

Chemical Kinetics . (Revision notes)

1. Chemical Kinetics - Branch of chemistry which deals with study of
 - i) rates (how slow or how fast is a reaction) of chemical reactions
 - ii) factors affecting the rate.
 - iii) mechanism by which the reactions proceed.
2. Rate of a reaction: Change of concentration of reactants or products per unit time.
For a general reaction of the type,



The rate of reaction = $-\frac{d[A]}{dt}$ \rightarrow []

Dimension
= $\frac{\text{Concentration}}{\text{Time}}$ or,

negative sign
 $\frac{d[B]}{dt}$ (consumed over time) time

[]
↓
denotes concentration

$+\frac{d[C]}{dt}$ (formation)
positive dt

The negative sign implies that concentration of the reactants i.e. A or B decrease as function of time. Similarly, +ve sign \Rightarrow concentration of products i.e. C (in this case) increase with time.

Unit for reaction rate = $\text{mol L}^{-1} \text{s}^{-1}$

3. Rate Law: It is a mathematical relationship between the rate of reaction and molar concentration of one or more reactants.

$$\text{Rate} = - \frac{dA}{dt}$$

For a reaction,



$$\text{Rate} = k [A]^m [B]^n$$

Order of a reaction

where, m & n are

experimentally determined

order of the reaction w.r.t A & B respectively.

$m + n =$ overall order of the reaction.

exponent

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$m + n =$ overall order of the reaction.

4. Order: Refers to the relationship between rate of a chemical reaction & the concentration of chemical entities participating in the reaction.

More specifically, order of a chemical reaction w.r.t. each reactant is defined as the exponent to which, the concentration term of that particular reactant in rate law is raised.

Order of a reaction can be zero, fractional or an integral number.

5. Molecularity: The number of reacting particles (e.g. atoms, or molecules, or any other species),

which collide simultaneously to bring about the chemical change in a reaction is called molecularity

A unimolecular reaction is a reaction in which only one reacting molecule participates in the reaction.

Bi molecular \rightarrow 2 reacting molecules collide
Termolecular / Trimolecular \rightarrow 3 " " "

Molecularity is a theoretical concept. It has always an integer (whole no.) value. Typically molecularity of a reaction ≤ 3 (not more than 3). It cannot be zero.

6. The rate of a reaction is never a constant quantity (except in the case of zero order reaction). The rate decreases as the reaction proceeds in the forward direction.

7. Rate constant: Rate of reaction when the concentration of each reacting species is unity. Typically, rate constant is denoted by 'k'. It is also called specific reaction rate or velocity constant of a reaction.

8. First order reaction. A reaction is said to be first order when the reaction rate is dependent on the variation of one concentration only.

Representation: First order reaction $\xrightarrow{\text{(reactant)}} A \rightarrow P \xrightarrow{\text{(product)}}$ linearly dependent

Differential representation

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

Integral representation

- i) Write the differential eqn.
- ii) Rearrange
- iii) Integrate it

9. The Integral Representation of 1st order reaction

Step I: Rate = $-\frac{d[A]}{dt} = k[A]$ ($A \rightarrow P$)
< differential form >

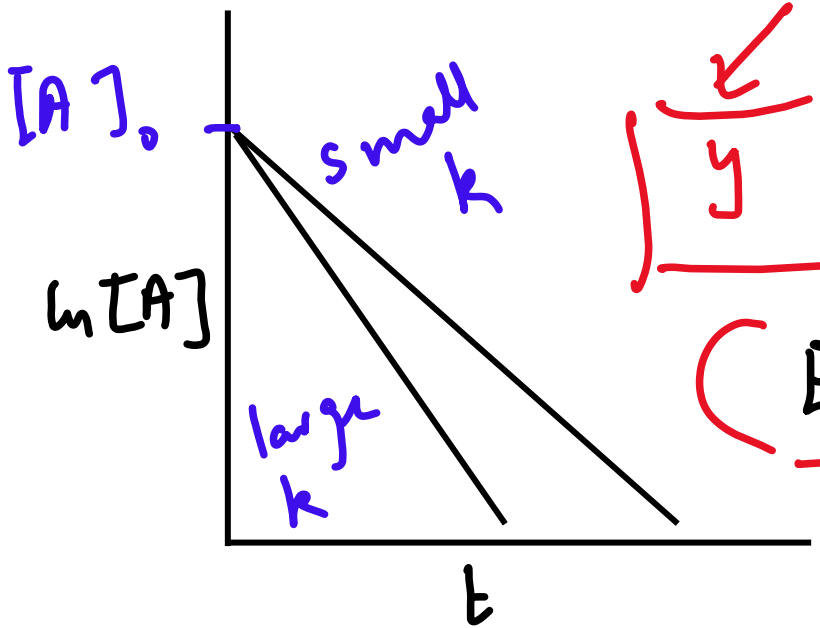
Step II: Rearrange to give: $\frac{d[A]}{[A]} = k \cdot dt$

Step III: Integrate both sides,

$\left\{ \int \frac{1}{x} = \ln \cdot x \right\}$
recall \Rightarrow

$$\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = - \int_{t_0}^t k dt \Rightarrow \int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = -k \int_{t_0}^t dt$$
$$\ln [A] - \ln [A]_0 = -kt + \ln [A]_0$$

$$\ln [A] = -kt + \underbrace{\ln [A]_0}_{\text{constant}}$$



$$y = -mx + c$$

Equation of a straight line

initial concentration of the reacting species at time t_0 .

$k =$ first order rate constant

$$\ln [A] - \ln [A]_0 = -kt$$

$$\Rightarrow \ln \frac{[A]}{[A]_0} = -kt$$

$$k = -\frac{1}{t} \ln \frac{[A]}{[A]_0}$$

$$\Rightarrow e^{-kt} \frac{[A]_0}{[A]} = \frac{[A]}{[A]_0}$$

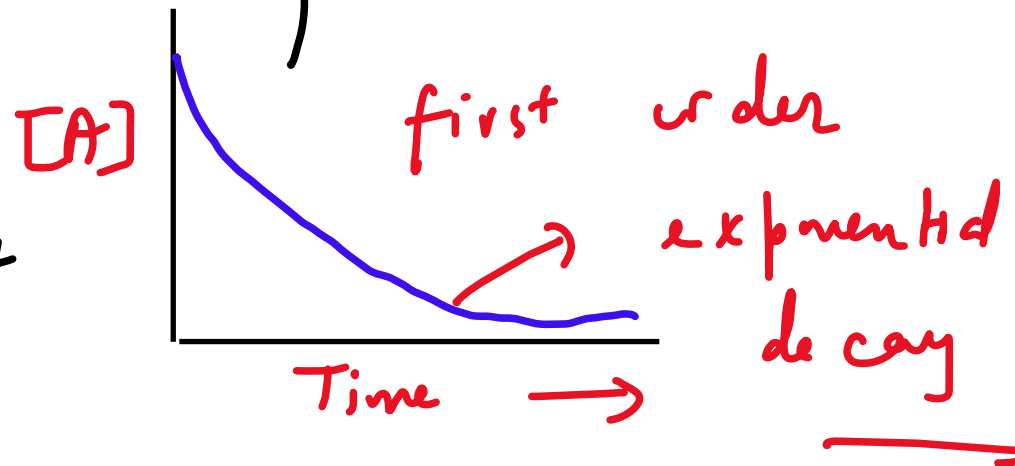
For first order reaction, unit of k is -
time⁻¹, s⁻¹, min⁻¹.

$$\frac{[A]}{[A]_0} = e^{-kt}$$

$$\Rightarrow [A] = [A]_0 e^{-kt}$$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

10. Half-life period - It is the time required for the reactant to reduce to



be reduced to half of its initial concentration.

For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$$

When a reactant reaches to its half-life, then, $t = t_{1/2}$ & $[A]_t = \frac{[A]_0}{2}$

$$\left[t_{1/2} = \frac{0.693}{k} \right] \quad k = \frac{2.303}{t_{1/2}} \log \frac{\cancel{[A]_0} \times 2^2}{\cancel{[A]_0}}$$

⑪ Second order reaction: The reaction in which sum of powers of concentration terms in rate law eqn. is - 2



$$\text{Rate} = \frac{dx}{dt} = k [A]^m [B]^n$$

where $m + n = 2$

⑫ Zero order reactions: Rate of reaction does not change with concentration of

reactants.

Rate law for a zero order reaction:

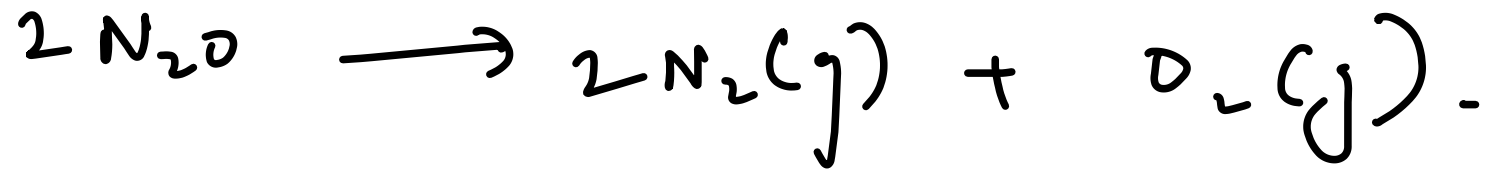
$$\text{Rate} = k [\text{A}]^0 [\text{B}]^0$$

Example



decomposition - 575°C.

This reaction in presence of hot platinum wire (which acts as a catalyst) is zero-order but when conducted in gas phase (centrally) follows a more conventional second order kinetics.



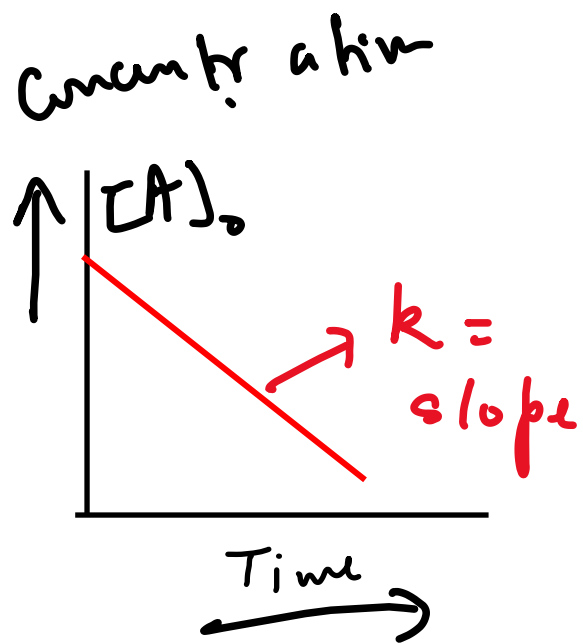
In this case, N_2O molecules that react are limited to those that could attach themselves to the surface of solid catalyst. Once all the sites of the limited surface of a catalyst have been occupied, additional gas-phase molecules must wait until the decomposition of one of the adsorbed molecules free up a surface site.

Two general conditions that give rise to zero order rates -

1) Only a small fraction of the reactant molecules are in a location or state in which they are able to react.

2) When two or more reactants are involved, the concentration of some are much greater than those of others.

⑬ Integrated form of the zeroth order
Rate Law:



When

$$\text{Rate} = k[A]^n$$



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

Rate

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

$$= k[A]^0 = k$$

⇒

$$-d[A] = k dt$$

⇒

$$-\int_{[A]_0}^{[A]} d[A] = k \int dt$$

⇒

$$-[A]_t + [A]_0 = kt$$

$$\Rightarrow [A] = -kt + [A]_0$$

$$y = -mx + c$$

14.

Temperature coefficient: It is the ratio of the rate constants of the reaction at two temperatures differing from one another by 10°C .

Two temp: 35°C , 25°C

Rate of a reaction is temperature dependent. Higher the temperature, faster is the reaction rate.

With rise in temp. by 10°C , the rate constant nearly gets doubled.

15. Arrhenius constant : Variation of rate constant with temperature.

Connects kinetics with thermodynamics

$$k = A \cdot e^{\frac{-E_a}{RT}}$$

where A = constant known as frequency factor.

E_a = activation energy - diff. temp.

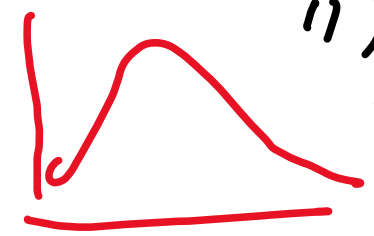
The rate constant at two

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

⑩ Two important theories of reaction rate:

i) Collision theory

ii) Transition state theory (activated complex theory)



Collision theory states that when suitable particles of the reactant hit each other only a certain amount of collision results in perceptible changes called successful collision.

No. of collision taking place per second per unit volume is known as collision frequency.