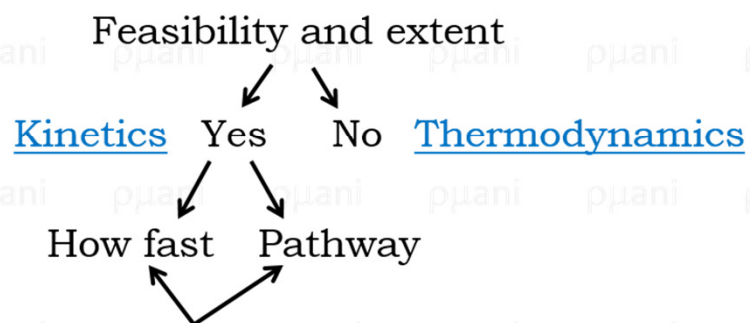# Lecture 21

In next few lectures we will learn about " Chemical Kinetics"

Suggested book: Physical Chemistry by Ira Levine

Why chemical kinetics is important?

Let us start with a macroscopic system, then move to microscopic system.

Feasibility and extent

Kinetics   Yes   No   Thermodynamics

How fast   Pathway

Factors affecting p, T, catalyst, photon etc. $\rightarrow$ pH, ε

Very slow experiment by Prof. Thomas Parnell, Pitch drop experiment $\rightarrow$ several years for a drop

Processes can be of physical, chemical or biological nature, for example – (a) photonic processes, (b) formation of HBr from H_2 and Br_2, (c) enzyme kinetics etc.

Let us assume a chemical reaction

$$aA + bB + \ldots\ldots \rightarrow cC + dD + \ldots\ldots \qquad (1)$$
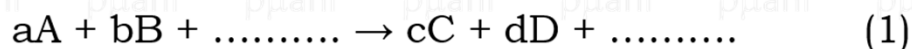
(i)   How will you measure the rate i.e. how fast is the reaction?

(ii) How would you know the relative value of a, b etc. (you have mixed the reactants, how do you know how the reaction will proceed?)

(iii) How will you know the mechanism of the reaction when it is complex in nature?

(iv) Is there any reaction intermediate? What is the nature of the reaction intermediate?

From the above equation (1),

The rate at which <u>any reactant is consumed</u> is proportional to its stoichiometric coefficient a, b etc.

$$\Rightarrow \frac{dn_A/dt}{dn_B/dt} = \frac{a}{b}$$

$$\Rightarrow \frac{1}{a}\frac{dn_A}{dt} = \frac{1}{b}\frac{dn_B}{dt} \qquad [n = \text{number of moles, t = time}]$$

<u>Convention:</u> For product it is (+)ve (as it is produced) and for reactant it is (−)ve (as it is consumed)

Thus, $(-)\dfrac{1}{a}\dfrac{dn_A}{dt} = (-)\dfrac{1}{b}\dfrac{dn_B}{dt} = (+)\dfrac{1}{c}\dfrac{dn_C}{dt} = (+)\dfrac{1}{d}\dfrac{dn_D}{dt}$
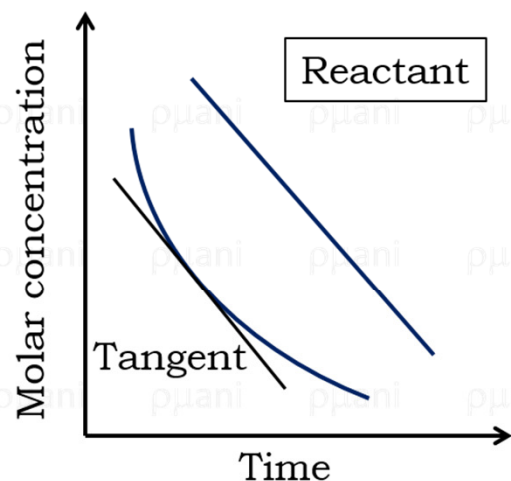
$$(-)\frac{1}{a}\frac{d[A]}{dt} = (-)\frac{1}{b}\frac{d[B]}{dt} = (+)\frac{1}{c}\frac{d[C]}{dt} = (+)\frac{1}{d}\frac{d[D]}{dt}$$
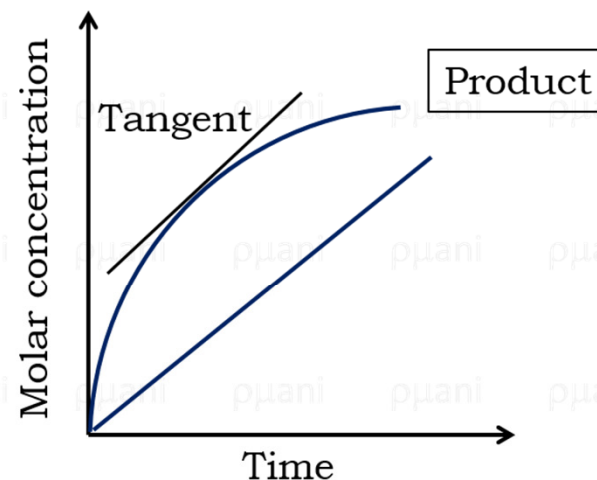
Thus, rate is refined as

$$v = \frac{1}{S_1} \times \frac{d[P]}{dt} = (-)\frac{1}{S_2} \times \frac{d[R]}{dt}$$

S → Stoichiometric number, P → Product, R → Reactant

How will you measure the rate?

Rate = Slope

(Also include method of initial rate)

So, what is the unit of rate?

$$mol\ L^{-1}\ s^{-1}\ or\ M\ s^{-1}$$

What is the typical time scale?

Million years – Months – Days – min – sec – m sec – μ sec – n sec – p sec – f sec

Geological

Biological

Chemical/physical

A brief discussion about different processes and their time scale.

Rate, order and Rate law:

Rate for reaction (1) is given by

$$r = k \times [A]^\alpha \times [B]^\beta \times \text{........} \quad [\alpha, \beta \text{ may be different from a, b}]$$

Where α, β could be integers or even non-integers.

The rate of the reaction depends also on pressure, temperature, etc. (other than molar concentration) $\rightarrow$ to be discussed later.

α, β etc. are termed as partial order w.r.t. A, B, ... etc.

Order of the reaction (n) = α + β + ...

Unit of r = M sec^{-1} , what is the unit of k?

k has the unit of (concentration)$^{1-n}$ time^{-1}

Thus the unit of rate constant depends on the order of the reaction.

Can order of a reaction be 4? Practical example?

Order can also depends on external condition like temperature, pressure etc.

Zero-order reaction:

When the value of the exponent/order = 0

This means rate is independent of the reactant concentration.

Does that mean reaction will happen without its presence?

→ No. It must be present but rate is independent of how much is present.

For example, catalytic decomposition of PH_3 over tungsten.

At high pressure, the rate law is r = k

PH_3 decomposes at a constant rate until it is completely disappeared. Heterogeneous reactions can have rate laws that are zero-order overall.
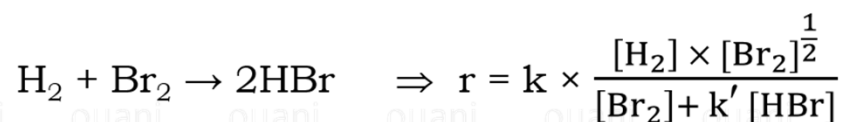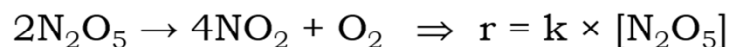
Homogeneous reaction:

Where the species involved in reaction are in single phase (i.e. either liquid, gas etc.)

Heterogeneous reaction:

Where the species involved in reaction are in more than phase.

Rate law:

The expression for rate as a function of concentration (at a fixed temperature) is called <u>rate law</u>.

$$H_2 + I_2 \rightarrow 2HI \quad \Rightarrow \quad r = k \times [H_2]^1 \times [I_2]^1$$

$$2N_2O_5 \rightarrow 4NO_2 + O_2 \quad \Rightarrow \quad r = k \times [N_2O_5]$$

$$H_2 + Br_2 \rightarrow 2HBr \quad \Rightarrow \quad r = k \times \frac{[H_2] \times [Br_2]^{\frac{1}{2}}}{[Br_2] + k'\,[HBr]}$$

Rate law <u>does not provide</u> any information about the stoichiometry of the reaction.

<u>Why is rate law important?</u>

(i) By integrating the rate law for a considerable period of time we can correlate <u>concentration change with time</u>.

(ii) <u>Rate constant</u> can be calculated from the values of concentration of unreacted reactants at different times using integrated rate expression.

(iii) It provides a guideline to establish <u>theoretically</u> the <u>mechanism</u> of the reaction in conformity with the integrated rate expression which is established on the basis of experimental observation.

Molecularity of a reaction:

It is actually a theoretical concept. Molecularity is defined as the number of molecules/species (molecules/atoms/ions etc.) involved in the reaction. Molecularity can be defined from the stoichiometric representation. For example, for $H_2 + I_2 \rightarrow 2HI$, molecularity is 2 or the reaction is bimolecular. For a complex reaction each sub-step has its own molecularity. Molecularity can never be zero or fraction. Molecularity of 4 or more is almost an impossibility.

Order	Molecularity
(1) It is the sum of exponents of a rate law expression.	(1) It is the number of species involved in a particular reaction or at a particular step of reaction.
(2) May or may not be a whole number /can be zero.	(2) Always whole number, /can never be zero.
(3) Can be determined experimentally.	(3) It is based on a theoretical concept.
(4) Order is for overall reaction.	(4) Molecularity can be of a step of a reaction.