

Chemical Kinetics

Presentation by
Dept. Of Chemistry

Theories of Chemical Kinetics: Collision Theory

- Before atoms, molecules, or ions can react, they must first *collide*.
- An *effective* collision between two molecules puts enough energy into key bonds to break them.
- The *activation energy* (E_a) is the minimum energy that must be supplied by collisions for a reaction to occur.
- A certain fraction of all molecules in a sample will have the necessary activation energy to react; that fraction increases with increasing temperature.
- The *spatial orientations* of the colliding species may also determine whether a collision is effective.

Application of collision theory to bimolecular reactions

The rate of the reaction can be calculated from the rate at which the reactant molecules are colliding

So the collision rate or collision number (number of collisions per unit volume per unit time) is expressed as

$$Z_{AB} = N_A N_B \pi (r_A + r_B)^2 \bar{u}_{rel}$$

$$Z_{AB} = N_A N_B \sigma \sqrt{\frac{8k_B T}{\pi \mu}}$$

$$\sigma = \pi (r_A + r_B)^2 = \text{Collision cross section}$$

Effect of concentration or temperature on the rate of a reaction

If the concentration or temperature of a reactant is increased the reaction goes faster.

When the reactants have a higher temperature, they move faster, thereby increasing the chance of a collision.

When the reactants have a lower temperature, they move slower, thereby decreasing the chance of a collision.

When the reactants are less concentrated there is less chance of a collision.

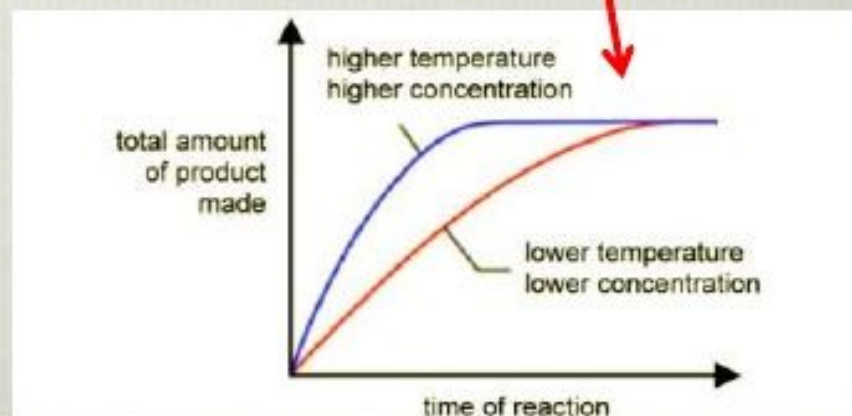
When the reactants are more concentrated there is more chance of a collision.



An animation on temperature:

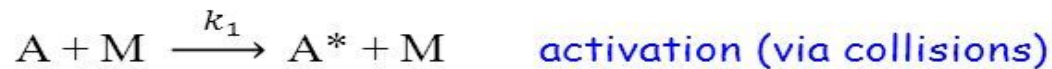
http://www.ltscotland.org.uk/higherciences/chemistry/animations/collision_theory.asp

Why does this graph have a plateau?



Application of collision theory to unimolecular reactions (Lindemann's Theory

Lindemann theory (1922)



M: any molecule (A, P or inert gas molecules added)

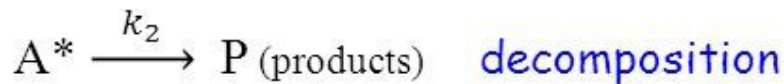
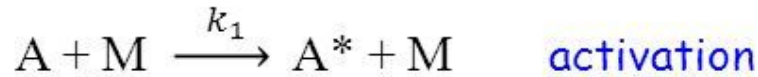
Rate equation for the energised molecules:

$$\frac{d[A^*]}{dt} = \underbrace{k_1[A][M]}_{\text{formation}} - \underbrace{k_{-1}[A^*][M] + k_2[A^*]}_{\text{removal}}$$

Considering A^* as a steady-state component:

$$k_1[A][M] \approx k_{-1}[A^*][M] + k_2[A^*] \longrightarrow [A^*] \approx \frac{k_1[A][M]}{k_{-1}[M] + k_2}$$

Lindemann theory



$$k_{\text{uni}}[A] = \frac{k_2 k_1 [M][A]}{k_{-1}[M] + k_2}$$



$$k_{\text{uni}} = \frac{k_2 k_1 [M]}{k_{-1}[M] + k_2}$$

$$\text{Low pressure limit: } k_{-1}[M] \ll k_2 \Rightarrow [M] \ll \frac{k_2}{k_{-1}} \Rightarrow k_{\text{uni}} = k_1[M] \quad \text{2nd order}$$

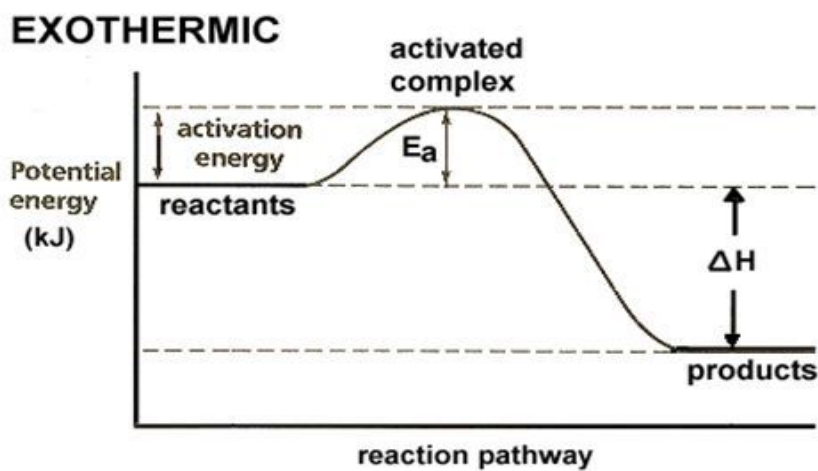
$$\text{High pressure limit: } k_{-1}[M] \gg k_2 \Rightarrow [M] \gg \frac{k_2}{k_{-1}} \Rightarrow k_{\text{uni}} = \frac{k_2 k_1}{k_{-1}} \quad \text{1st order}$$

In accordance with experiments

Activated complex theory or transition state theory

• Transition State Theory

- The energy changes in a chemical reaction can be shown in a graph called a **potential energy diagram**
- the high energy product is called an **activated complex** or a **transition state complex**
- the energy needed to form the activated complex is the **activation energy**
- The **reaction pathway** represents time or the progress of the reaction
- **The potential energy** shows the amount of energy the chemicals have at different points in the reaction



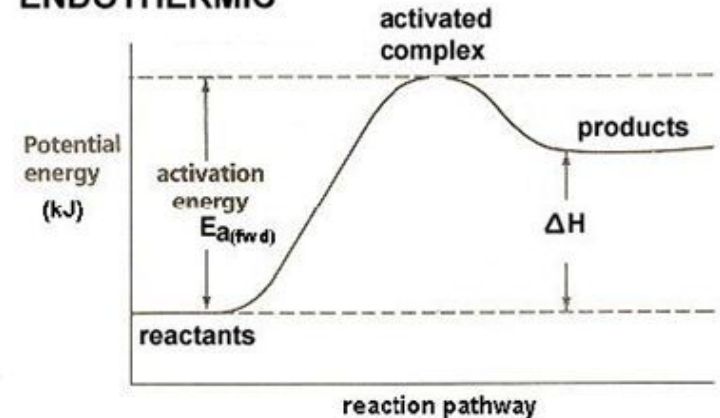
Transition State Theory

• Activated complexes

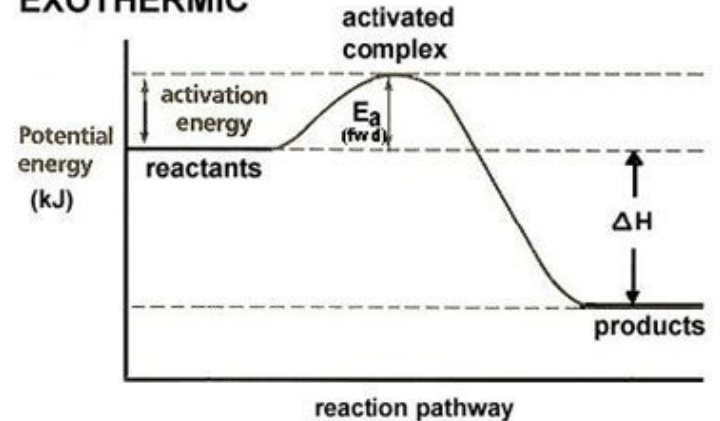
- exist for only brief periods of time while the atoms rearrange themselves
- have **high energy** due to their formation by **high energy collisions**
- **they are unstable** but need to form in order to make the final product(s)
- the energy needed to form the activated complex is called the **activation energy**

POTENTIAL ENERGY DIAGRAMS

ENDOTHERMIC



EXOTHERMIC



The equilibrium constant K^\ddagger can be expressed in terms of standard Gibbs free energy change of activation ($\Delta^\ddagger G^\circ$)

$$\Delta^\ddagger G^\circ = -RT \ln K^\ddagger \quad \Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$$

$$K^\ddagger = e^{-\Delta^\ddagger G^\circ / RT} = e^{-\Delta^\ddagger H^\circ / RT} e^{\Delta^\ddagger S^\circ / R}$$

$$k_2 = k^\ddagger e^{-\Delta^\ddagger H^\circ / RT} e^{\Delta^\ddagger S^\circ / R}$$

$$k_2 = \left(\frac{k_B T}{h} \right) e^{-\Delta^\ddagger H^\circ / RT} e^{\Delta^\ddagger S^\circ / R} \quad \text{Eyring Equation}$$

$\Delta^\ddagger S^\circ =$ *entropy of activation*

$\Delta^\ddagger H^\circ =$ *enthalpy of activation*

Difference Between Collision Theory and CTST

- Collision theory is only for reaction involving gaseous reactantswhile transition state theory can be applied to reactions taking place in solution as well as in the gas phase.
- In the collision theory reaction occurs when two molecules collide, but only if the collision is sufficiently vigorous
- transition state theory is used to explain in detail what happens when reactant molecules come together in a collision .

1.1.3 Classification of Reactions

Table 1.1.1

Classification of Chemical Reactions

Type	$K \text{ dm}^3 \text{ m}^{-1} \text{ s}^{-1}$	Half time ($t_{1/2}$)
(1) slow	10^{-7}	10^8 (About 3 years)
(2) Fast	10^2 to 10^5	10^{-1} to 10^{-4}
(3) Ultrafast	About 10^{11}	10^{-12} to 10^{-15}

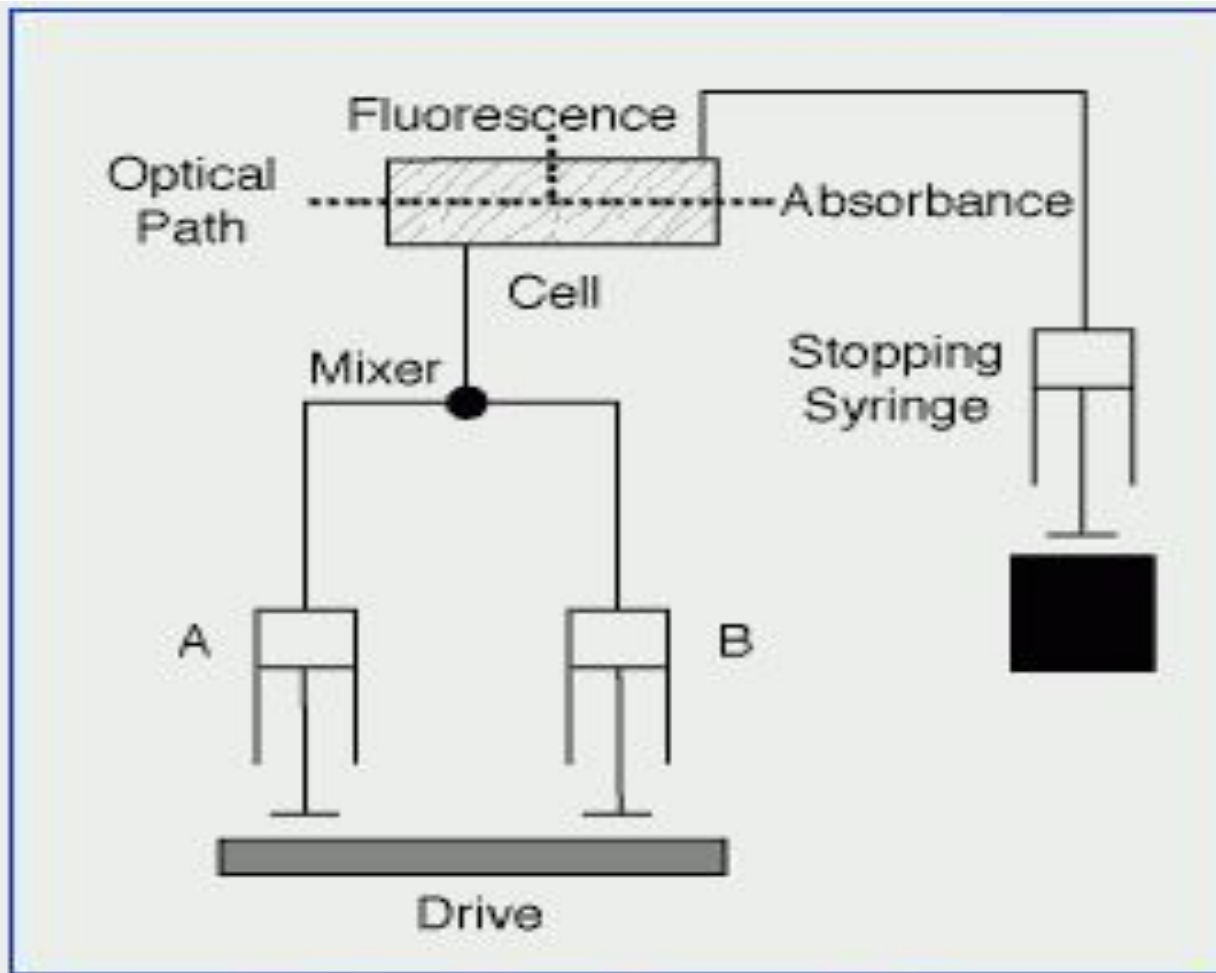
Examples

Slow: Reaction between hydrogen & oxygen to give water in absence of catalyst.

Fast: (a) Organic substitution reactions like bromination of aromatic amines and phenols

(b) Reaction of haemoglobin with O_2 and CO_2 .

Stop flow method to study fast reactions



Single Mixing Stopped-Flow

Polymers

Polymers

- **Definition** – A polymer is a molecule with a very high molecular weight which is composed of repeating simple structural units called monomers. Often referred to as macromolecules.
 - Homopolymer – single recurring monomer
 - Heteropolymer or Copolymer – at least 2 different monomer subunits

Classification of Polymers

- **Classification based on Source**

1. *Natural polymers*

E.g., Proteins, Cellulose, Starch, Rubber

2. *Semi-synthetic polymers*

E.g., Cellulose derivatives - Cellulose acetate
(Rayon)

3. *Synthetic polymers*

E.g., Buna-S, Buna-R, Nylon, Polythene, Polyester.



Classification

i) On the basis of origin

- Natural
- Synthetic

ii) On the basis of nature of monomer

- Homopolymers (comprise of monomers of the same type)
 - Linear (homochain or heterochain)
 - Branched
 - Cross-linked
- Heteropolymers/ Copolymers (Different repeating units)
 - Linear; Branched; Graft (regular/irregular); Block (regular/irregular)

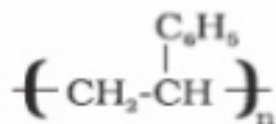
iii) On the basis of chemical nature

- Organic (polymer backbone chain made up of carbon atom)
- Inorganic (No carbon atoms in the backbone chain, eg., Silicone rubbers)

By Thermal Response

❖ Thermoplastic Polymers

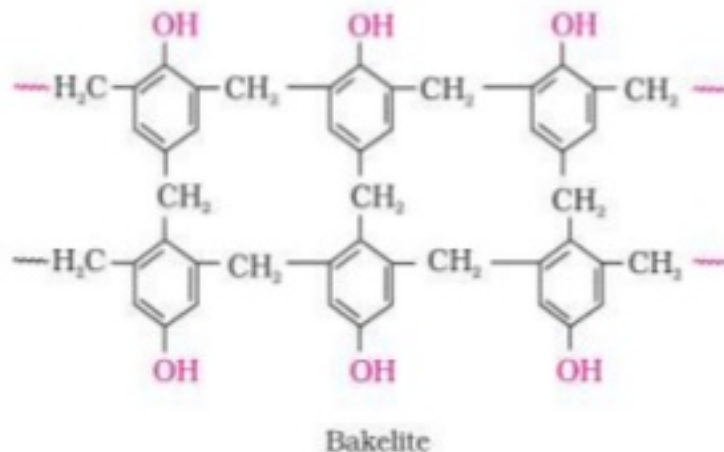
- They are easily moulded in desired shapes by heating and subsequent cooling at room temperature.
 - They are soft in hot and hard on cooling.
 - They may be linear or branched chain polymers.
- E.g. PE, PVC, PS, PP



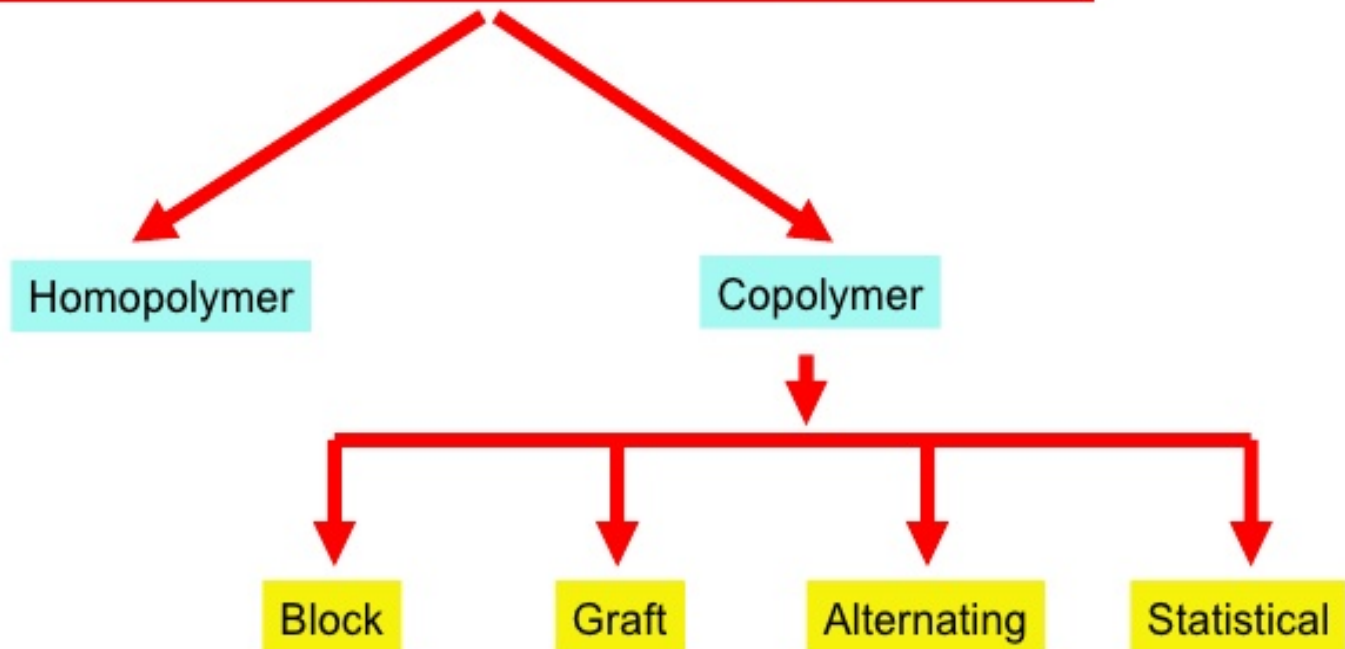
❖ Thermosetting Polymers

- This polymer is hard and infusible on heating.
- These are not soft on heating under pressure and they are not remolded.
- These are cross linked polymers and are not reused.

E.g. Bakelite



Classification by Monomer Composition



Homopolymer

Consist of only one type of constitutional repeating unit (A)

AAAAAAAAAAAAAAAA

copolymer

Consists of two or more constitutional repeating units (A.B)

Classification by Thermal Behavior

Thermoplastics - materials become fluid and processible upon heating, allowing them to be transformed into desired shapes that are stabilized by cooling.

Thermosets - initial mixture of reactive, low molar mass compounds reacts upon heating in the mold to form an insoluble, infusible network

Classification by Application

- Plastics
- Fibers
- Elastomers
- Coatings
- Adhesives

Classification Based on Kinetics or Mechanism

Step-growth

Chain-growth

Molecular weight averages

To create a solid with useful mechanical properties the chain must be long !!

One may describe chain length in terms of polymer **average molecular weight**, which can be defined in several ways:

1. A number-average molecular weight M_n : divide chains into series of size ranges and then determine the number fraction N_i of each size range

$$\overline{M}_n = \sum M_i N_i / \sum N_i$$

where M_i represents the mean molecular weight of the size range i , and N_i is the fraction of total number of chains within the corresponding size range

2. A weight average molecular weight M_w is based on the weight fraction w_i within the size ranges:

$$\overline{M}_w = \sum M_i W_i / \sum W_i$$

(1) The **number-average molecular weight** for a discrete distribution of molecular weights is given as

$$\bar{M}_n = \frac{\sum_{i=1}^N N_i M_i}{\sum_{i=1}^N N_i} = \frac{\sum_{i=1}^N W_i}{\sum_{i=1}^N (W_i/M_i)}$$

where N is the total number of molecular-weight species in the distribution.

(2) The **weight-average molecular weight** is given as

$$\bar{M}_w = \frac{\sum_{i=1}^N N_i M_i^2}{\sum_{i=1}^N N_i M_i} = \frac{\sum_{i=1}^N W_i M_i}{\sum_{i=1}^N W_i}$$

A measure of the molecular-weight distribution is given by the ratios of molecular-weight averages.

For this purpose, the most commonly used ratio is M_w/M_n , which is called the polydispersity index or **PDI**.

$$\text{PDI} = M_w/M_n$$

$M_w/M_n = 1$ monodisperse

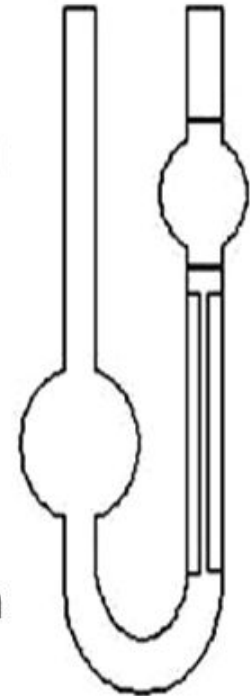
Polymer sample consisting of molecules all of which have the same chain length

$M_w/M_n > 1$ polydisperse

Polymer consisting of molecules with the variety of chain length

Determination of Viscosity of liquids

- **Using Ostwald Viscometer (Capillary-type viscometer):**
 - It is U-shaped glass apparatus with a wide arm and a narrow one with a capillary tube in the narrow part.
 - There are two marks; above and below the bulb in the narrow part.
 - In this method the viscosity of a liquid (η_1) can be determined in relation to another liquid of known viscosity (η_2).



VISCOSITY MEASUREMENT

Ubbelohde Viscometer, for measuring viscosity of dilute solution



upper and lower level

(measure the flow time t , of solution, drop from upper level to lower level)

$$\eta = k\rho t$$

k = viscometer constant

ρ = density of solution

t = flow time

If, t = time for solution

t_0 = time for solvent

$\rho = \rho_0$ \therefore dilute solution

ρ_0 = solvent density

Viscometry

IUPAC suggested the terminology of solution viscosities as following.

Relative viscosity :
$$\eta_{rel} = \frac{\eta}{\eta_o} = \frac{t}{t_o}$$
$$\eta : \text{solution viscosity}$$
$$\eta_o : \text{solvent viscosity}$$
$$t : \text{flow time of solution}$$
$$t_o : \text{flow time of solvent}$$

Specific viscosity :
$$\eta_{sp} = \frac{\eta - \eta_o}{\eta_o} = \frac{t - t_o}{t_o} = \eta_{rel} - 1$$

Reduced viscosity :
$$\eta_{rel} = \frac{\eta_{sp}}{c} = \frac{\eta_{rel} - 1}{c}$$

Inherent viscosity :
$$\eta_{inh} = \frac{\ln \eta_{rel}}{c}$$

Intrinsic viscosity :
$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c \rightarrow 0} = (\eta_{inh})_{C = 0}$$

Mark-Houwink equation

- Mark-Houwink equation is valid for **broad** molecular weight distribution:

$$[\eta] = K_m \overline{M}_v^a$$

$[\eta]$ = intrinsic viscosity

\overline{M}_v = viscosity average molecular weight

K and a = constants for particular polymer-solvent combination

For flexible polymer chains a is 0.5 - 0.8, for stiff and rod like chains a is 2.0.

Thank you