Unit - II

Rheology

The term rheology has been derived from the greek word rheo means "To flow" and logos means "Science".

Rheology may be defined as the science concerned with the flow of liquid and deformation of matter under the influence of stress. applied perpendicularly to the surface or at any angle to the surface of body.

Newtonian System

Liquids which exhibit newton's law of flow are k/as newtonian liquid.

Newton's law of flow -!
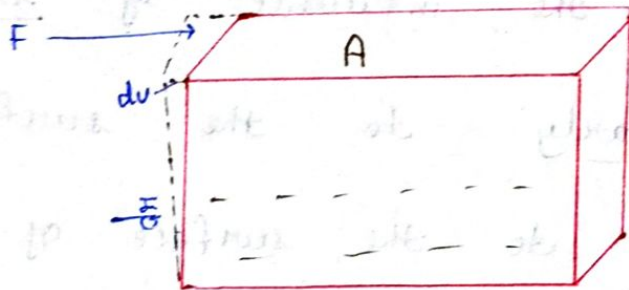Newton's law of flow states that rate of shear is

directly proportional to the shearing stress.

$$\boxed{\text{Rate of shear} = \frac{dv}{dr}}$$

where -: dv = Velocity difference b/w two planes of liquid separated by distance dr.

$$\boxed{\text{Shearing stress} = \frac{F}{A}} \text{ (Force per area).}$$
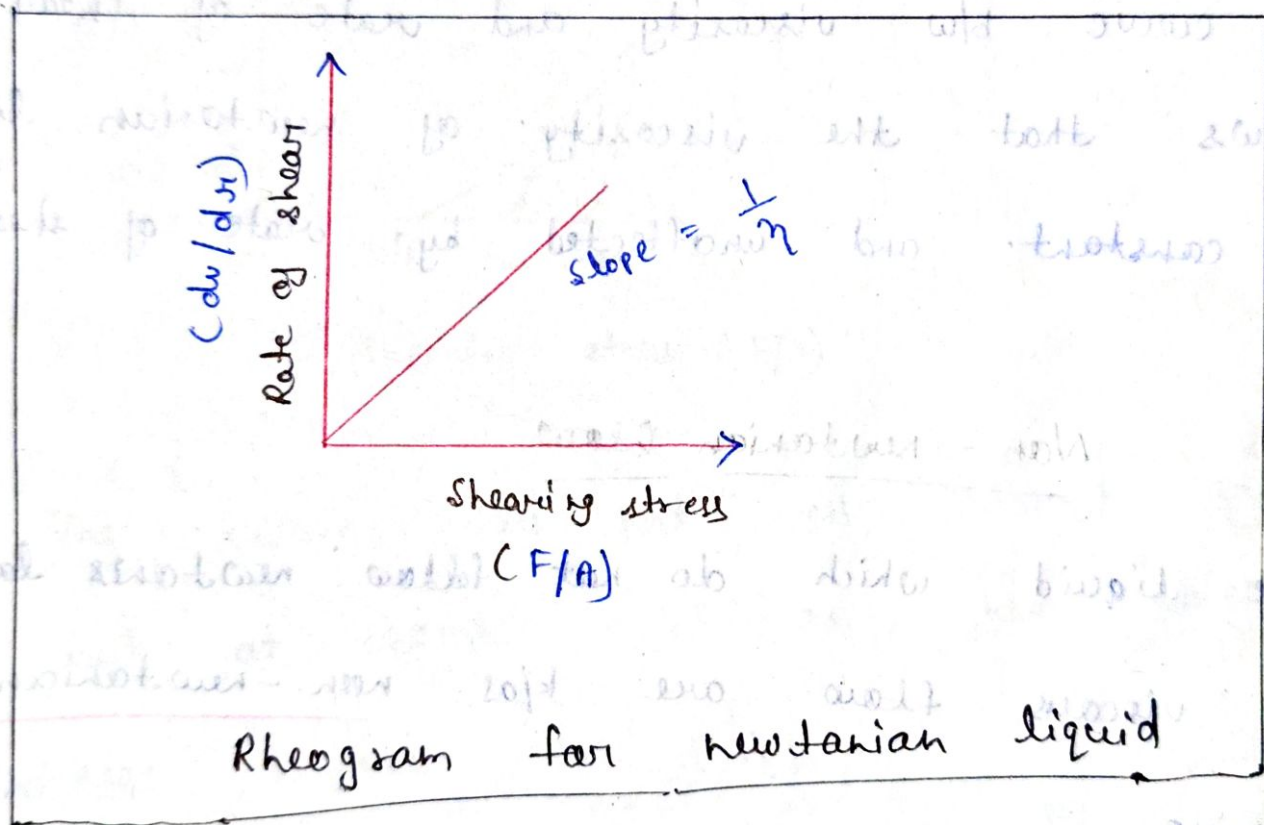

According to newton's law :-

$$\frac{dv}{dr} \propto \frac{F}{A}$$

$$\boxed{\frac{dv}{dr} = \eta \, \frac{F}{A}}$$
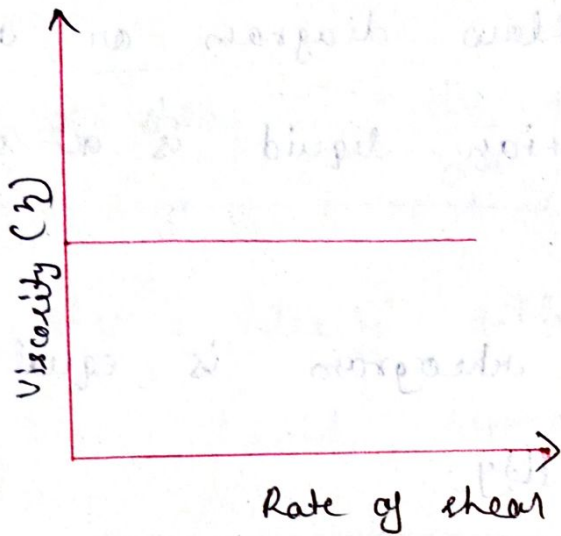
where - η = coefficient of viscosity.

* The rheological property of liquids are expressed in the form of flow diagram or rheograms.

* The plot of newtonian liquid is a strate line.

* The slope of this rheogram is equal to reciprocal of viscosity.

Rheogram for newtanian liquid

(y-axis: Rate of shear (du/dy))
(x-axis: Shearing stress (F/A))
slope $= \frac{1}{\eta}$

* The linear curve indicate that a mild force can induce flow in this system.

Ex $\rightarrow$ Benzene, water, CCl_4, hexane

The graph shows Viscosity (η) on the y-axis and Rate of shear on the x-axis, with a horizontal line indicating constant viscosity.

* The curve b/w viscosity and rate of shear shows that the viscosity of newtonian liquid is constant. and unaffected by rate of shear.

Non - newtonian flow

* Those liquid which do not follow newton's law of viscous flow are k/as non-newtonian fluids.

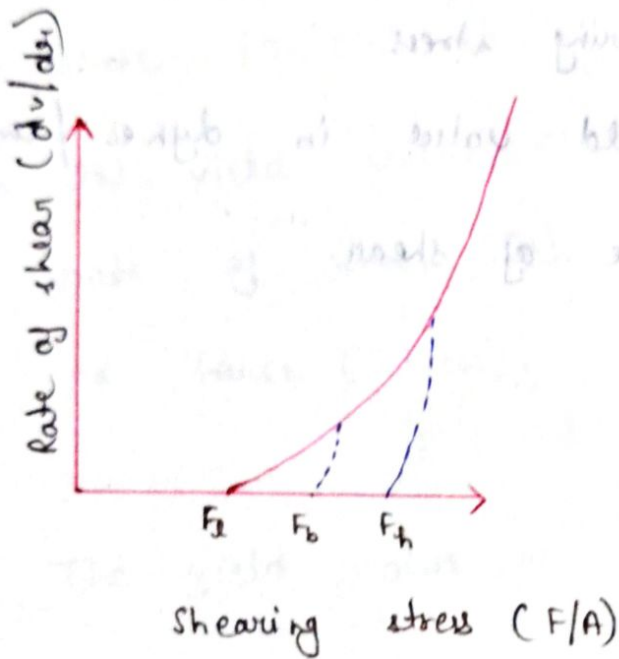* Viscosity of non-newtonian fluids changes with change in applied shear stress.

* Ex-! Emulsion, ointment, gel, colloidal dispersions are non-newtonian fluids.

* There are following types of non-newtonian fluids

1- Plastic flow —:

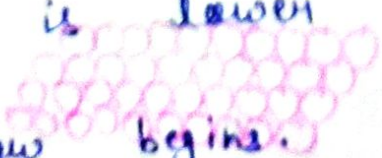* The characteristics of material which exhibit plastic flow are k/as bingham bodies.

* The curve does not pass through origin, but at some point on shear stress axis intersect k/as bingham yield (F_b).

* F_h is high yield value beyond which flow curve become linear.

* F_1 is lower yield value, where actual flow begins.

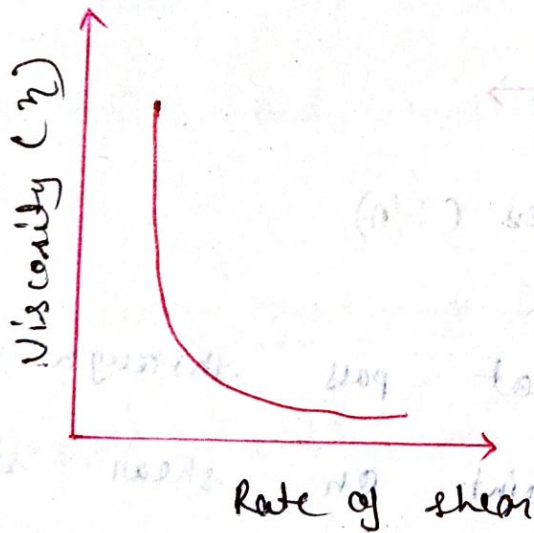* The plastic viscosity (U) can be calculated from equation –

$$U = \frac{F - F_B}{G}$$

Where →

F = shearing stress.

F_B = Yield value in dynes/cm^2.

G = Rate of shear.

* Example of plastic flow are zinc oxide in mineral oil paints.

Mechanism –

* Plastic flow is due to contact of flocculated particles.

* Friction b/w the moving particles and force of flocculation contributes yield value.

* The shearing stress in dynes/cm² require to over come these force.

* When the yield value exceed and flow begins, the rate of shear (Cr) becomes directly proportional to the force (stress).

Q-1 → The yield value of a plastic material was determined experimentally to be 6000 dynes/cm² and shearing stress above the yield value, F was found to ↑ linearly with Cr. If the rate of shear was 120 s⁻¹, when F was 8500 dynes/cm² calculate the plastic viscosity of sample.
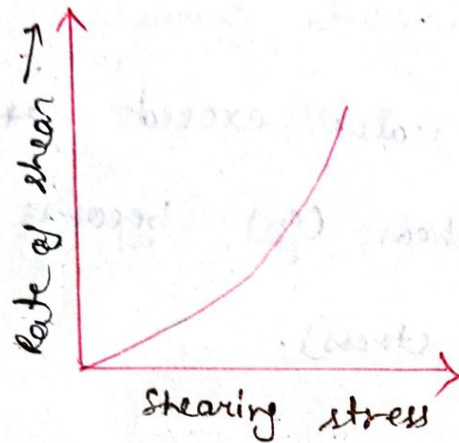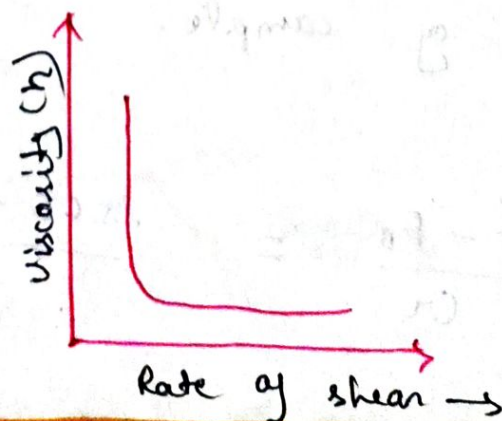
$$U = \frac{F - F_B}{Cr} = \frac{8500 - 6000}{120} = 20.8 \text{ poise}$$

2- Pseudoplastic flow

Pseudoplastic materials are characterised by rheological curve which pass through the origin.

* Pseudoplastic flow curve is not linear.
* The shear stress F does not ↑ linearly with the rate of shear.
* Viscosity does not remains constant.
* Viscosity ↓ es with rate of shear.

Eg → Sol^n of tragacanth , gelatine , CMS
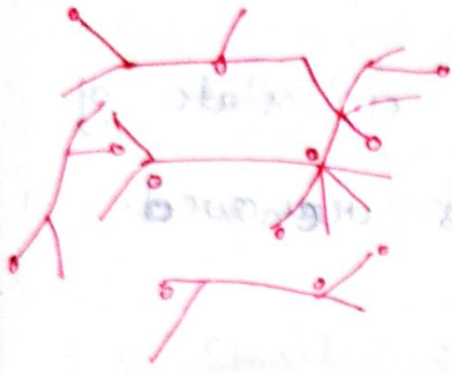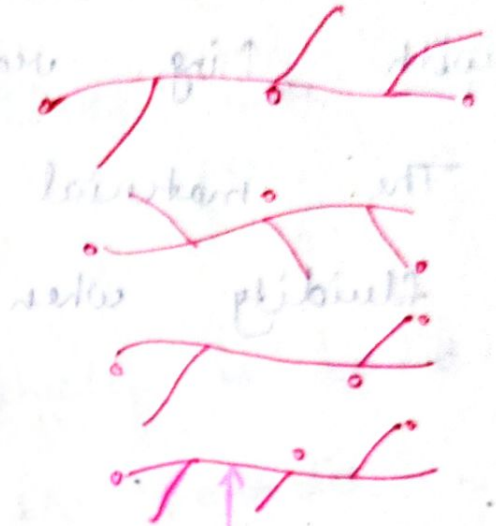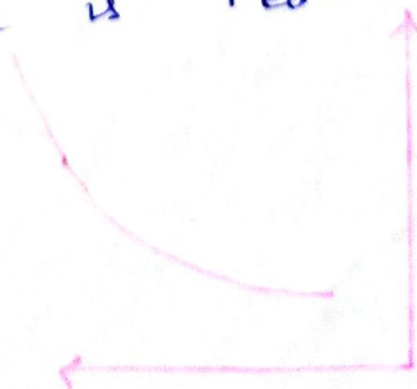and gums —

Mechanism -:

Polymer at
resting stage

Polymer under flow
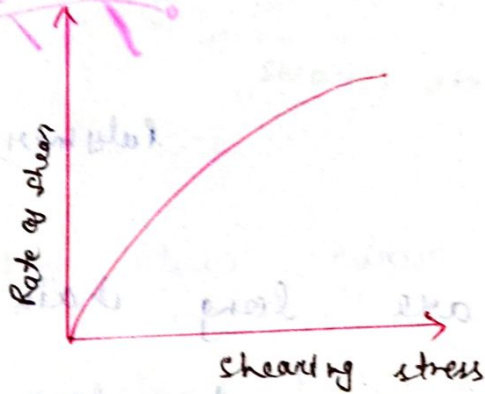
* These materials are long chain molecules
which are dis arrange at low shear rates
* At high rate of shear they become aligned
* Thus material becomes less viscous as
the shear rate is ↑ed.

3- Dilatant flow

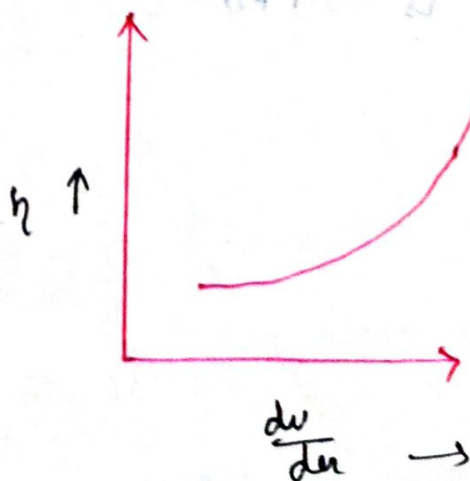* Dilatancy is a phenomena in which material show an ↑ in resistance to flow with ↑ing rate of shear.

* The material returns to a state of fluidity when the shear is removed.

* This phenomena is k/as shear thickening

* Viscosity ↑es with ↑ing rate of shear.

Mechanism

1→ Dilatant flow is found in suspension containing high concentration of very fine particles.

2→ When deflocculated particles of a suspension settle, they pack closely with minimum void volume.

3→ Small quantity of vehicle is needed to fill the voids b/w particles but suspension can flow freely.

4→ When mass agitated, bulk is ↑ed.

5→ The vehicle become insufficient to fill the voids.

6→ Particles show and ↑ed resistance to flow.
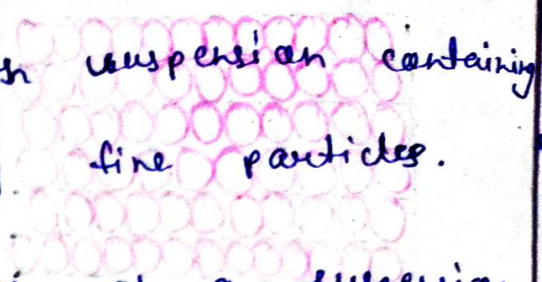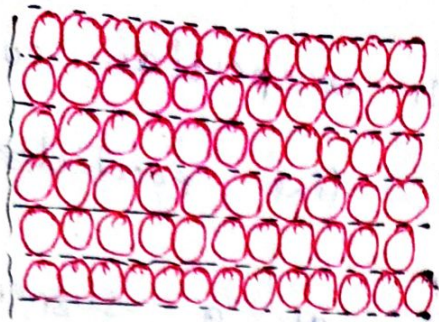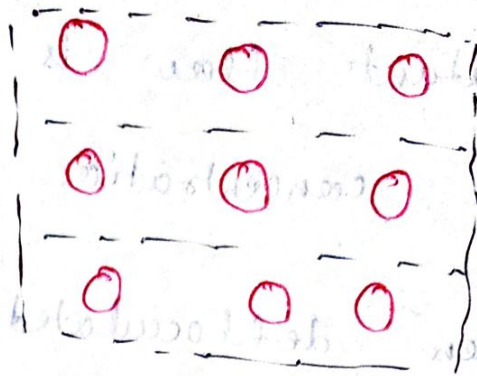
$$\text{Shear} \longrightarrow$$

Close packing minimum
Void volume

Open packing high
void volume

Phixotropy

Plastic and pseudoplastic system -:

* Viscosity $\downarrow$es on $\uparrow$ing the shearing stress, at any given temperature.

* On removing the shearing stress, the viscosity is regained but after some time lead.

  This phenomena is k/as phixotropy.

* It is reversible isothermal process.

$$\text{Gel} \xrightarrow[\text{shear stress}]{\text{Application of}} \text{Sol} \xrightarrow[\text{shear stress}]{\text{Removal of}} \text{Gel}$$

* Rheogram is obtained by plotting the rate of shear at various shearing stress.
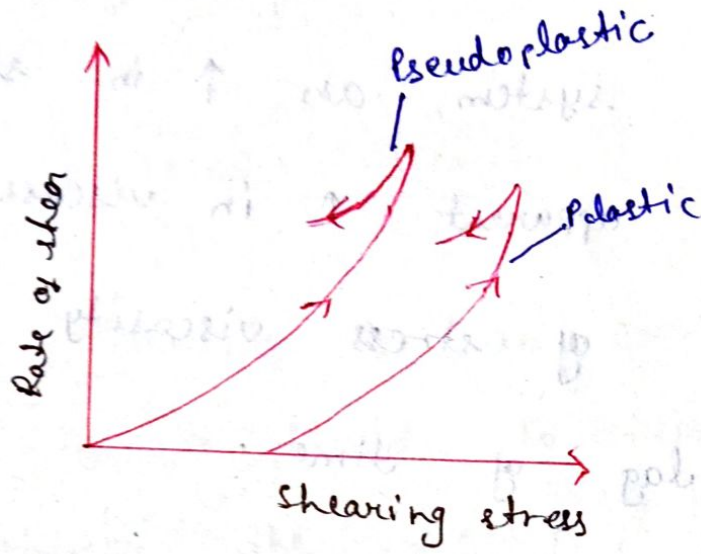
* As shearing stress is ↑es and upcurve is obtained.

* On reducing the shearing stress a down curve is obtained.

* The down curve sifted to the left side means the viscosity of down curve is lower than the upcurve.

Ex-: ① Example of plastic system showing thixotropy or bentonite gel.

⑪ Pseudo plastic system showing thixotropy or

dispersions of synthetic suspending agents.

Thixotropy in dilatant system —:

* In dilatant system, an ↑ in shearing stress causes an apparent ↑ in viscosity.

* On removal of stress viscosity ↓es but after a lag of time.

* It is reversible isothermal transformation from solution to gel.

Sol^n $\xrightarrow[\text{shear stress}]{\text{Application of}}$ Gel $\xrightarrow[\text{shear stress}]{\text{Removal of}}$ Sol^n

* Rheogram for dilatant system are as follows —
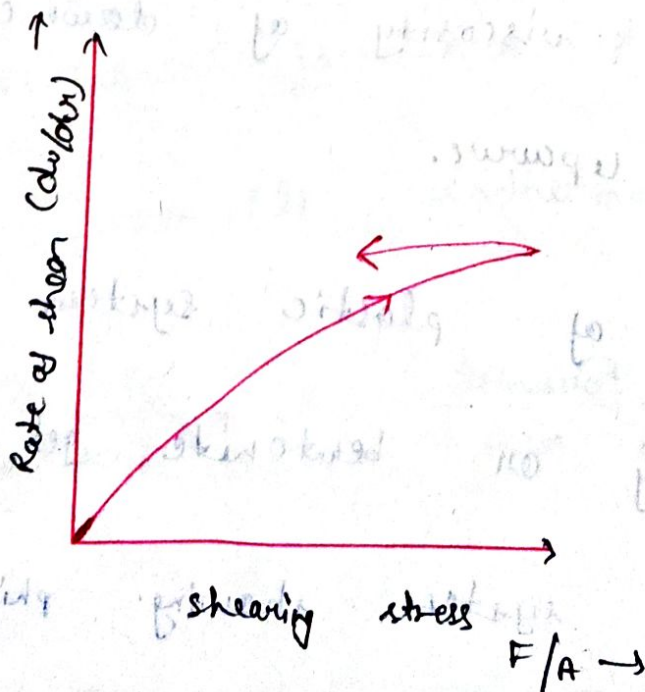
* Viscosity of system ↑es with application of stress.
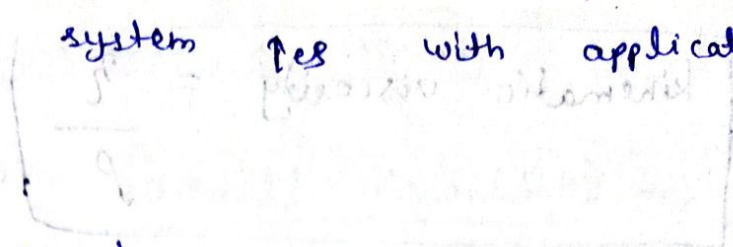
eg → Sand suspension

Kinematic viscosity

Viscosity → Viscosity is an expression of the resistance of a fluid to flow under applied stress, higher the viscosity, greater the resistance (overall)

Coefficient of viscosity →

It is determined with from equation

$$\eta = \frac{F}{G}$$

where — F = Force per unit area.

G = Rate of shear.

The unit of viscosity is paise or senti poise.

1 Cp = 0.01 poise.

Kinematic viscosity →

The kinematic viscosity of a liquid is its absolute viscosity divided by the density at a definite temperature.

$$\boxed{\text{kinematic viscosity} = \frac{\eta}{\rho}}$$

Effect of temperature -:

Viscosity of a gas ↑es with temperature.

In case of liquid the viscosity ↓es with ↑ in temperature.

Genereally speed of many rxn can be ↑ed 2-3 times with ↑ of of 10°C temp.

The dependence of viscosity of a liquid on temperature is given by Arrhenius equation —

$$\boxed{\eta = A\,e^{-E_V/RT}}$$

where -: T = Temperature in kalvin.

η = Vixosity of liquid.

R = Gas constant.

A = Frequeny of chotizen challision b/w mole cules.

E_V = Energy of activation reuired for collision b/w mole cules

Determination of viscosity

1→ Capillary viscometer (Ostwald viscometer) :—
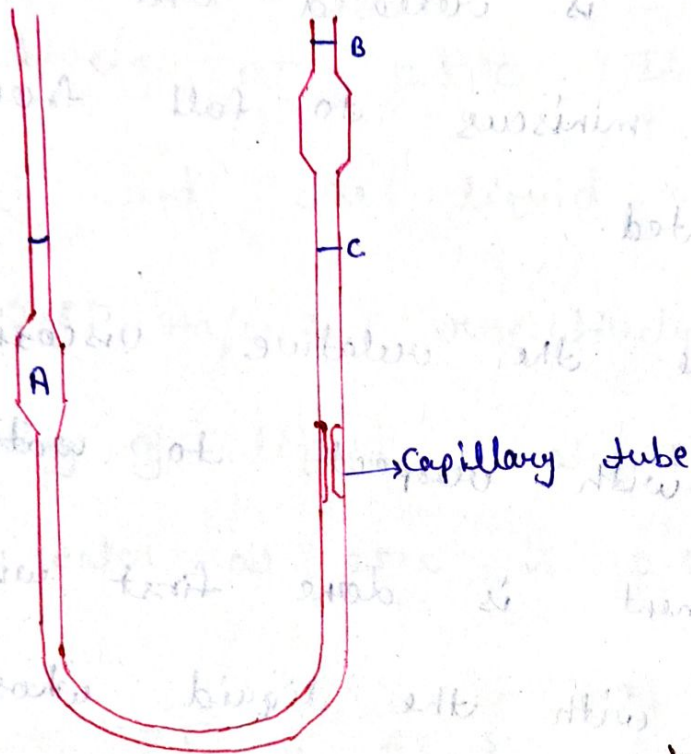
→ capillary tube

Ostwald viscometer

* Capillary viscometer is accurate for measurement of viscosity of newtonian liquids (fluids) having low viscosity.

* Liquid is introduced into the ostwald viscometer through left arm upto mark A.

* The viscometer is fixed vertically an a water bath.

* The liquid is sucked through right arm
untill the mark B.

* The pressure is released and time taken
from the miniscus to fall from B to
C is noted.

* To determine the relative viscosity of
a liquid with respect to water.

* The experiment is done first with water
and then with the liquid whose viscosity
is to be determined.

* The time taken for the liquid T_1 and
for water T_2 are determined.

* The relative viscosity is determined
by calculation as —

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

Q-1 → The time required for water and liquid B to flow through a ostwald viscometer was found to be 48 sec. and 20 sec. respectively. at 25°C. If the density of water and the liquid at 25°C are 1 and 0.85 gm/cm3 respectively, calculate the viscosity of liquid B at 25°C. Given viscosity of water at 25°C is 0.89 (m. paise).

Answer →

$$T_1 = 48 \text{ sec.} \qquad T_2 = 20 \text{ sec.}$$

$$P_1 = 1 \text{ gm/cm3} \qquad P_2 = 0.85 \text{ gm/cm3}$$

$$\eta_1 = 0.89 \text{ c.m. paise} \qquad \eta_2 = ?$$

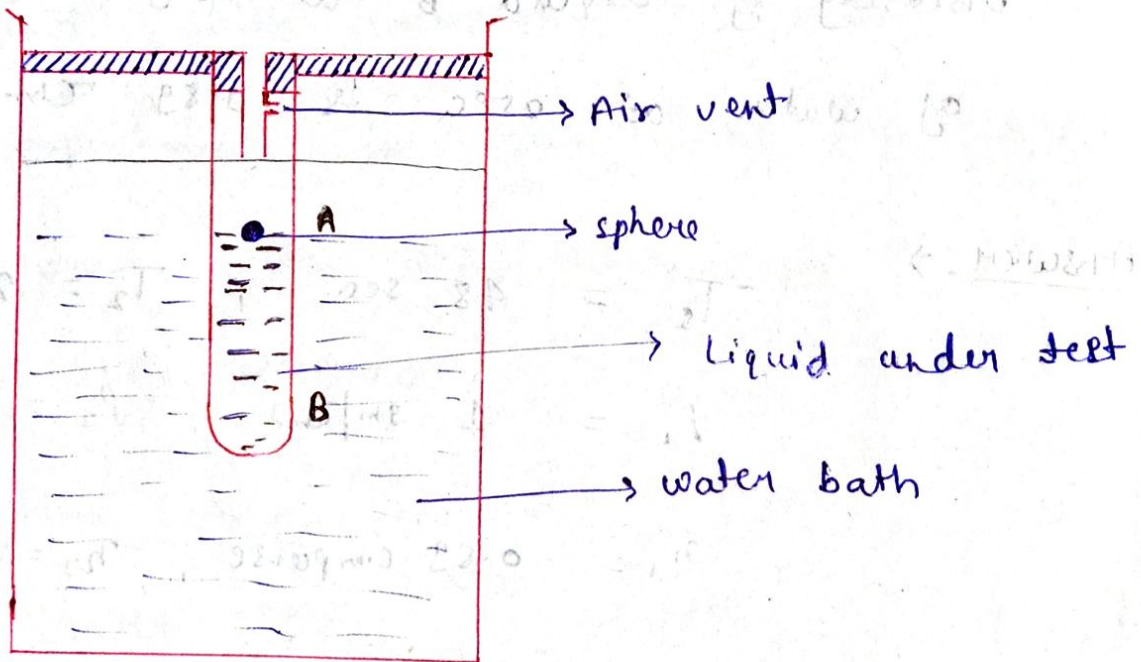$$\frac{\eta_1}{\eta_2} = \frac{P_1 t_1}{P_2 t_2}$$

$$\frac{0.89}{\eta_2} = \frac{1 \times 48}{0.85 \times 20}$$

$$\eta_2 = 0.31 \text{ c.m. paise}$$

2 - Falling sphere viscometer :-

This instrument is based on stok's law which states that when a body falls through a viscous medium, it experiences a resistance which opposes the motion of the body.

* It consist of a tube having two mark A and B on the outer surface.

* The tube is filled with the liquid whose viscosity is to be determined.

* The tube is clamped vertically inside a

temperature bath.

* A ball of suitable material such as steel or glass is allowed to fall through the guide tube inside the falling tube.

* The time taken for the sphere to fall from the point A to B is noted.
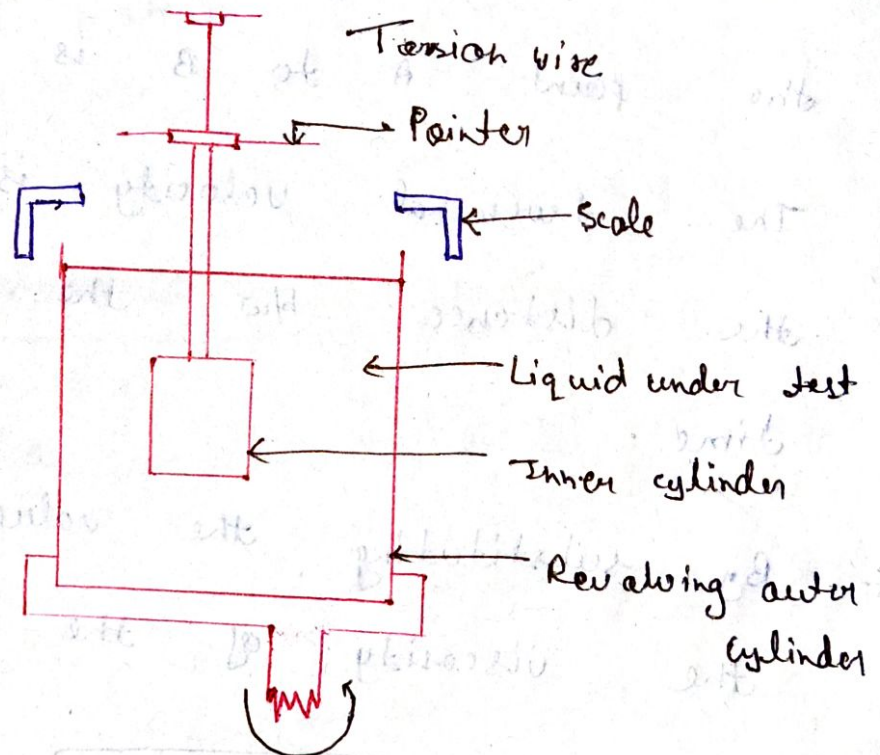
* The terminal velocity is obtained by dividing the distance b/w the 2 marks and the time.

* By substituting the values in the equation, the viscosity of the liquid is determined.

$$\eta = \frac{d^2 g (\rho_s - \rho_o)}{18 V}$$

3 - Rotational viscometer - (cup and bob viscometer)

* It works on the viscous drag exerted on a body when it is rotated in the fluid whose viscosity is to be determined.

Cup and Bob visco-meter

* It consists of 2 cylinders of different diameter.

* The outer cylinder forms the cup into which the inner cylinder or bob is fixed.

* The sample to be analysed is placed

in the space b/w the outer wall of the bob and inner wall of the cup.

The torque set up in the bob is measured by angular diflection (θ) of a pointer that moves on a scale.

(change)
Deformation of solid

* Deformation refers to any change in the shape or size of an object due to applied force (energy through work) or change in temperature (heat).

* Applied force can be result of tensile (pulling) forces, compressive (pushing) forces, bending or twisting.

* Temperature can result in structural defect, point vacancies, line and screw dislocation in both crystalline and non-crystalline solids.

* As deformations occurs, internal intermolecular forces arise that appose the applied force.

* If the applied force is not too great, these forces may be sufficient to resist the applied force.

* The object return to it's original state, when the load is removed.

* A larger applied force may lead to a permanent deformation of the object.

Types of deformation

(i) Elastic deformation → Small
                        → large

(ii) Plastic deformation.

(iii) Fracture deformation.

(iv) True stress and strain deformation.

① Elastic deformation -:

* This is also k/as ~~Temporary~~ deformation.

* It depend upon the stress level in material.

* The temporary deformation is recoverabl as it disappears after the removal of applied force.

* Upon removal of load, a complete recovery to the undeformed configurati should takes place.

* There are 2 types of elastic deform-ation-

ⓐ small elastic deformation → in case of material such as concrete and steel.

(i) large elastic deformation → Deformation in case

of elastomer and polymer.

(ii) Plastic deformation →

* This types of deformation is irreversible.

* An object in the plastic deformation range will first undergo elastic deformation and then plastic deformation which is irreversible.

* It depends on both the stress level and strain history of the material.

* Plastic deformation in metals occurs after a metal has reached its yield point.

* It results due to dislocation of micro structural sources which are not fully recoverable on removal of load.

* Soft thermo plastic have large plastic deformation such as copper, silver and gold.

* Hard thermo setting plastic have small plastic deformation such as rubber, crystalls and ceramics.

Elastic modulus

* Elastic modulus is the ratio of stress, below the proportional limit to the strain.

* It is the ratio of stress to strain when the deformation is totally elastic.

* This modulus may be thought as a materials resistance to elastic deformation.

* A rigid material has a higher

modulus.

* Elastic modulus is also klas young's modulus.

Ex-i Magnisium has magnitude of modulus b/w
45 gigapascale and tungsten has 407
gigapascale.

* The parameter's used to describe the
stress - strain curve is tensile strength,
yield strength and % elongation.

* There are 3 types of moduli —

1- Elastic modulus (young's modulus) —→ The
ratio of longitudinal stress to strain.

2- Bulk modulus —→ The ratio of stress
to the fractional decrease in the
volume of the body.

3- Shear modulus —→ The ratio of tangential
force per unit area to the angular
deformation.

Stress →

It is defined as force per unit area.

strain →

It is defined as elongation or contraction per unit length.

Heckel equation

* The heckel analysis is a most popular method of deformation reduction under compression pressure.

* Powder packing with fing compression load affect particle rearrangement, elastic and plastic deformation and particle fragmentation.

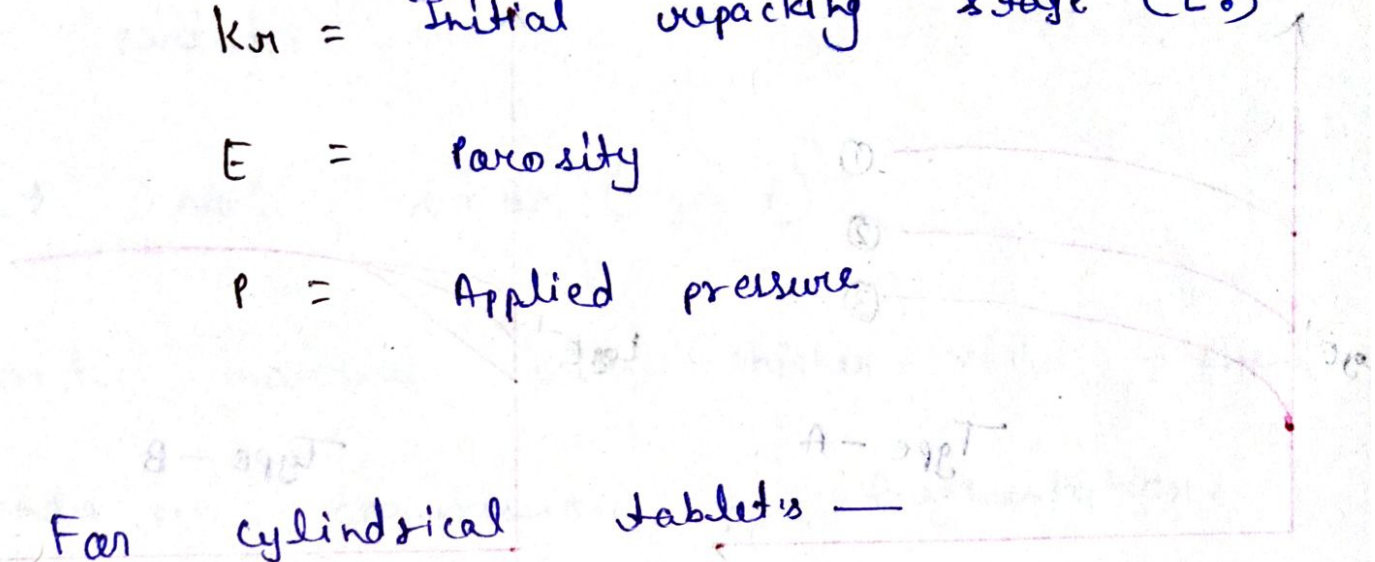* It follow first order with there's the pores in the powder are the reactant. (Depend on concentration).

$$\boxed{\text{Log } \frac{1}{E} = K_y \cdot P + K_r}$$

where →
    K_y = material constant.

    K_r = Initial repacking stage (E_o)

    E = Porosity

    P = Applied pressure

* , For cylindrical tablets —

$$\boxed{P = 4F / \pi \cdot D^2}$$

where →
    D = Tablet diameter,
    F = compression force.

* Porosity can be calculated by equation —

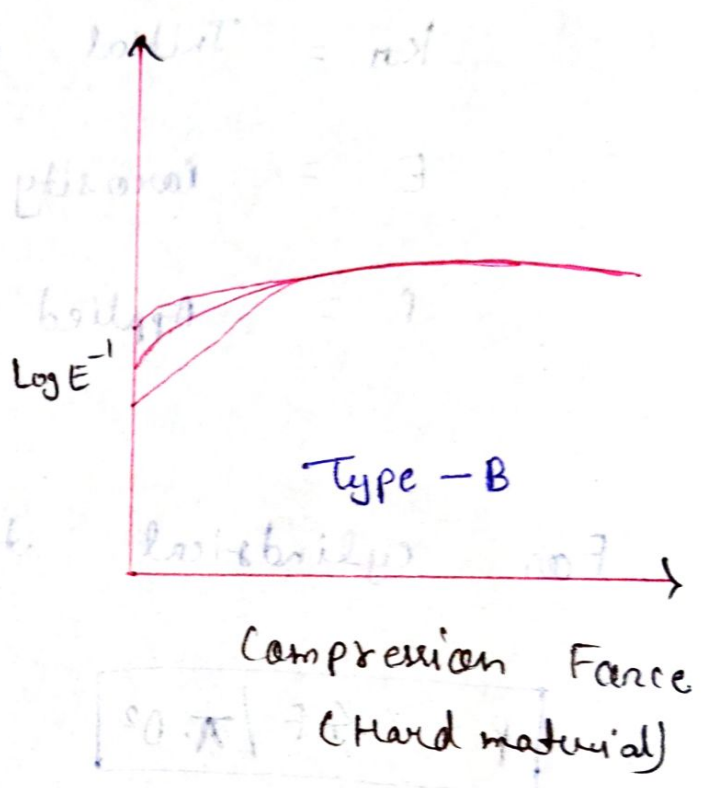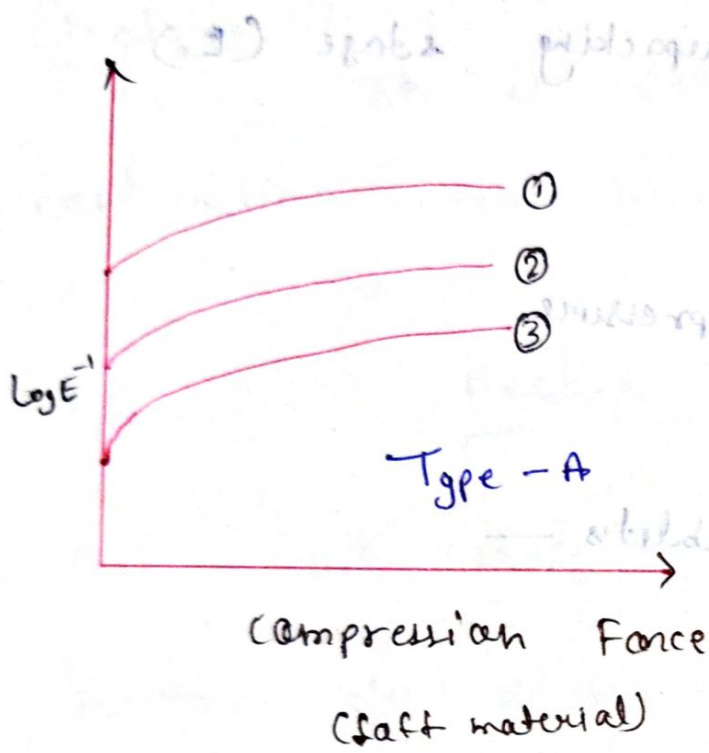$$\boxed{E = 100 \left(1 - 4w/P_t \cdot \pi D^2 H\right)}$$

where →
    w = weight of tablet.

    P_t = True density.

    H = Thickness of tablet.

Heckel's plots —:

Type — A

Type — B

Type — A → Higher slope and lower yield stress.

Type — B → Lower slope and high yield stress (Hard material).

* It follow first order kinetics.

* Ass porosity ↑es , compression force also ↑es.

* materials which are soft undergo plastic deformation.

* It depend upon shape and size distribution of particles.

  Ex → NaCl , NaBr (Type A)

* Harder material with higher yield pressure undergo compression by fragmentation.

  Ex → Lactose and sacrose (Type B)

Coarse dispersions are heterogeneous dispersed system in which the dispersed phase particles are larger than 1000 nm.