CY 1020: Dynamics of Chemical Systems

Syllabus on Chemical Kinetics

Introduction to Chemical Kinetics: Order, molecularity, 1st-2nd-3rd –nth order derivations, half life, determining order of reaction, effect of Temperature on Reaction Rate, Collision and Transition State Theory

Books Recommended for Chemical Kinetics

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1. **Principles of Physical Chemistry: Puri, Sharma, Pathania**

2. **A Textbook Of Physical Chemistry (Vol. 5) by K L Kapoor**

3. **Physical Chemistry: P.W. Atkins**

Why do we want to study reaction kinetics?

To fully **understand or apply any chemical reaction**, we must know more than just the **identities of the reactants and the products**.

We must know: *if* the reaction will occur (is it **thermodynamically favorable**?)
• *how long it will take* to occur (is it **kinetically feasible**?) For a complete understanding, we should also know *how* it occurs.

When a chemist asks: "*how* does this reaction occur" they are asking for a **reaction mechanism**

and a model of chemical kinetics (collisions, effect of temperature…).

What is Chemical Kinetics?

The study of the RATE (Speed) of chemical reaction and the mechanism by which they occur.

Chemical reactions:

(i) Instantaneous reaction

$Ag^+ + Cl^- \rightarrow AgCl$ (ppt). t = 10^{-4}s, biological processes (photo synthesis),

(ii) Slow reaction: Corrosion of Iron, Formation of water

(iii) Reaction at which proceed at a measurable speed: Hydrolysis of cane sugar

What are the factors that affect the RATE of a chemical reaction?

➢ **The nature of the reactants and products**

➢**Concentration of Reactants**

- As the concentration of reactants increases, so does the likelihood that reactant molecules will collide. **Rate α collision frequency α concentration**

•**Temperature:** **Rate α collision frequency α temperature**

- At higher temperatures, reactant molecules have more kinetic energy, move faster, and collide more often and with greater energy.

•**Catalysts-** Not all the reactions have catalysts
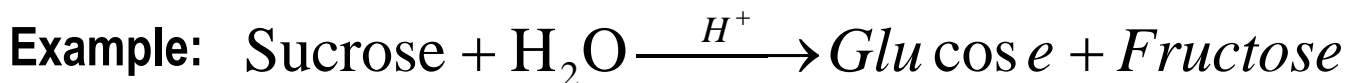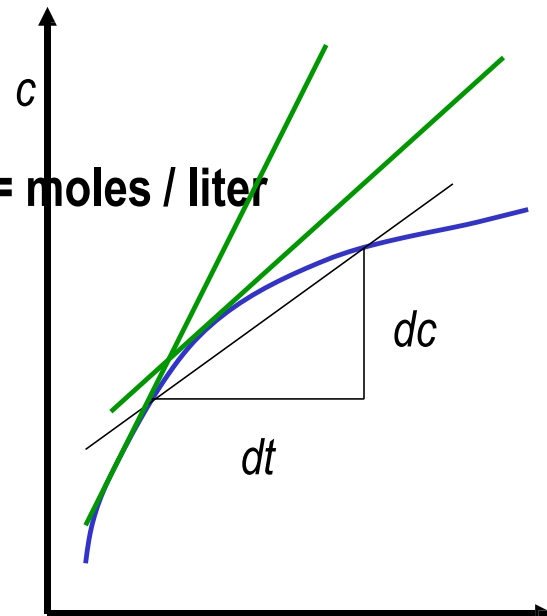
•Speed the reaction by changing mechanism.

Reaction Rate

❖ **Reaction Rate = either the increase in concentration of product per unit time or the decrease in concentration of reactant per unit time;**

$$Reaction\ rate = -\frac{dc}{dt}$$

→ Change in conc with time

Note: [c] = moles / liter

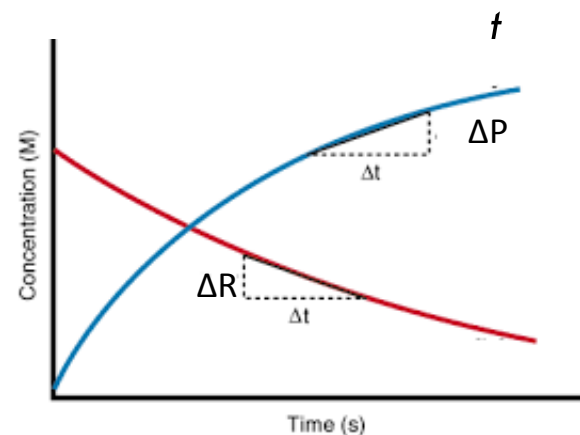**Example:**

$$Sucrose + H_2O \xrightarrow{H^+} Glu\cos e + Fructose$$

Rate = rate of formation of product.

$$Rate = +\frac{d[Glu\cos e]}{dt} = +\frac{d[Fructose]}{dt}$$

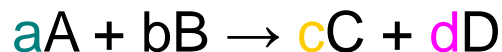**Or Rate = rate of disappearance of reactant.**

$$Rate = -\frac{d[Sucrose]}{dt}$$

- **In order to obtain rate, we need a way to measure concentration of any reactant or product with respect to time.**

In General

aA + bB → cC + dD

$$Rate \quad R = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{c}\frac{d[C]}{dt} = +\frac{1}{d}\frac{d[D]}{dt}$$

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Why do we define our rate in this way?

1. To remove ambiguity in the measurement of reaction rates.

2. Obtain a single rate for the entire equation, not just for the change in a single reactant or product.

Common unit of R : dc/dt= mol dm^{-3}s^{-1}

- Consider the simple reaction aA + bB ⟶ Product

$R = f\ ([A][B])$

And, **R** α [A]^a [B]^b

$$Rate \quad R = -\frac{1}{a}\frac{d[A]}{dt} \quad = -\frac{1}{b}\frac{d[B]}{dt} \quad = k[A]^a[B]^b$$

k is the proportionality constant, called as **rate constant** (independent of conc. but dependent on temp.).
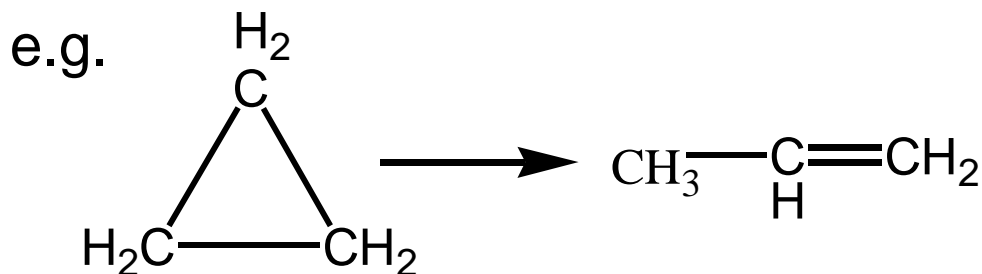
This equation is called the rate law

8

Molecularity

- Molecularity is the number of molecules coming together to react in an elementary step.

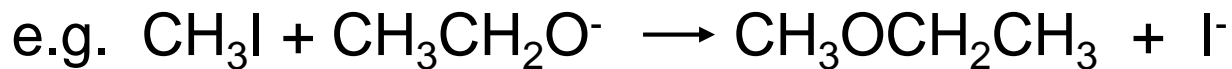- Elementary reactions are simple reactions (described by molecularity)

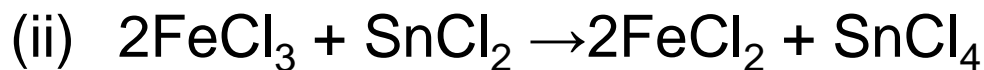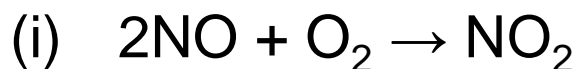(a) A $\longrightarrow$ Products   UNI-molecular reaction

e.g.

$$\underset{\underset{H_2C \rule{1.2cm}{0.4pt} CH_2}{}}{\overset{\overset{H_2}{C}}{\bigtriangleup}} \longrightarrow CH_3 \rule{0.6cm}{0.4pt} \underset{H}{\overset{}{C}} = CH_2$$

(b) A + A $\longrightarrow$ Products or A + B $\longrightarrow$ Products $\longrightarrow$ Bi-molecular reaction

e.g. $CH_3I + CH_3CH_2O^- \longrightarrow CH_3OCH_2CH_3 + I^-$

(c) 2A + B $\longrightarrow$ P or A + B + C $\longrightarrow$ P $\longrightarrow$ Termolecular reaction

(i) $2NO + O_2 \rightarrow NO_2$

(ii) $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

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9

Order of reaction

The order of a reaction is given by the number of atoms or molecules whose concentration alter during the chemical change.

Or

The order of reaction is given by the total # of molecules or atoms **whose concentration determine the velocity of the reaction**.

- Molecularity ≠ Order of reaction
- Reaction order is determined by experiment only
- Reaction order is an empirical quantity (values range -2 to 3).
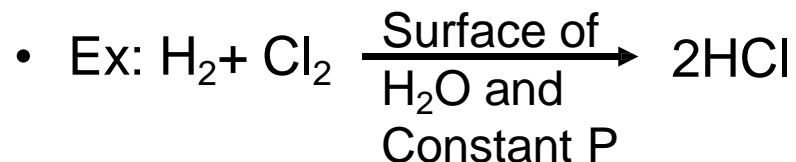- Can be fractional
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Can be negative, $R = k[A]^{-m}[B]^n = \dfrac{k[B]^n}{[A]^m}$ A is an inhibitor (decreases the rate)

Zero order reaction

- The concentrations of the reactants does not influence the rate of reaction. Because they do not change during the reaction.
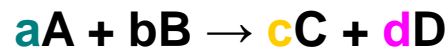
  - Ex: $H_2 + Cl_2 \xrightarrow[\text{Constant P}]{\text{Surface of H}_2\text{O and}} 2HCl$

  - Initial concentration is constant, amount of reactant species may change.

  - **Unit: moles/liter/s (mole dm^{-3} s^{-1})**

Order of the reaction

$$aA + bB \rightarrow cC + dD$$

➤The exponents a and b are the <u>order</u> of the reaction with respect to reactant A and the order of the reaction with respect to reactant B respectively.

➤The order of the reaction = a + b

➤If a = b =1, then the reaction is first-order in A and first-order in B, but in <u>overall it is</u> second-order, therefore: $R = k$ [A][B]

Hence, $k = \dfrac{R}{[A][B]} = \dfrac{mol\ dm^{-3}\ s^{-1}}{(mol\ dm^{-3})^2} = dm^3\ mol^{-1}\ s^{-1}$

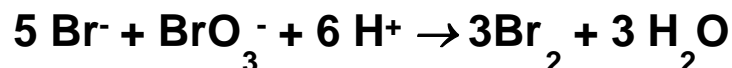**Units for rate constant for 2nd order reaction**

If first-order overall????

$$k = \dfrac{R}{[A]} = \dfrac{mol\ dm^{-3}\ s^{-1}}{mol\ dm^{-3}} = s^{-1}$$

Units for rate constant for 1st order reaction

For example,

$$5\ Br^- + BrO_3^- + 6\ H^+ \rightarrow 3Br_2 + 3\ H_2O$$

rate = k [Br⁻] [BrO₃⁻] [H⁺]

$rate = k\,[Br^-]\,[BrO_3^-]\,[H^+]$

The reaction is **1st order** w.r.t. all three reactants, **total order 3**.

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12

Broken order

In **broken-order reactions or fractional order** reactions, the order is a non-integer, which often indicates a chemical chain reaction or other complex reaction mechanism.

Ex.: The decomposition of phosgene (COCl$_2$) to carbon monoxide and chlorine has order 1 with respect to phosgene itself and order 0.5 with respect to chlorine: CoCl$_2$ → CO + Cl$_2$↑

$$r = -\frac{dx}{dt} = k[COCl_2][Cl_2]^{\frac{1}{2}}$$

Mixed order

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More complex rate laws have been described as being **mixed order** if they approximate to the laws for more than one order at different concentrations of the chemical species involved.

or example, a rate law of the form $r = k_1[A] + k_2[A]^2$
Ex- Pseudo unimolecular reaction

Another example is the **oxidation of an alcohol to a ketone** by a ruthenate (RuO$_4{}^{2-}$) and a hexacyanoferrate.

| Molecularity	Order of reaction
Common points. 1. Its value does not exceed 3. 2. Depends on the condition of the reaction	**Common points.** 1. Its value does not exceed 3. 2. Depends on the condition of the reaction
1. Number of species taking part in a single step reaction. 2. It's a whole number 3. Molecularity pertains single step reaction which involves several steps for its completion. 4. It can be obtained from a simple balanced equation	1. Order of reaction is the sum of exponents of molar concentrations of reactants involved in the rate equation of a chemical reaction. 2. It may be whole number, zero or a fraction. 3. Order of reaction pertains to reactions as a whole respective of the intermediate steps involved for its completion. 4. Can not be obtained from a simple balance chemical equation. Can be determined experimentally.

Mechanism, Rate – determining step and Intermediates

- Assembly of elementary steps (to give products(s)) is called the reaction *mechanism.*

e.g. $H_2 + Cl_2 \rightarrow 2HCl$. HCl is NOT formed in this one step, but proceeds by a series of elementary steps:

$$Cl_2 \rightarrow 2Cl^\bullet$$

$$Cl^\bullet + H_2 \rightarrow HCl + H^\bullet$$

$$Cl^\bullet + H^\bullet \rightarrow HCl$$
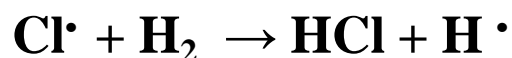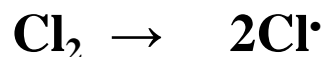
Mechanism – arrived at from theory and experiment

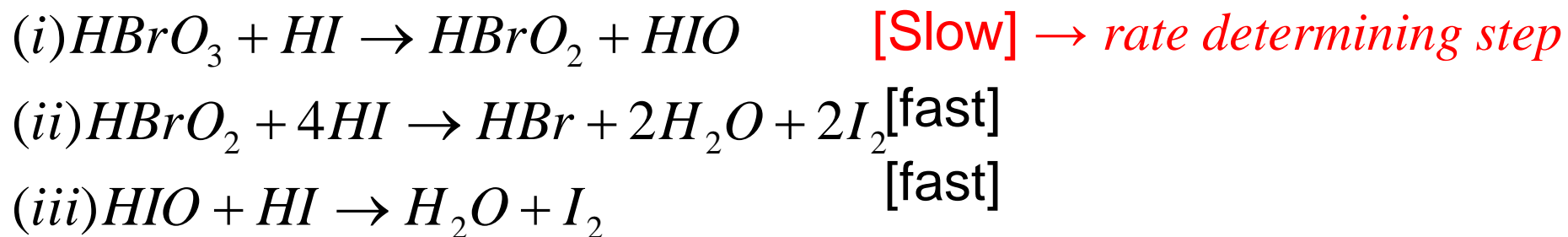$$H_2 + Cl_2 \rightarrow 2HCl \quad \text{Overall reaction}$$

- <u>Rate-determining step</u> (RDS) is the slowest elementary reaction in the mechanism and **controls the overall rate** of the reaction.

e.g.   Reduction of bromic acid to hydrobromic acid by hydroiodide

$$HBrO_3 + HI \rightarrow HBr + 3H_2O + 3I_2 \quad (1)$$

mechanism: rate determining step

$$(i) HBrO_3 + HI \rightarrow HBrO_2 + HIO \qquad \text{[Slow]} \rightarrow rate\ determining\ step$$

$$(ii) HBrO_2 + 4HI \rightarrow HBr + 2H_2O + 2I_2 \text{[fast]}$$

$$(iii) HIO + HI \rightarrow H_2O + I_2 \qquad \text{[fast]}$$

1st *step is slow→ the reaction is of* ***2nd*** *order. The molecularity of complex reaction (1) as such has no significance.*

The **elementary step** *involved in the complex reaction has its* **own molecularity.** *Molecularity of step (i), (ii) and (iii) are 2,5,2 respectively.*

17

The Study of Half-Life

- The half-life, $t_{1/2}$, of a reaction is the time taken for the concentration of a reactant to fall to half its initial value.

- It is a useful indication of the rate of a chemical reaction.

Kinetics of zero-order reaction

A reaction said to be zero-order when rate is independent of concentration of the reactants.
Alternatively: if the concentration of the reactants remains unaltered during the course of a reaction it is said to be zero order.

Rate of disappearance of reactant in a zero order process, we can write

Or Mathematically $R = \dfrac{-d[A]}{dt} = k_o \quad \Rightarrow -d[A] = k_o dt \quad ---(1)$

Where [A]= conc. of the product and k_o is the rate constant

Integrating eqn 1 w.r.t. *t* we get

$$-\int d[A] = k_o \int dt \quad \Rightarrow -[A] = k_o t + consant \quad ---(2)$$

Since [A]=[A]$_0$, when *t*=0 (beginning of reaction, no product has formed), the equation (2) can be written as

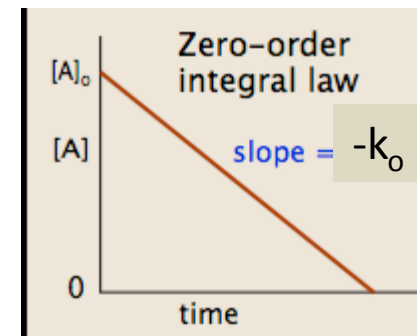$$\Rightarrow -[A]_o = k_o \times 0 + consant \quad \Rightarrow consant = -[A]_o \quad ---(3)$$

On substituting eqn. 3 in 2, we get

$$\Rightarrow -[A] = k_o t - [A]_o$$

$$\Rightarrow [A] = [A]_o - k_o t \quad ----(4)$$

Zero–order integral law

[A]$_o$

[A]

slope = -k$_o$

0

time

Which is in the form of y = mx + C
Plot of [A] vs. time should be linear with slope of –k and intercept [A]$_o$
Dimensions of k_o are conc./time, moles/liter/s

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Half life of Zero Order Reaction

In order to calculate half life of this reaction: At time t = 0, $[A] = [A]_0$, Then at time t = $t_{1/2}$ (half-life), $[A]_{t_{1/2}} = [A]_0/2$ **From eqn # 4:**

$$[A] = [A]_o - k_o t - - - -(4)$$

$$\Rightarrow [A]_o - \frac{[A]_o}{2} = k_o t_{1/2}$$
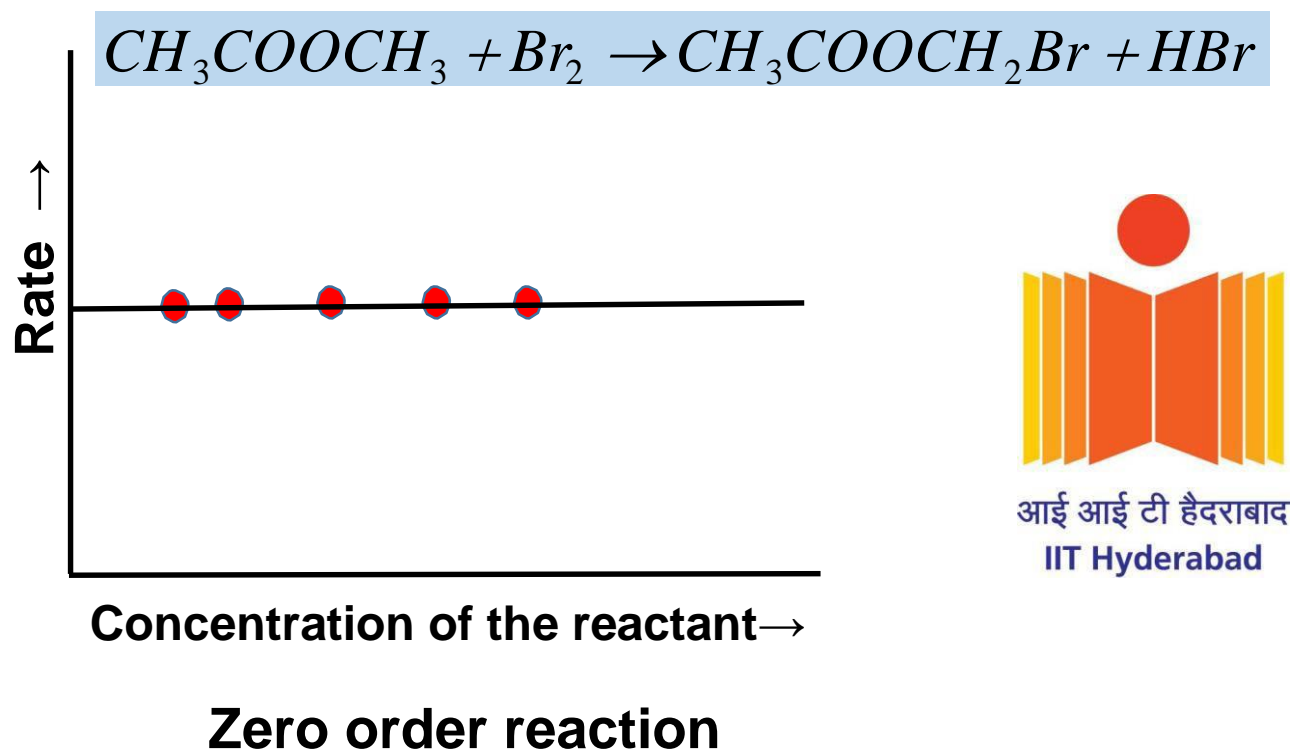
$$\Rightarrow \frac{[A]_o}{2} = k_o t_{1/2}$$

$$\Rightarrow t_{1/2} = \frac{[A]_o}{2k_o}$$

$$\boxed{\Rightarrow t_{1/2} \propto [A]_o}$$

In zero order reaction half life is proportional to initial concentration of the reactant.

Example of zero order reaction:

The reaction between Br_2 and acetone is zero order w.r.t Br_2 as this reaction proceeds at the same rate irrespective of the concentration of Br_2.

$$CH_3COOCH_3 + Br_2 \rightarrow CH_3COOCH_2Br + HBr$$

Zero order reaction

Integrated Rate Expressions: First-order reactions

A $\xrightarrow{k}$ P, then the rate of disappearance of A is:

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

Rearranging gives: $\dfrac{-d[A]}{[A]} = kdt$

At time t = 0, $[A] = [A]_0$, and when t = t, $[A] = [A]_t$

Integrating:

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k\int_0^t dt \quad \Rightarrow -[\ln[A]]_{[A]_0}^{[A]_t} = kt$$

Remember

$$\int \frac{1}{x} dx = \ln x$$

$$\Rightarrow -(\ln[A]_t - \ln[A]_0) = kt$$

$$\Rightarrow \ln[A]_t = \ln[A]_0) - kt \quad ---(5)$$

Integrated form of the
1st order rate expression

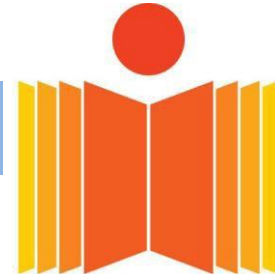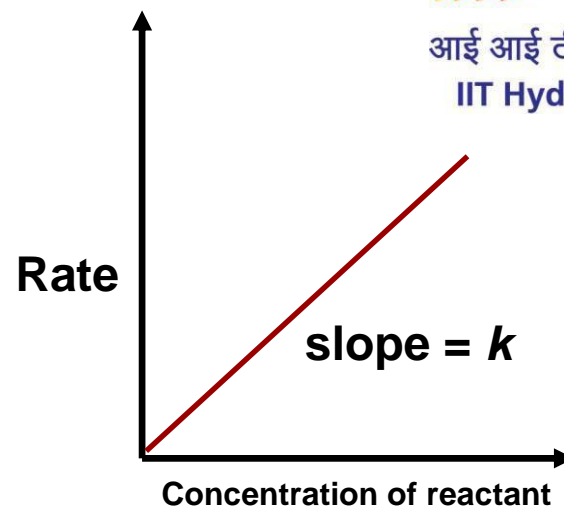आई आई टी हैदराबाद
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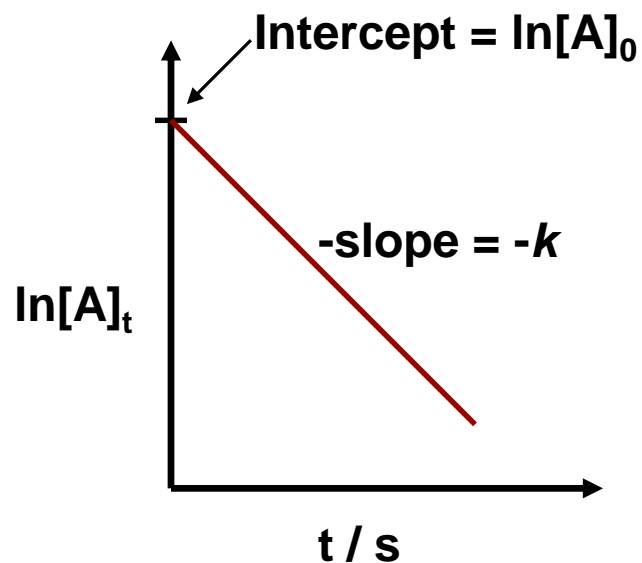
22

$$\ln[A]_t = \ln[A]_0) - kt \quad ---(5)$$

Intercept = ln[A]$_0$

-slope = -k

ln[A]$_t$

t / s

Rate

slope = k

Concentration of reactant

Recall $\ln[A]_t = \ln[A]_0) - kt \implies \ln\left(\dfrac{[A]_t}{[A]_0}\right) = -kt$

Antilog gives:

$$[A]_t = [A]_0 e^{-kt} \qquad ---(6)$$

Intercept = $[A]_0$

$[A]_t$

t / s
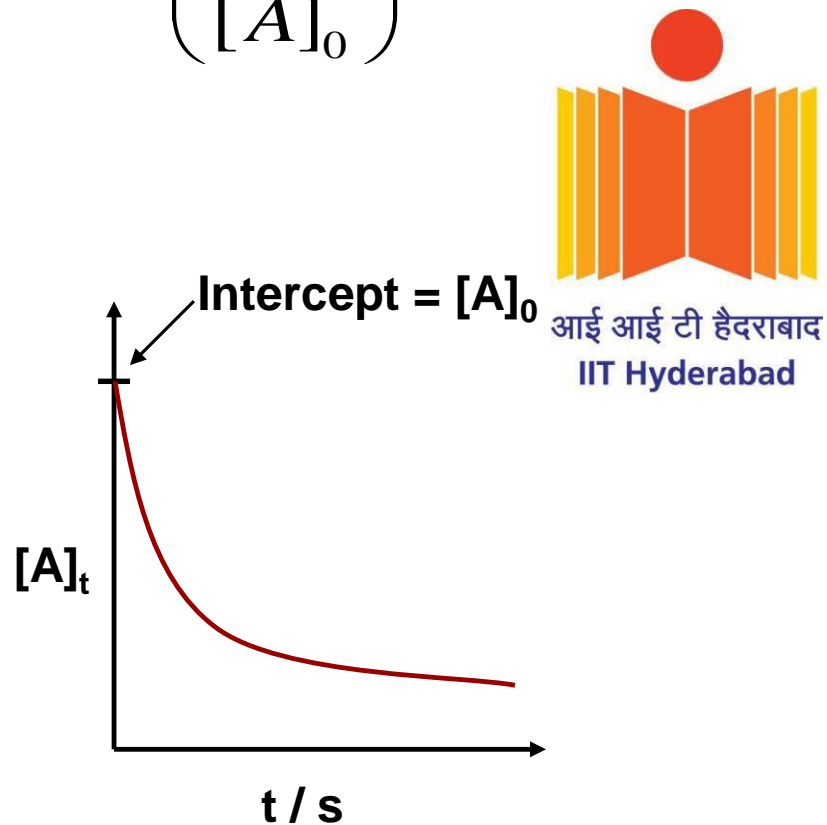
First-order reactions continuing…. Half-life

Remember that for a 1st order reaction $\ln[A]_t = \ln[A]_0) - kt --- (5)$

At time $t = 0$, $[A] = [A]_0$

Then at time $t = t_{1/2}$ (half-life), $[A]_{t_{1/2}} = [A]_0/2$

Substituting into above equation,

$$\ln\left(\frac{[A]_0}{2}\right) = \ln[A]_0 - kt_{1/2}$$

$$\Rightarrow \ln\left(\frac{[A]_0}{2}\right) - \ln[A]_0 = -kt_{1/2}$$

$$\Rightarrow \ln\left(\frac{[A]_0/2}{[A]_0}\right) = -kt_{1/2}$$

$$\Rightarrow \ln\left(\frac{1}{2}\right) = -kt_{1/2}$$

$$\Rightarrow \ln 1 - \ln 2 = -kt_{1/2} \quad (NB : \ln 1 = 0)$$

$$\Rightarrow \ln 2 = kt_{1/2}$$

2

Hence,

$$t_{1/2} = \frac{\ln 2}{k} \qquad \text{or} \qquad t_{1/2} = \frac{0.693}{k} \qquad ---(6)$$

What is/are the main point(s) to note from this expression??

➢For a 1st order reaction, the half-life is independent of reactant concentration but dependent on *k.*

➢**The half-life is constant for a 1st order reaction**

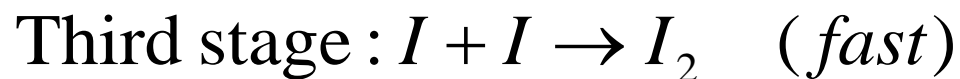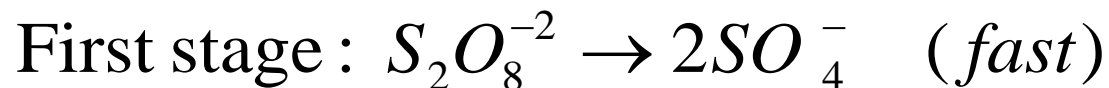**Therefore, larger initial concentrations imply shorter half-lives (so faster the reaction).**

Recall: $[A]_t = [A]_0 e^{-kt}$

Concentration $[A]_0$

$t_{1/2}$

$[A]_0/2$

$t_{1/2}$

$[A]_0/4$

$t_{1/2}$

$[A]_0/8$

Time

26
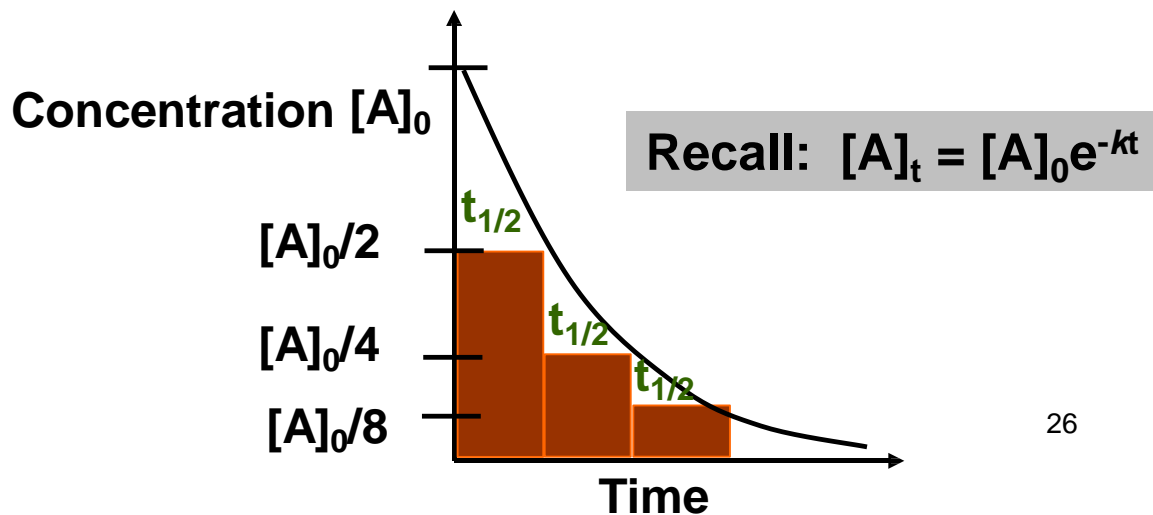
Second order reactions

1. $K_2S_2O_8 + 2KI \rightarrow 2K_2SO_4 + I_2$ the reaction looks like of 3rd order
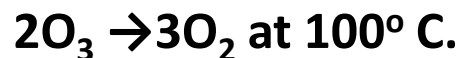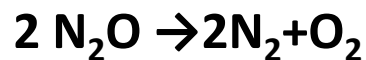**But let us consider the mechanism of this reaction:**
(fast)

$$First\ stage:\ S_2O_8^{-2} \rightarrow 2SO_4^{-} \quad (fast)$$

$$Second\ stage:\ SO_4^{-} + I^{-} \rightarrow I + SO_4^{-2} \quad (slow)$$

$$Third\ stage:\ I + I \rightarrow I_2 \quad (fast)$$

1st and 3rd stage are fast and 2nd stage is slow, is 2nd order.

$$The\ experimental\ rate\ of\ reaction\ \frac{dx}{dt} = k_2[I^{-}][SO_4^{-}]$$

2. Decomposition of ozone into oxygen:
$2O_3 \rightarrow 3O_2$ at 100° C.

3. Thermal decomposition of N_2O:
$2\ N_2O \rightarrow 2N_2 + O_2$

Second-order reactions continuing

Two possible cases:

Case I : A + A $\rightarrow$ P (Products)

   or   2A $\rightarrow$ P

Case II : A + B $\rightarrow$ P

$$r = -\frac{1}{2}\frac{d[A]}{dt} = k_2[A]^2$$

Rearranging gives: $-\dfrac{d[A]}{[A]^2} = 2k_2 dt \quad ---(7)$

At time t = 0, [A] = [A]$_0$
And when t = t, [A] = [A]$_t$

27

Integrating equation (7)

$$-\frac{d[A]}{[A]^2} = k_2 dt \quad ----(7)$$

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = k_2 \int_0^t dt$$

$$\Rightarrow -\left[-\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k_2 t$$

$$\int \frac{1}{x^2} dx = \int x^{-2} dx = \frac{x^{-2+1}}{-2+1} = -x^{-1} = -\frac{1}{x}$$

$$\Rightarrow \left[\frac{1}{[A]}\right]_{[A]_0}^{[A]_t} = k_2 t$$

$$\Rightarrow \frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t \quad ----(8)$$

Integrated form of the
2nd order rate expression

$$y = c + mx$$

28

Second-order reactions continuing

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t \quad ---(8)$$

y   =   c   +   m*x*

slope = *k2*

(1/[A]$_t$) / dm^3 mol^{-1}

Intercept = 1/[A]$_0$

t / s

Half-life: Second-order reaction

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + k_2 t \quad ---(8)$$

At time t = 0, [A] = [A]$_0$
And when t = t$_{½}$, [A]$_{t½}$ = [A]$_0$/2

$$\Rightarrow \frac{1}{\dfrac{[A]_0}{2}} = \frac{1}{[A]_0} + k_2 t_{1/2}$$

$$\Rightarrow \frac{2}{[A]_0} = \frac{1}{[A]_0} + k_2 t_{1/2}$$

$$\Rightarrow \frac{1}{[A]_0} = k_2 t_{1/2}$$

$$\therefore t_{1/2} = \frac{1}{k_2 [A]_0} \quad ---(9)$$

So $t_{1/2}$ for 2nd order reactions
depends on initial concentration

Comparison of Zero Order, 1ˢᵗ Order and 2ⁿᵈ Order Reactions

	Zero Order	First Order	Second Order
Rate law	rate $= k$	rate $= k[A]$	rate $= k[A]^2$
Units for k	mol/L·s	1/s	L/mol·s
Half-life	$\dfrac{[A]_0}{2k}$	$\dfrac{\ln 2}{k}$	$\dfrac{1}{k[A]_0}$
Integrated rate law in straight-line form	$[A]_t = -kt + [A]_0$	$\ln [A]_t = -kt + \ln [A]_0$	$1/[A]_t = kt + 1/[A]_0$
Plot for straight line	$[A]_t$ vs. t	$\ln [A]_t$ vs. t	$1/[A]_t$ vs. t
Slope, y intercept	$-k, [A]_0$	$-k, \ln [A]_0$	$k, 1/[A]_0$

31

Partial fractions are used to evaluate the rate constants when the reactants are different.

To use the method of partial fractions to evaluate an integral of the form

$$\int \frac{1}{(a-x)(b-x)} \, dx, \text{ where } a \text{ and } b \text{ are}$$

constants, we write

$$\frac{1}{(a-x)(b-x)} = \frac{1}{b-a}\left(\frac{1}{a-x} - \frac{1}{b-x} \right)$$

and integrate the expression on the right. It follows that

$$\int \frac{dx}{(a-x)(b-x)} = \frac{1}{b-a}\left[\int \frac{dx}{a-x} - \int \frac{dx}{b-x} \right]$$

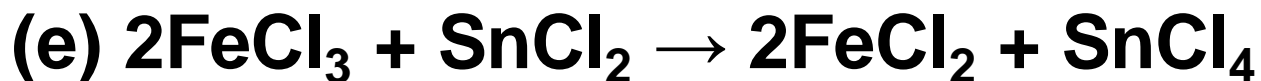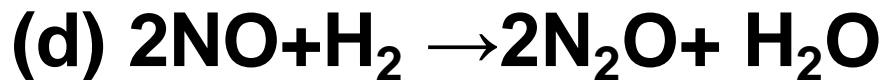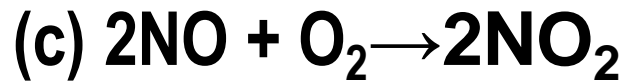$$-\frac{1}{b-a}\left(\ln\frac{1}{a-x} - \ln\frac{1}{b-x} \right) + \text{constant}$$

32

Third order reactions: Depends on 3 concentration terms

Examples of 3rd order of reaction

(a) $2NO + Cl_2 \rightarrow 2NOCl$

(b) $2NO + Br_2 \rightarrow 2NOBr$

(c) $2NO + O_2 \rightarrow 2NO_2$

(d) $2NO + H_2 \rightarrow 2N_2O + H_2O$

(e) $2FeCl_3 + SnCl_2 \rightarrow 2FeCl_2 + SnCl_4$

Third order reactions: Depends on 3 concentration terms

Case I: $3A \rightarrow P$ (Products)

Case II: $2A + B \rightarrow P$

Case III: $A+B+C \rightarrow P$

Let's consider for the Case -1

$3A \rightarrow P$ (Products): $\qquad Rate \quad R = -\dfrac{d[A]}{dt} = k_3[A]^3 \quad ---(10)$

Rearranging gives: $\qquad -\dfrac{d[A]}{[A]^3} = k_3 dt \quad ---(10A)$

At time t = 0, [A] = $[A]_0$, and when t = t, [A] = $[A]_t$.

Integrating:

$$k_3 = \dfrac{1}{2t}\left[\dfrac{[A]_0^2 - [A]_t^2}{[A]_o^2[A]_t^2}\right] \quad ---(11)$$

This is called as kinetic equation of 3 order reaction

Half life: At time t = 0, $[A] = [A]_0$
And when $t = t_{1/2}$, $[A]_{t_{1/2}} = [A]_0/2$

$$\Rightarrow t_{1/2} = \frac{3}{2k_3[A]_o^2}$$

$$\Rightarrow t_{1/2} \propto \frac{1}{[A]_o^2}$$

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So $t_{1/2}$ for 3rd order reactions inversely proportional to square of initial concentration

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Kinetic of nth order reaction

- nA $\rightarrow$ P (Products)

$$Rate \quad R = -\frac{d[A]^n}{dt} = k_n[A]^n \quad ---(12)$$

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

$$\int x^n dx = \frac{x^{n+1}}{n+1}; n \neq 1$$

Solving

$$\Rightarrow k_n = \frac{1}{(n-1)t}\left[\frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}\right] \quad ---(15)$$

13

Half life for the nth order Reaction

At time t = 0, [A] =[A]$_0$ And when t = t$_{1/2}$, [A]$_{t1/2}$ =[A$_0$/2]

Solving

$$\Rightarrow t_{1/2} = \frac{2^{n-1} - 1}{k_n(n-1)[A]_o^{n-1}}$$

$$\Rightarrow t_{1/2} \propto \frac{1}{[A]_o^{n-1}}$$

Summary of the Kinetics of Zero-Order, First-Order Second-Order ……..Reactions

Order	Rate Law	Concentration-Time Equation	Half-Life
0	rate = k	$[A] = [A]_0 - kt$	$t_{1/2} = \dfrac{[A]_0}{2k}$
1	rate = $k\,[A]$	$\ln[A] = \ln[A]_0 - kt$	$t_{1/2} = \dfrac{0.693}{k}$
2	rate = $k\,[A]^2$	$\dfrac{1}{[A]} = \dfrac{1}{[A]_0} + kt$	$t_{1/2} = \dfrac{1}{2k[A]_0}$
3	rate = $k\,[A]^3$	$k_3 = \dfrac{1}{2t}\left[\dfrac{[A]_t^2 - [A]_o^2}{[A]_o^2 [A]_t^2}\right]$	$t_{1/2} = \dfrac{3}{2k_3[A]_o^2}$
n	rate = $k\,[A]^n$	$k_n = \dfrac{1}{(n-1)t}\left[\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}}\right]$	$t_{1/2} = \dfrac{2^{n-1} - 1}{k_n(n-1)[A]_o^{n-1}}$

What can we conclude about RATE LAWS

versus

INTEGRATED RATE EXPRESSSIONS??

➢ **a rate law can tell us the rate of a reaction,**

once the composition of the reaction mixture is known.

➢**An integrated rate expression can give us the concentration of a** species as a function of time. **(Ex:** $\ln[A] = \ln[A]_0 - kt$**)**

➢ It can also give us the **rate constant** and **order of the reaction** by plotting the appropriate graph.

Determining Order of Reaction

Rate laws have to be determined *experimentally*.

Techniques for monitoring the progress of a reaction include:

➢ **Absorption measurements (using a spectrophotometer)**

➢ **Conductivity (reaction between ions in solution)**

➢ **Polarimetry (if reactants/products are optically active, e.g. glucose)**

➢ **employing titration technique**

Recall
A + B→ P, $r = k[A]^m[B]^n$

1. Half life method:

$$t_{\frac{1}{2}} \propto \frac{1}{[A]_o^{n-1}}$$

Suppose we start with two independent reactions with initial concentration $[A_1]_0$ and $[A_2]_0$ and let the corresponding times be t_1 and t_2 respectively. Then

$$t_1 \propto \frac{1}{[A_1]_o^{n-1}} \quad and \quad t_2 \propto \frac{1}{[A_2]_o^{n-1}}$$

$t_{1/2}$
$\dfrac{[A]_0}{2k} \rightarrow Zero\ order$
$\dfrac{0.693}{k} \rightarrow 1st\ order$
$\dfrac{1}{k_2[A]_0} \rightarrow Second\ Order$
$\dfrac{2^{n-1}-1}{k_n(n-1)[A]_o^{n-1}} \rightarrow nth\ order$

$$\Rightarrow \frac{t_1}{t_2} = \frac{[A_2]_o^{n-1}}{[A_1]_o^{n-1}} \qquad \Rightarrow \log \frac{t_1}{t_2} = (n-1)\log \frac{[A_2]_o}{[A_1]_o}$$

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$$\Rightarrow \log \frac{t_1}{t_2} = (n-1)\log \frac{[A_2]_o}{[A_1]_o}$$

$$\Rightarrow (n-1) = \frac{\log \dfrac{t_1}{t_2}}{\log \dfrac{[A_2]_o}{[A_1]_o}}$$

$$\Rightarrow n = 1 + \frac{\log \dfrac{t_1}{t_2}}{\log \dfrac{[A_2]_o}{[A_1]_o}}$$

From this order of reaction n can be calculated.

In case of gaseous reactions the initial pressure (P) can be taken instead of initial concentration [A]$_0$. So

$$\Rightarrow n = 1 + \frac{\log \dfrac{t_1}{t_2}}{\log \dfrac{P_2}{P_1}}$$

(2) Isolation Method:

This technique simplifies the rate law by taking the **concentrations of all the reactants except one**, in large excess and the order of the reaction is determined by any method w.r.t. that the reactant which is not taken excess.

mA+ nB →Product

Using as example: $r = k[A]_t^m \; [B]_t^n$

Make [B] in excess, so [B]>>[A].

Hence, by the end of the reaction [B] would not have changed that much, although all of A has been used up

And we can say, $[B] \cong [B]_0$

dependent on A, and we can say

$$\boxed{r = k'[A]_t^m}, \text{ where } k' = k[B]_0^n$$

Created a 'false' first-order (imitating first-order) PSEUDO-FIRST-ORDER,

where k' is the pseudo-first-order rate constant

Ex: Hydrolysis of an ester

RCOOR'+$H_2O \leftrightarrow$ RCOOH + R'OH

Logging both sides gives:

$$\log r = \log k' + m \log [A]_t$$

$$y \;\; = \;\; c \;\;\;\; + m \;\;\; x$$

A plot of log r vs. log $[A]_t$ gives a straight line with slope = m, and intercept log k'

If m = 1, the reaction is said to be pseudo-first-order

With the roles of A and B reversed, **n** can be found in a similar manner

k can then be evaluated using any data set along with the known values of **m** and **n**

The advantage of this method is that the mode of action of each components can be determined separately.

For a reaction: $n_1A + n_2B + n_3C \rightarrow$ Product
The order of reaction = $n_1 + n_2 + n_3$

(3) Initial Rate Method:

- **conjunction with the isolation method**

In this method, the rate of **initial rate of reaction is measured when the concentration of one of the reactants is varied** and that of the others are kept constant.

The initial reaction rates are determined by measuring the slopes of concentration time curves at time t=0.

Initial rate

$[A]_t$

t / s

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21
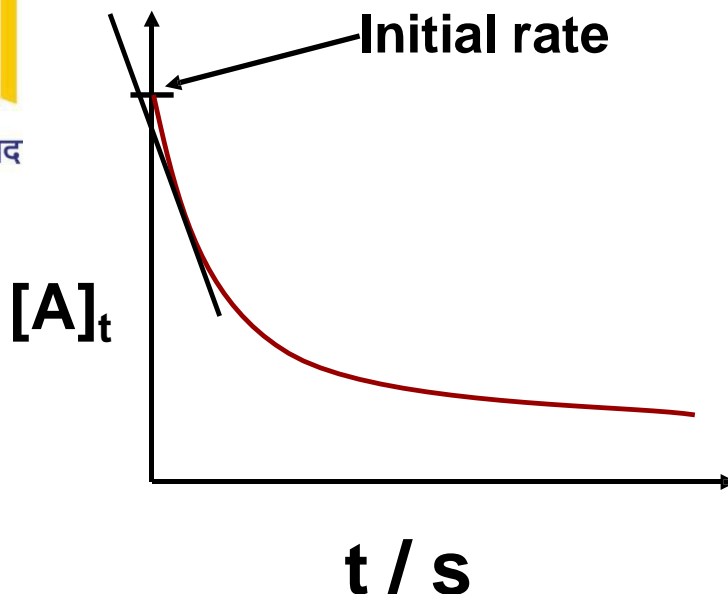
Recall aA + bB→P; *Rate $R_0 = k[A]_0^a[B]_0^b$*

Taking 'logs $\log R_0 = \underbrace{\log k + a \log [A]_0}_{c} + b \underbrace{\log[B]_0}_{x}$

$\underset{y}{} \qquad \underset{c}{} \qquad \underset{m}{} \quad \underset{x}{}$

** Keep $[A]_0$ constant for varying values of $[B]_0$ to find b

Log R_o

slope = b

Intercept = log k + a log$[A]_0$

log$[B]_0$

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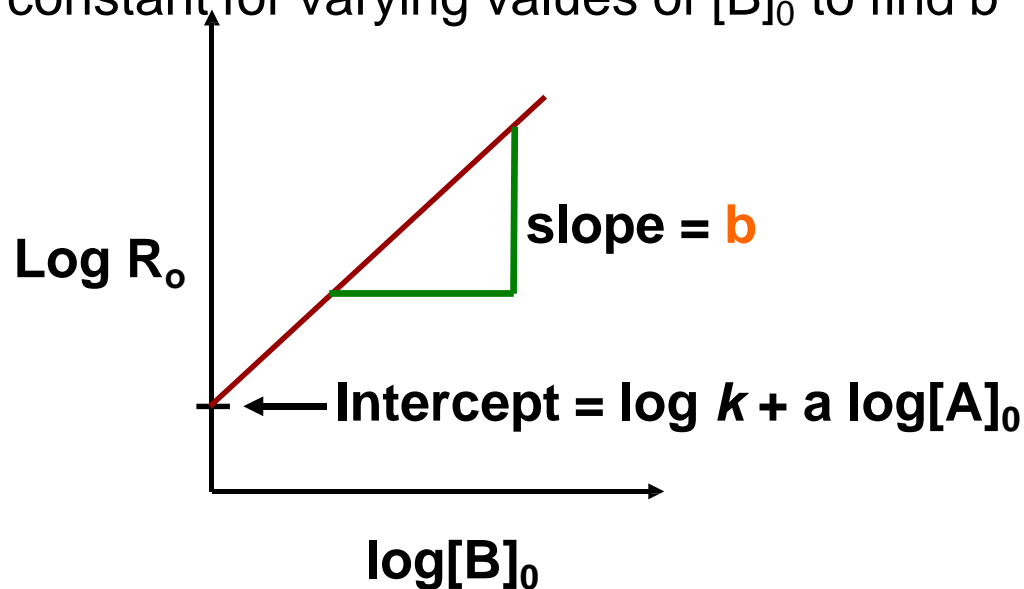
** Keep $[B]_0$ constant for varying values of $[A]_0$ to find **a** from the slope of the graph, $\log R_0$ vs $\log [A]_0$

** Substitute values of **a**, **b**, **$[A]_0$**, **$[B]_0$** to find ***k***.

However, in some cases, there may be no need to use the plots as shown previously.

EXAMPLE

$R_1 = k[A]^a[B]^b$

$R_2 = k[nA]^a[B]^b$

For these experiments, B is kept constant while A is varied and R_1 and R_2 are known.

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Dividing R_2 by R_1

$$\therefore \frac{R_2}{R_1} = \frac{k[nA]^a[B]^b}{k[A]^a[B]^b} = \frac{[nA]^a}{[A]^a} = \frac{n^a[A]^a}{[A]^a} = n^a$$

$$\therefore \frac{R_2}{R_1} = n^a$$

$$\therefore \log\left(\frac{R_2}{R_1}\right) = a\log n$$

$$\therefore a = \frac{\log\left(\frac{R_2}{R_1}\right)}{\log n}$$

(a) If $R_2 = 2R_1$, and n=2, then a = 1, so 1st order with respect to A

(b) If $R_2 = 4R_1$, and n=2, then a = 2, so 2nd order with respect to A

Concluding: if n=2,

and rate doubles→   1st order

rate increases by a factor of 4 → 2nd order

rate increases by a factor of 8 → 3rd order

4. Graphical method

nA $\rightarrow$ P ; Products

rate $R = k [A]^n$

$\therefore \log R = \log k + n \log[A]$

$(y = c + mx)$

The slope gives the value of n.

Rate

Concentration of reactant

slope = _n_

5. Van't Hoff Differential methods

In 1884 Van't Hoff suggested that the rate of reaction of nth order is proportional to the nth power of concentration

$$-\frac{dc}{dt} \propto c^n \Rightarrow -\frac{dc}{dt} = kc^n \quad ---(1)$$ **c is the concentration of the reactants.**

$Taking \log$

$$\log\left[-\frac{dc}{dt}\right] = \log k + n\log c$$

Suppose, we start the experiments having two reactants, initial concentrations c_1 and c_2, then

$$\log\left[-\frac{dc_1}{dt}\right] = \log k + n\log c_1 \quad -(2) \qquad And \quad \log\left[-\frac{dc_2}{dt}\right] = \log k + n\log c_2 \quad -(3)$$

Subtracting equation (3) from (2)

$$\log\left[-\frac{dc_1}{dt}\right] - \log\left[-\frac{dc_2}{dt}\right] = n(\log c_1 - \log c_2) \Rightarrow n = \frac{\log\left[-\frac{dc_1}{dt}\right] - \log\left[-\frac{dc_2}{dt}\right]}{(\log c_1 - \log c_2)} \quad ---(4)$$

Equation 4 can be used for calculating the order of a reaction provided the initial concentrations are known.

These values are measured by plotting c against time t.

Order of reaction

(A) Isolation Method

For a reaction: $n_1A + n_2B + n_3C \rightarrow$ Product
The order of reaction = $n_1 + n_2 + n_3$

(B) Initial Rate Method:

$$a = \frac{\log\left(\dfrac{R_2}{R_1}\right)}{\log n}$$

(C) Half life method

$$n = 1 + \frac{\log\dfrac{t_1}{t_2}}{\log\dfrac{[A_2]_o}{[A_1]_o}}$$

$$n = 1 + \frac{\log\dfrac{t_1}{t_2}}{\log\dfrac{P_2}{P_1}}$$

(D) Graphical method

rate $R = k[A]^n$

$$\therefore \log R = \log k + n\log[A]$$

$$(y = c + mx)$$

(E) Van't Hoff Differential Methods

$$n = \frac{\log\left[-\dfrac{dc_1}{dt}\right] - \log\left[-\dfrac{dc_2}{dt}\right]}{(\log c_1 - \log c_2)}$$
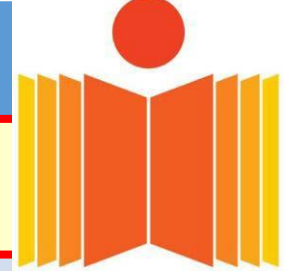
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Disturbing factors that opposes determination of Oder of reactions:

1st, 2nd or 3rd order reactions are straight forward, others are complicated because the interpretation of rate becomes difficult due several other simultaneous reactions.
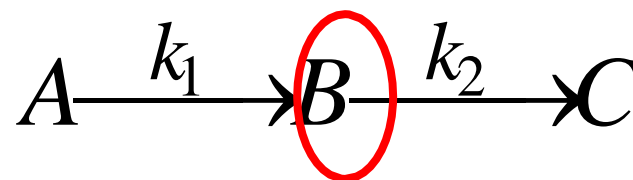
Typical Complex Reactions

(1) Reversible reaction   Opposing reaction $A \xrightarrow[k_b]{k_f} C$
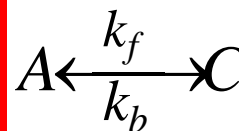
(2) Consecutive reaction $A \xrightarrow{k_1} B \xrightarrow{k_2} C$

(3) Competing reaction   Parallel reaction $A \xrightarrow{k_1} C$
$A \xrightarrow{k_2} D$

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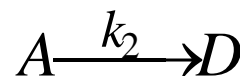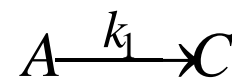
Reversible First-Order Reactions

There are certain reactions in which the product of a chemical change react to form the original reactants are called counter, reversible or opposing reaction.

In this reaction, the net rate of reaction will be influenced by both forward and backward rates and hence causes disturbance in the measurement of reaction rates.

$$A \xleftrightarrow[k_b]{k_f} C$$
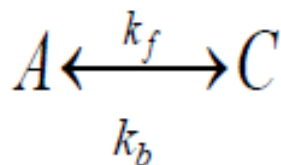
A= reactant, c= Product, k_f and k_b are the rate constants for forward and backward reaction

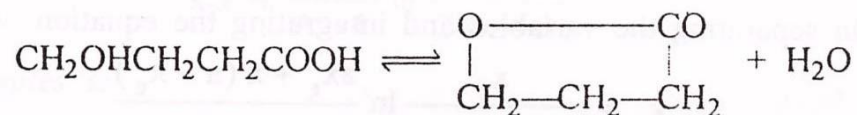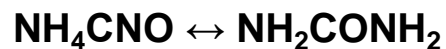The first order in both forward and back directions

Examples of Reversible First-Order Reactions

1. **Conversion of γ-hydroxyl bytyric acid into lactone.**

$$CH_2OHCH_2CH_2COOH \rightleftharpoons \begin{array}{c} O\text{---------}CO \\ | \qquad\qquad | \\ CH_2\text{---}CH_2\text{---}CH_2 \end{array} + H_2O$$

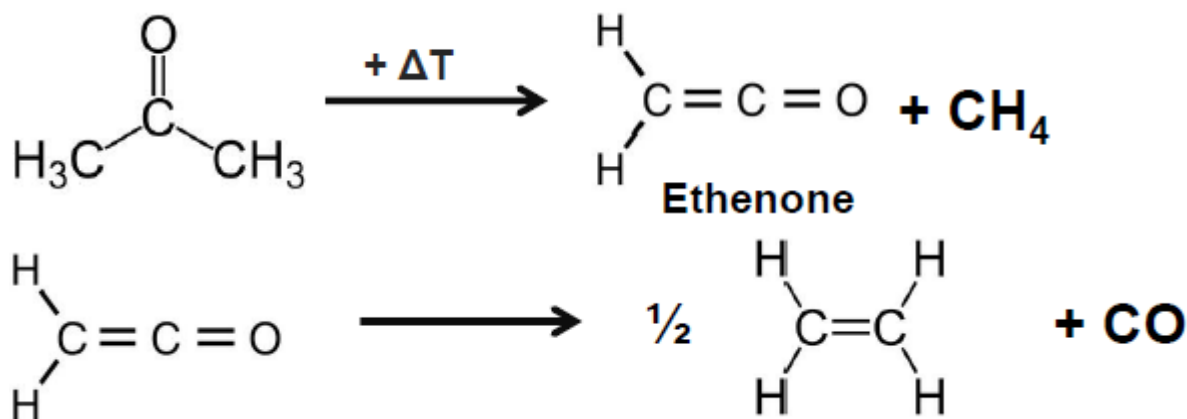2. **Conversion of ammonium cyanate into urea.**
   $NH_4CNO \leftrightarrow NH_2CONH_2$
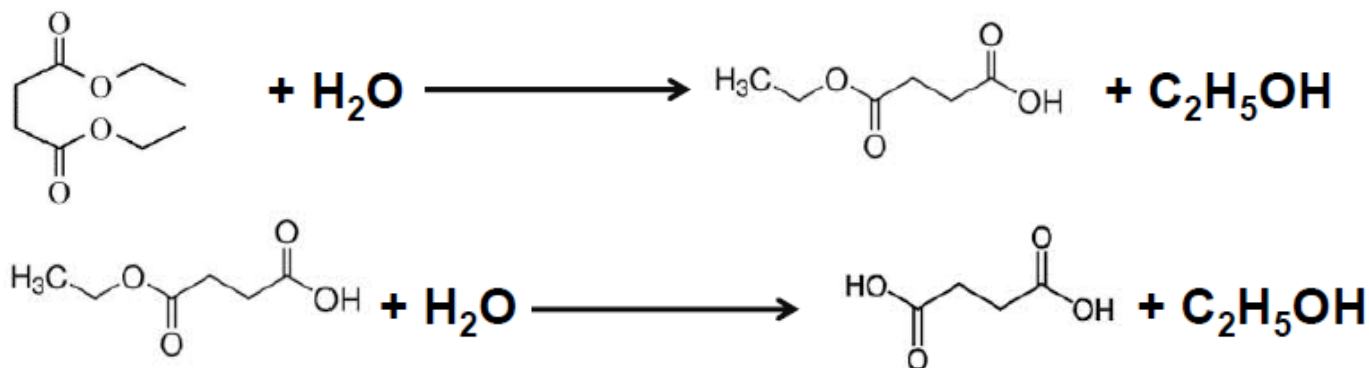
Consecutive reactions

In such reactions the products obtained in the 1st stage react with each other or with the reactants to form new product. That means consecutive reaction proceed in stages.

(a) Thermal decomposition of acetone occurs in two stages.
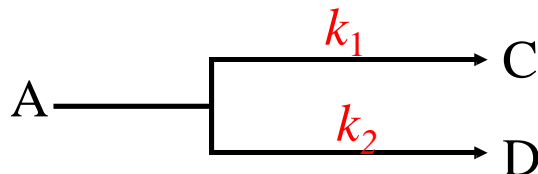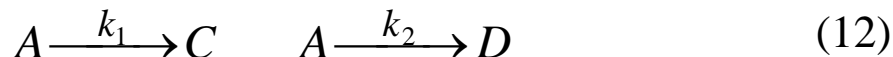

(b) The acid hydrolysis of ester of dibasic acid (e.g., diethyl succinate) occur in two stages.

Parallel reactions or side reactions

When a reactant [A] undergoes two or more independent reactions at the same time, it is the case of side reactions. Each independent reactions gives its own sets of products.

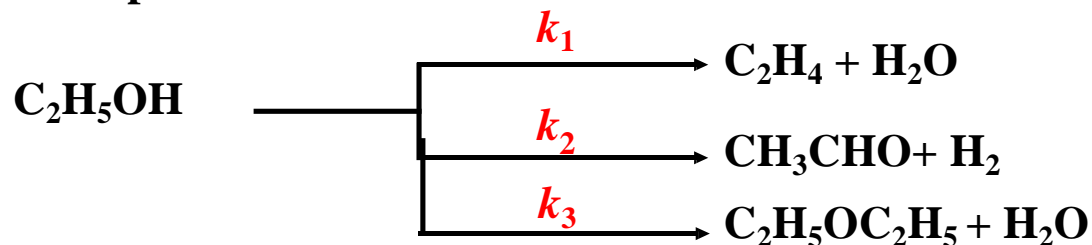**Consider two competing irreversible first-order reactions**

$$A \xrightarrow{k_1} C \qquad A \xrightarrow{k_2} D \qquad (12)$$

$$A \begin{cases} \xrightarrow{k_1} C \\ \xrightarrow{k_2} D \end{cases}$$

Parallel reactions

Example

$$C_2H_5OH \begin{cases} \xrightarrow{k_1} C_2H_4 + H_2O \\ \xrightarrow{k_2} CH_3CHO + H_2 \\ \xrightarrow{k_3} C_2H_5OC_2H_5 + H_2O \end{cases}$$

From the Ex., it is possible to convert any of the side reactions into main reactions by adjusting favorable exp. condition.