = \frac{r_a}{-a} = \frac{r_b}{b}$	}	$r_a = -a r_1$
$bB \xrightarrow{k_2} cC$		$r_2 = \frac{r_b}{-b} = \frac{r_c}{c}$		$r_b = b r_1 - b r_2$
		$r_c = c r_2$		

If both of the rates of rxn \rightarrow 1st order

$r_1 = k_1[A]$	$r_a = -ak_1[A]$
$r_2 = k_2[B]$	$r_b = bk_1[A] - bk_2[B]$
	$r_c = ck_2[B]$

Reversible Reactions



Note:

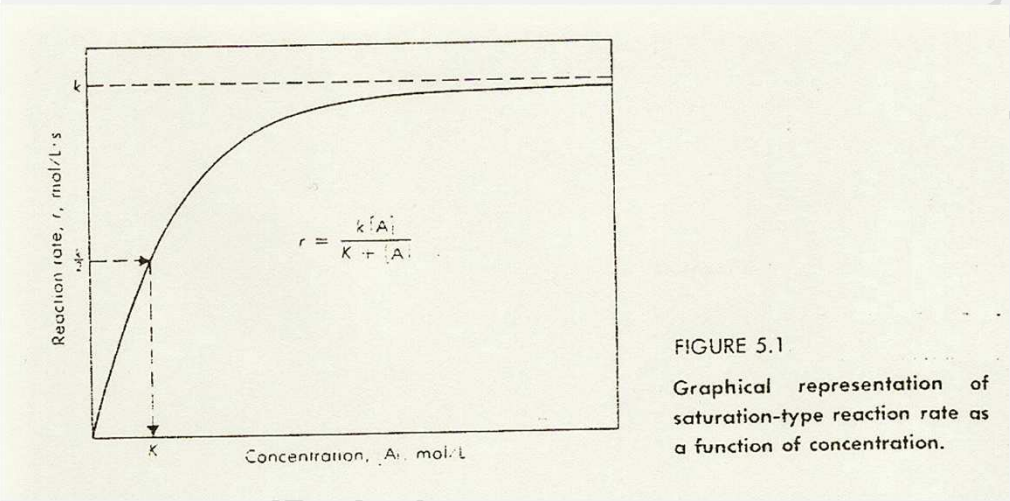
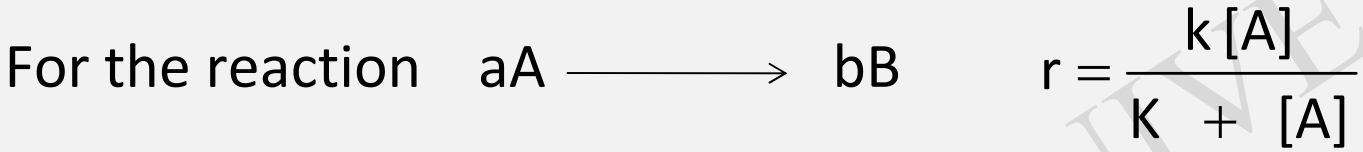
for reversible rxns → signs of stoichiometric coefficients
 (both reactants & products) are always positive (+)

If both of the rates of rxn → 1st order

$$\begin{array}{ll}
 r_1 = k_1[A] & r_a = ak_1[A] + ak_2[B] \\
 r_2 = k_2[B] & r_b = bk_1[A] + bk_2[B]
 \end{array}$$

Saturation Type Reactions

Saturation type reactions have a maximum rate that is a point at which the rate becomes independent of concentration A.



- r = rate of rxn, mol /Lt
- [A] = conc. of reactant, mol / L
- k = rxn rate constant, mol/ Lt
- K = half saturation constant, mol/ L

Fig.1.Graphical representation of Saturation –Type Reaction

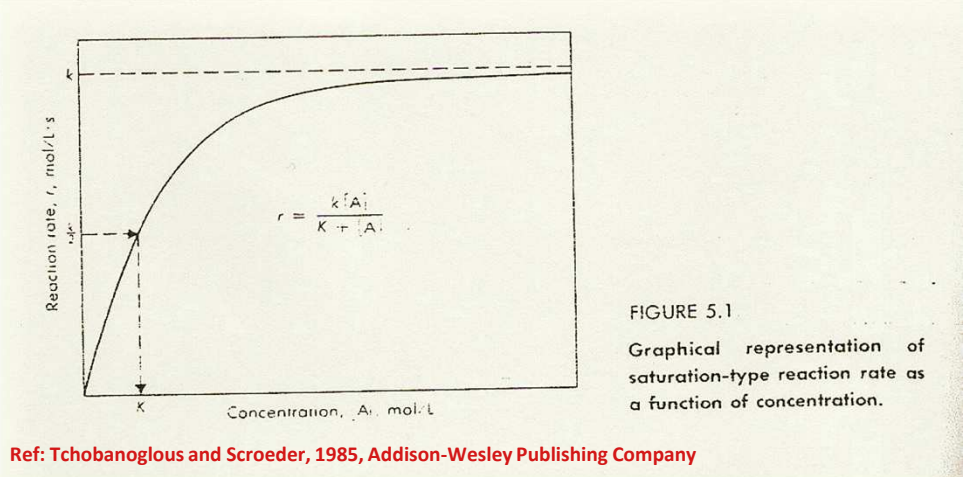
Ref: Tchobanoglous and Schroeder, 1985, Addison-Wesley Publishing Company

Saturation Type Reactions (continue)

$$r = \frac{k[A]}{K + [A]}$$

• When $K \ll [A] \rightarrow r = \frac{k[A]}{K + [A]} \approx k$ (zero order)

↓
Negligible



• When $K \gg [A] \rightarrow r = \frac{k[A]}{K + [A]} \approx \frac{k[A]}{K}$ (first order)

↓
Negligible

Saturation Type Reactions (continue)

For the reaction $A + B \xrightarrow{k} P$

$$r = \frac{k [A] [B]}{K + [A]} = k \left(\frac{[A]}{K_1 + [A]} \right) \left(\frac{[B]}{K_2 + [B]} \right)$$

Autocatalytic Reactions

Autocatalytic reaction rates are functions of the product concentration.

Example: Bacterial growth

(rate of increase in bacterial number is proportional to the number present)

Autocatalytic rxns can be → 1st order

2nd order

Saturation Type

Partially Autocatalytic (function of reactant & product)

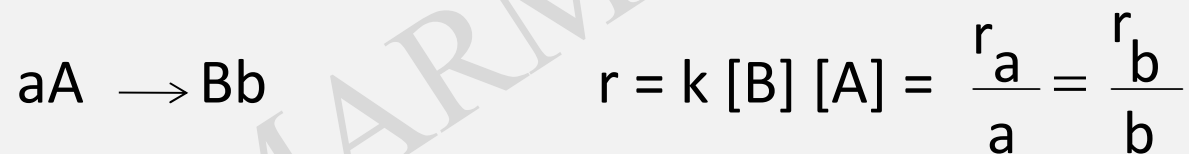
1st order Autocatalytic Rxn.



$$r_a = a k [B]$$

$$r_b = b k [B]$$

2nd order Autocatalytic Rxn.



$$r_a = a k [A][B]$$

$$r_b = b k [A] [B]$$

Effects of Temperature On Reaction Rate Coefficients

The temperature dependence of the rate constant is given by

Van't Hoff- Arrhenius relationship

$$\frac{k_2}{k_1} = \theta^{(T_2 - T_1)}$$

Analysis of Experimental Data

Methods to determine the order of a reaction from experimental data

- 1-) Method of Integration
 - 2-) Differential Method
 - 3-) Time Reaction Method
 - 4-) Isolation Method
- } Most commonly used

I. Method of Integration

- Integrated forms of the various rate expressions (0^{th} order, 1^{st} order etc)
- Plotting the experimental data functionally based on the integrated form of the rate expression

If straight line plot is obtained



It is assumed that the order of the rxn corresponds to the rxn. plotted

- Determine the reaction rate constant from the plotting

a) Irreversible Zero-Order Reaction $A \rightarrow P$

$$\rightarrow r_A = \frac{d[A]}{dt} = -k[A]^0 = -k$$

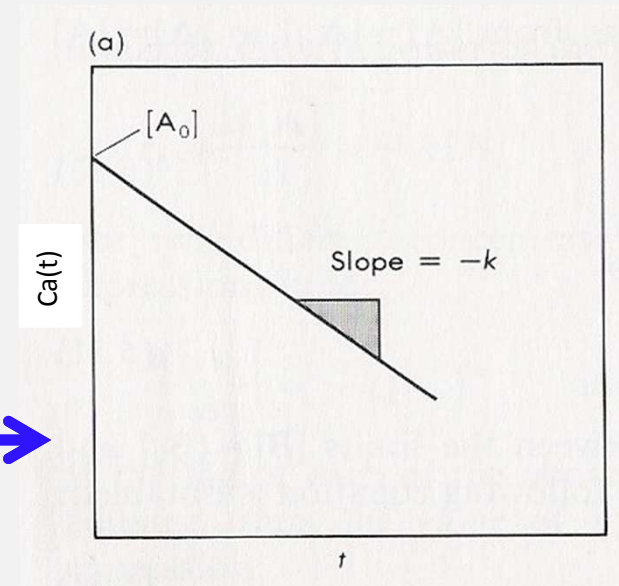
$$\rightarrow r_A = \frac{d[A]}{dt} = -k$$

$$\rightarrow \int_{C_a(0)}^{C_a(t)} d[A] = \int_0^t -k \cdot dt$$

$$\rightarrow C_{a(t)} = C_{a(0)} - kt$$

To determine reaction rate constant (k)

Plot $C_a(t)$ versus t \rightarrow



b) Irreversible First Order Reaction $A \longrightarrow P$

→ $r_A = \frac{d[A]}{dt} = -k[A]$

→ $\int_{C_{a(0)}}^{C_{a(t)}} \frac{d[A]}{[A]} = -k \int_0^t dt$

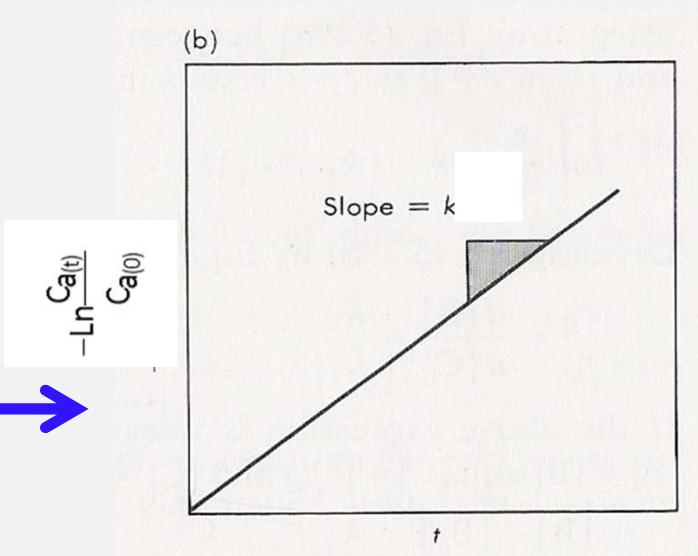
→ $\ln C_{a(t)} - \ln C_{a(0)} = -kt$

→ $\ln \frac{C_{a(t)}}{C_{a(0)}} = -kt$

→ $C_{a(t)} = C_{a(0)} e^{-kt}$

To determine reaction rate constant (k)

Plot $-\ln \frac{C_{a(t)}}{C_{a(0)}}$ versus **t** →



Half Life

Time required for the amount of substance to decrease to half its initial value

$$C_{a(t_{1/2})} = \frac{C_{a(0)}}{2}$$

For 1st order rxn :

$$\rightarrow C_{a(t)} = C_{a(0)} \cdot e^{-kt}$$

$$\rightarrow C_{a(t_{1/2})} = C_{a(0)} \cdot e^{-k \cdot t_{1/2}}$$

$$\rightarrow \frac{C_{a(0)}}{2} = C_{a(0)} \cdot e^{-k \cdot t_{1/2}}$$

$$\rightarrow \frac{1}{2} = e^{-k \cdot t_{1/2}}$$

$$\rightarrow \ln \frac{1}{2} = \ln \cdot e^{-k \cdot t_{1/2}} \rightarrow \ln \frac{1}{2} = -k \cdot t_{1/2} \rightarrow$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

c) Irreversible Second Order Reaction $A+A \longrightarrow P$

→ $r_A = \frac{d[A]}{dt} = -k[A]^2$

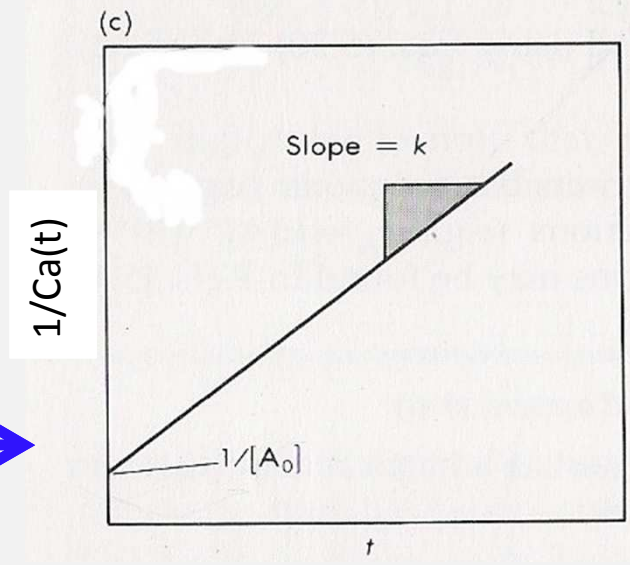
→ $\int_{C_a(0)}^{C_a(t)} \frac{d[A]}{[A]^2} = -k \int_0^t dt$

→ $-\frac{1}{[A]} \Big|_{C_a(0)}^{C_a(t)} = -kt$

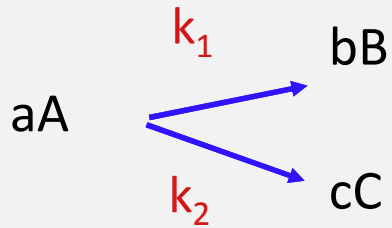
→ $-\frac{1}{C_a(t)} = kt + \left(\frac{1}{C_a(0)}\right)$

To determine reaction rate constant (k)

Plot $\frac{1}{C_a(t)}$ versus **t** →



d) Irreversible Parallel Reaction (1st order)



$$r_1 = k_1[A] = \frac{r_a}{-a} = \frac{r_b}{b}$$

$$r_2 = k_2[A] = \frac{r_a}{-a} = \frac{r_c}{c}$$

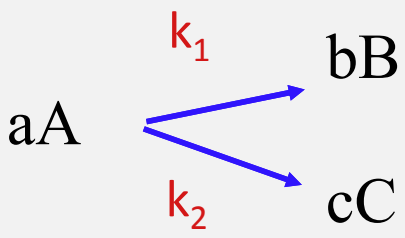
$$a, b, c = 1$$

$$r_a = \frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$r_b = \frac{d[B]}{dt} = k_1 \cdot [A]$$

$$r_c = \frac{d[C]}{dt} = k_2 [A]$$

d) Irreversible Parallel Reaction (1st order-continue)



$$\rightarrow r_a = \frac{d[A]}{dt} = -k_1[A] - k_2[A]$$

$$\rightarrow -\frac{d[A]}{dt} = (k_1 + k_2) \cdot [A]$$

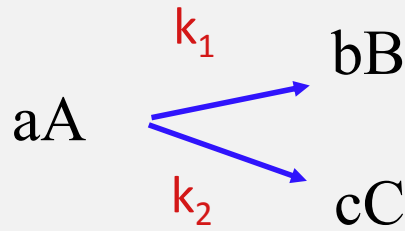
$$\rightarrow -\int_{C_{a(0)}}^{C_{a(t)}} \frac{d[A]}{[A]} = (k_1 + k_2) \cdot \int_0^t dt$$

$$\rightarrow -(\ln C_{a(t)} - \ln C_{a(0)}) = (k_1 + k_2) \cdot t$$

$$\rightarrow \ln C_{a(t)} - \ln C_{a(0)} = -(k_1 + k_2) \cdot t$$

$$\rightarrow \ln \frac{C_{a(t)}}{C_{a(0)}} = -(k_1 + k_2) \cdot t$$

$$\rightarrow \boxed{C_{a(t)} = C_{a(0)} \cdot e^{-(k_1 + k_2) \cdot t}}$$



$$\frac{r_b}{r_c} = \frac{d[B] / dt}{d[C] / dt} = \frac{k_1 \cdot [A]}{k_2 \cdot [A]}$$

$$\frac{r_b}{r_c} = \frac{d[B]}{d[C]} = \frac{k_1}{k_2} \longrightarrow k_2 \int_{C_{b(0)}}^{C_{b(t)}} d[B] = k_1 \int_{C_{c(0)}}^{C_{c(t)}} d[C]$$

$$k_2 \cdot [C_{b(t)} - C_{b(0)}] = k_1 \cdot [C_{c(t)} - C_{c(0)}]$$

$$k_1 = \frac{k_2 [C_{b(t)} - C_{b(0)}]}{[C_{c(t)} - C_{c(0)}]}$$

II. Differential Method

Assumption: The rate of rxn is proportional to the n^{th} power of concentration.

$$r_A = \frac{d[A]}{dt} = -k[A]^n$$

For 2 different concentrations at 2 different times;

$$t = t_1, \quad A = A_1 \quad \longrightarrow \quad \frac{d[A_1]}{dt} = -k[A_1]^n$$

$$t = t_2, \quad A = A_2 \quad \longrightarrow \quad \frac{d[A_2]}{dt} = -k[A_2]^n$$

If logarithm of each of the above equation is taken and the k values are equated:

$$\frac{d[A_1]}{dt} = -k[A_1]^n \rightarrow \log\left(\frac{-d[A_1]}{dt}\right) = \log k + n \log[A_1]$$

$$\frac{d[A_2]}{dt} = -k[A_2]^n \rightarrow \log\left(\frac{-d[A_2]}{dt}\right) = \log k + n \log[A_2]$$

$$n = \frac{\log(-d[A_1]/dt) - \log(-d[A_2]/dt)}{\log[A_1] - \log[A_2]}$$

Example:

Determine the order of the reaction and the reaction rate constant for the following data derived from an experiment carried out in a batch reactor.

Solve the problem

- a) Using Integration Method
- b) Using Differential Method

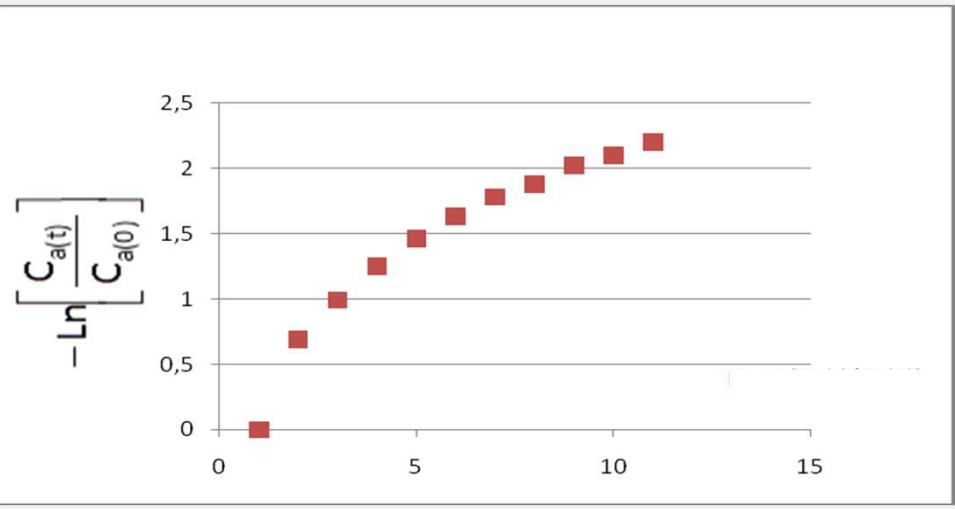
Time (min)	[A] mol/L
0	100
1	50
2	37
3	28.6
4	23.3
5	19.6
6	16.9
7	15.2
8	13.3
9	12.2
10	11.1

A) Integration Method

For 1st order rxn ; $C_{a(t)} = C_{a(0)} e^{-t}$ \longrightarrow $\ln \frac{C_{a(t)}}{C_{a(0)}} = -kt$

For 1st Order Reaction

Time (min.)	[A] mol/L	Time	-Ln [Ca(t)/Ca(0)]
0	100	0	0
1	50	1	0.69
2	37	2	0.99
3	28.6	3	1.25
4	23.3	4	1.46
5	19.6	5	1.63
6	16.9	6	1.78
7	15.2	7	1.88
8	13.3	8	2.02
9	12.2	9	2.10
10	11.1	10	2.20

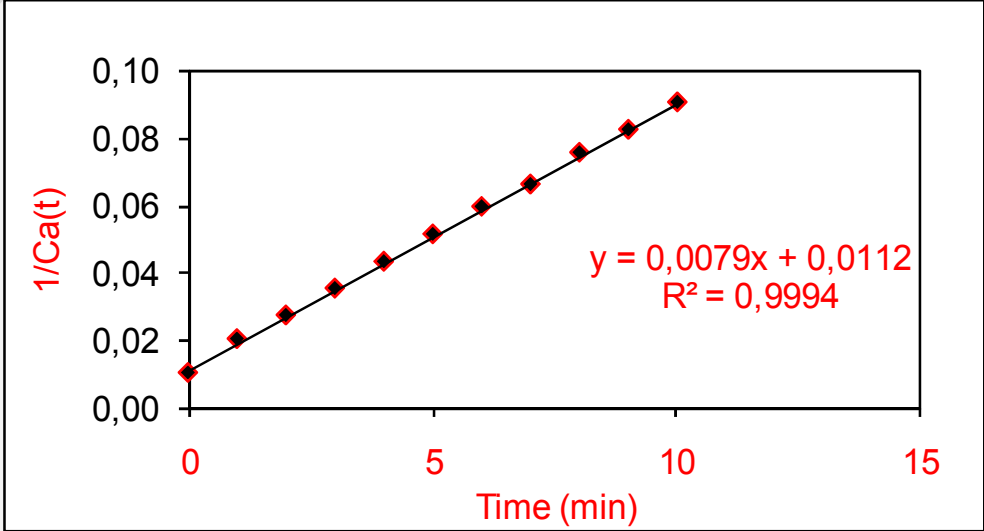


For 2nd order rxn; $\longrightarrow \frac{1}{C_{A(t)}} = kt + \frac{1}{C_{A(0)}}$

For 2nd Order Reaction

Time (min.)	[A] mol/L
0	100
1	50
2	37
3	28.6
4	23.3
5	19.6
6	16.9
7	15.2
8	13.3
9	12.2
10	11.1

Time	$\frac{1}{C_a(t)}$
0	0.01
1	0.02
2	0.03
3	0.03
4	0.04
5	0.05
6	0.06
7	0.07
8	0.08
9	0.08
10	0.09



Slope(k) 0,0079 L/mol.t

B) Differential Method

$$n = \frac{\log(-d[A_1]/dt) - \log(-d[A_2]/dt)}{\log[A_1] - \log[A_2]}$$

$$\frac{[A_{t+1}] - [A_{t-1}]}{dt}$$

Choose any data;

Time	[A], mol/L	d[A]/dt
2	37	$\frac{28.6 - 50}{3 - 1} = -10.7$
6	16.9	$\frac{15.2 - 19.6}{7 - 5} = -2.20$

$$n = \frac{\log(-(-10.7)) - \log(-(-2.20))}{\log[37] - \log[16.9]} = \frac{1.029 - 0.34}{0.34} = 2$$

To find k;

@ t=2min $\rightarrow \frac{d[A]}{dt} = -10.7$

[A]=37 mol/L

$$r_A = \frac{d[A]}{[dt]} = -kC^2$$

$$-10.7 = -k \cdot 37^2$$

$$\mathbf{k = 0.0078}$$

@ t=6min $\rightarrow \frac{d[A]}{dt} = -2.20$

[A]=16.9 mol/L

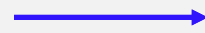
$$r_A = \frac{d[A]}{[dt]} = -kC^2$$

$$-2.20 = -k \cdot 16.9^2$$

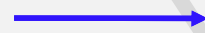
$$\mathbf{k = 0.0078}$$

Materials Balance

Materials Balance
(mass balance)



quantitative description of all materials that **enter, leave and accumulate** in a system with defined boundaries.

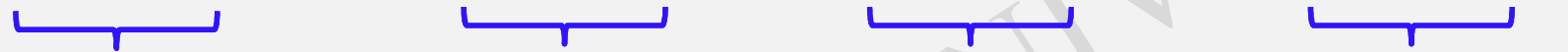


based on the law of conservation of mass (*mass is neither created nor destroyed*)

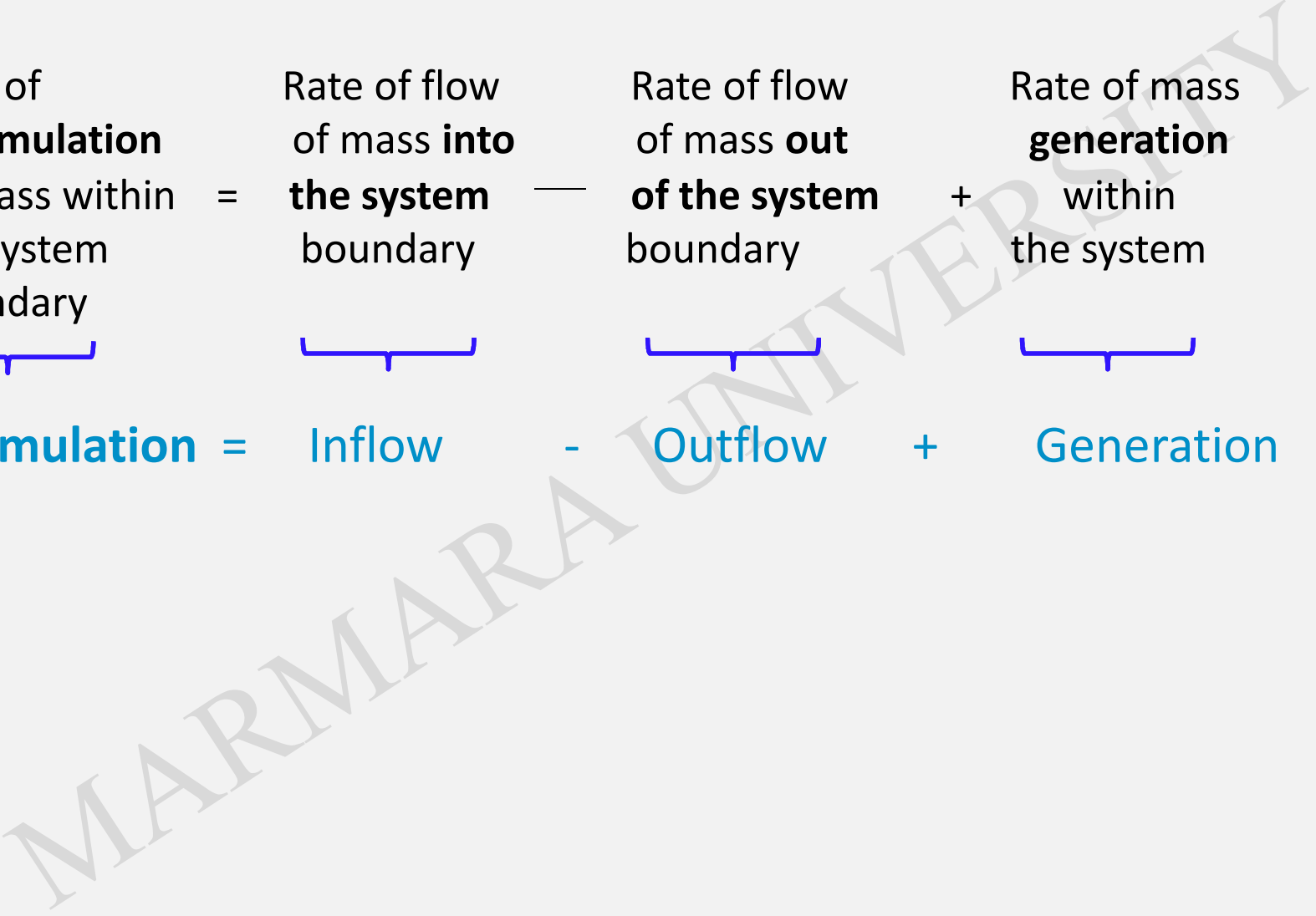


is developed on a chosen control volume.

Rate of **accumulation** of mass within the system boundary = Rate of flow of mass **into the system** boundary — Rate of flow of mass **out of the system** boundary + Rate of mass **generation** within the system



Accumulation = Inflow - Outflow + Generation



$$\text{Accumulation} = \text{Inflow} - \text{Outflow} + \text{Generation}$$

Generation term. can be “+” or “-“

[Most of the materials of interest disappear and therefore generation term is “-“ in most cases.]

Symbolic Representation:

$$\text{Accumulation} = \text{Inflow} - \text{Outflow} + \text{Generation}$$

$$\forall \frac{dC}{dt} = (QC_0) - QC \pm r \forall$$

\forall = volume of the reactor, m^3

$\frac{dc}{dt}$ = rate of change of reactant concentration within the reactor ($g / m^3 \text{ sec}$)

Q = flow into and out of the reactor (m^3 / sec)

C_0 = concentration of reactant in the influent (g / m^3)

C = concentration of reactant in the reactor and effluent (g / m^3)

r = rate of generation ($g / m^3 \text{ sec}$)

Operational states that must be considered in the application of materials balances:

→ **Steady state:**

There is no accumulation in the system.

All rates and concentration do not vary with time.

$$\frac{\partial C_A}{\partial t} = 0$$

Example: Pump discharging constant value of water within time.

→ **Unsteady (transient) State:**

Rate of accumulation is changing with time

$$\frac{\partial C_A}{\partial t} \neq 0$$

Example: Filling a reservoir pumping, of the contents of a tank.