Rheology

Rheology → Rheo + logos

Rheo ⇓ to Flow

logos ⇓ study/science

⇒ Rheology is the branch of science that concerns with the flow of liquid and the deformation of solids.

- Deformation means a change in matter, be it shape or volume or both.
- The flow of liquids is induced by applying stress (Shear stress).

Applications:-

① Standards of liquids: The viscosity (a term of expressing the flow) of common liquid of pharmaceutical importance are standardized and reported.

- liquid paraffin has viscosity less than 64 centistrokes at 37.8°C.

② Manufacturing of dosage form:- Materials undergo process namely as mixing, flowing through pipes, filling into containers etc.

③ Handling of drugs for administration: The syringibility of the medicines, pouring of liquid from container, extrusion of ointment from, all depend on the changes in flow behaviour of dosage forms.

④ Identification of disease: A change in consistency of the body fluids, mucus, blood, saliva etc. is used as an indicator of the severeness of the disease

⑤ model for treatment of disease : the effectiveness of drug against diseases such as mucoviscidosis can be tested by studying the consistency at changes.

- Rheological principles are also applied in the study of paints, inks, cosmetics, dairy products etc.

Flow/fluids

- Newtonian
  - Water
  - Glycerin
  - Chloroform
- Non-Newtonian
  - Time independent
    - Plastic flow
    - Pseudoplastic flow
    - Dilatant flow
  - Time dependent
    - Thixotropy
    - Rheopexy

⇒ Newtonian System :-

- Newton was the first to study the flow properties of liquids in quantitative terms.

⇒ Liquids that obey Newton's law of flow are called as Newtonian fluids.

- The viscosity of such a fluid is constant at a given temperature and pressure.

This class includes liquids such as:

Water
Glycerin
Chloroform
Solution of syrups
Very dilute colloidal solution

★ molten Vaseline behaves Newtonian, whereas Vaseline is classified as non-Newtonian at room temperature.

Newton's law of flow: It states that

"The shear stress is directly proportional to the rate of shear strain."

$$\boxed{\tau \propto \frac{dv}{dr}}$$

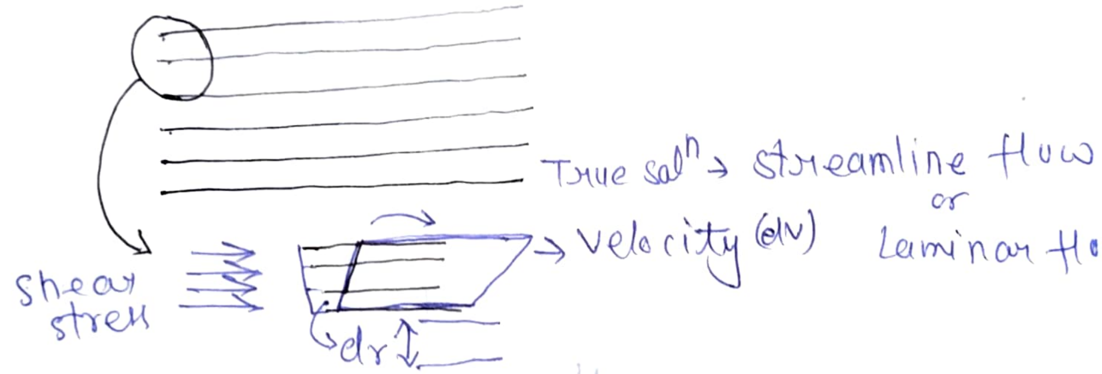
$$\tau = \eta \frac{dv}{dr}$$ ✓

Where,

τ = shear stress

$\frac{dv}{dr}$ = shear strain

η = coefficient of viscosity ✓



- **Shear Stress** :- It is defined as the force per unit area, which is applied to bring about the flow.

$$\boxed{\tau = \frac{F}{A}}$$

- **Rate of shear ~~stress~~ or strain** :- It may be defined as the change in velocity between top and bottom planes of liquid separated by a distance (dr)

Shear strain (G) = $\frac{dv}{dr}$. G = Rate of shear strain.

Relationship between shear stress and rate of shear (strain)

shear stress ∝ Rate of shear strain

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

or $$\frac{F}{A} = \eta \frac{dv}{dr}$$

or = $$\tau = \eta \frac{dv}{dr}$$

$\tau = \eta G$. or $\boxed{\eta = \frac{\tau}{G}}$

- Coefficient of viscosity is defined as the force per unit area required to maintain unit difference in velocity between two parellel ~~to~~ layers in the liquid, one meter apart.

CGS unit = poise
SI = Pascal ·second (Pa.s)

- Fluidity ÷ This term fluidity, ϕ, is used to denote the reciprocal of viscosity.

Fluidity, $\phi = \frac{1}{\eta}$.

Viscosity

Dynamic Viscosity (Absolute viscosity)
⇓
External force applied

Kinemetic Viscosity

⇒ **Kinematic viscosity** :- It is the ratio of viscosity of fluid to its density.

$$\underset{(\nu)}{\text{Kinematic viscosity}} = \frac{\eta}{\rho} \qquad \text{SI unit} = m^2/s$$

Where, η = viscosity of fluid
ρ = density of fluid
ν = kinetic viscosity

⇒ The unit of kinematic viscosity is stokes (s) and centistokes (cs).

1 stoke (s) = 10^{-4} m^2/s.

- It is a measure of the resistive flow of the fluid under influence gravity.

Factors influencing the viscosity

- Effect of temperature :- Viscosity is highly dependent on temperature.

In case of liquids,

Viscosity decrease with increases in temp.

$\boxed{\text{Temp} \uparrow = \text{Viscosity} \downarrow}$ → For liquids. {Exp → methyl cellulose.

eg. water:
↳ Viscosity
→ at 20°C ⇒ 1.0016
→ at 80°C ⇒ 0.35
→ at 100°C ⇒ 0.2822.

In case of gases,

Viscosity increases with increase in temp.

$\boxed{\text{Temp} \uparrow = \text{Viscosity} \uparrow}$ for gases.

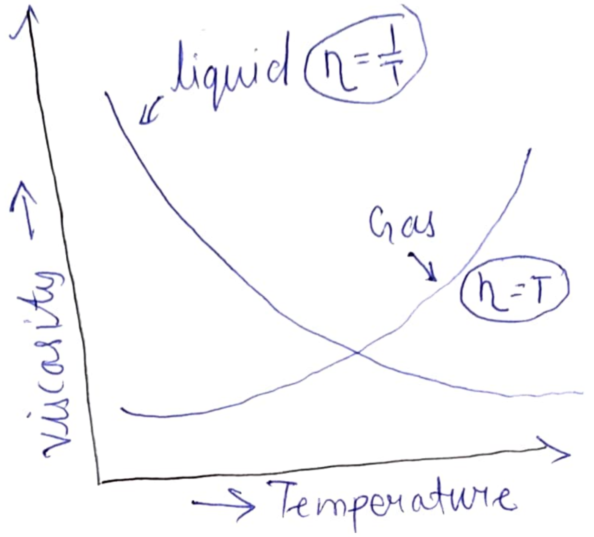
eg-

Oxygen → 20°c → 2.04

100°c → 2.44

400°c → 3.76.

Relationship curve b/w viscosity & temp. for liquids and gases.



The relationship b/w temp. and viscosity is expressed by Arrhenius equation–

$$\boxed{\eta = Ae^{EV/RT}} \qquad \eta = Ae^{E_v/RT}$$

where,

η = viscosity

A = constant which depends on the molecular weight & molar volume

E = E_v = Activation energy required to initiate flow

T = Temperature

R = Boltzmann's constant.

Non-newtonian system :- Non-Newtonian fluid (flow) are those, which does not fallow Newton law of flow.

- In which, shear stress and rate of shear is not constant.
- Viscosity is not constant.

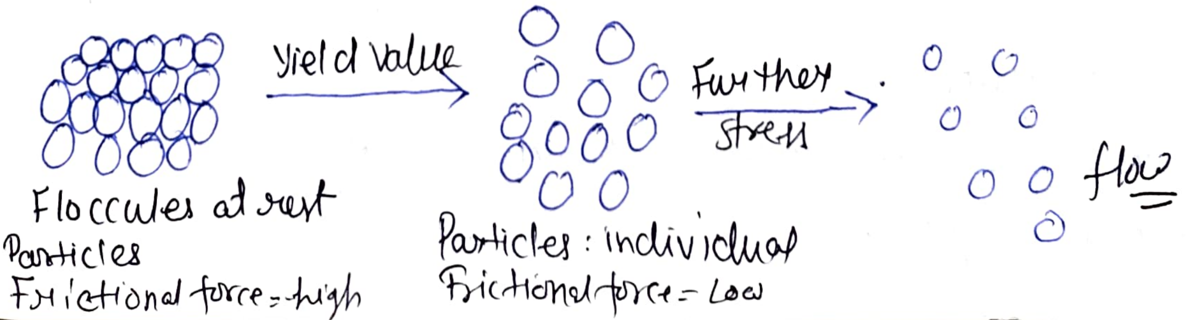
Ⓐ **Time independent** : Plastic flow
Pseudoplastic flow
Dilatant flow

Ⓑ **Time dependent** : Thixotropy
Rheopexy

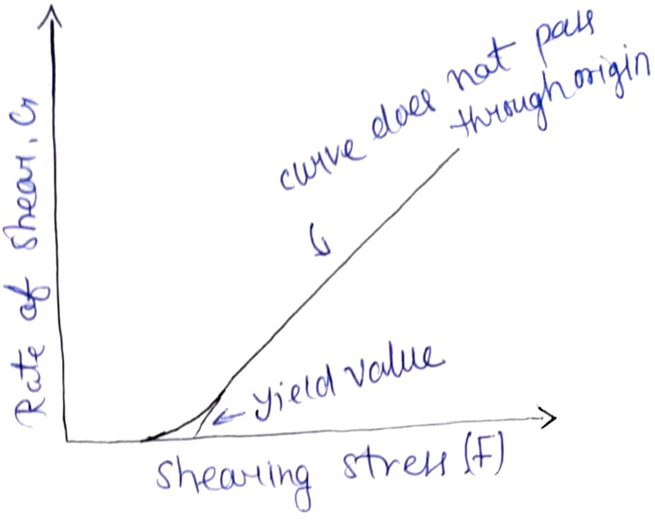
A

① Plastic Flow :-

- Those material/substance which fallow plastic flow are called Bingham bodies.
- In this flow, when we apply shear stress initially their are no change in shear strain (Rate of shear) until shear stress reaches yield value.
- Yield value - the amount of shear stress are required to break the floccules is called yield value (f)



- After yield value, they follow Newton law of flow.



- Mathmetically expressed as

Plastic Viscosity $\boxed{U = \frac{F-f}{G}}$

Acc. to Newton law
Shear stress ∝ Rate of shear
$F-f \propto G$ or $\frac{dv}{dr}$
$F-f = UG$
$U = \frac{F-f}{G}$

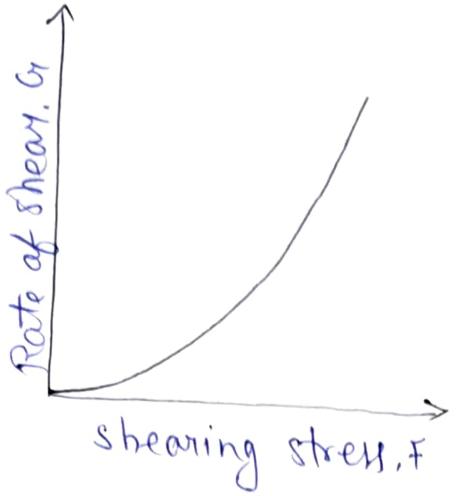
where, F = Shear stress (N/m²)
f = yield value (N/m²)
G = Rate of shear (s⁻¹)
U = Plastic Viscosity.

eg. Flocculated system, suspension of zinc oxide in mineral oil etc.

2. Pseudoplastic Flow

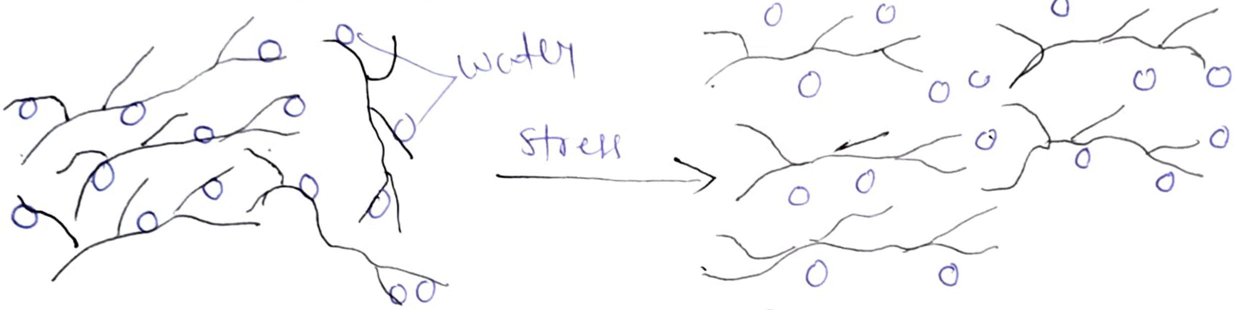
- The materials are known as shear thinning materials.
- In this system flow begins at the origin in curve.
- As the shear stress increases progressively, shear rate also increases, but the trend is not linear.
- Pseudoplastic flow can be found in emulsions, suspensions etc.

→ ~~In gener~~



- In general, pseudoplastic flow is exhibited by polymer dispersions such as :

→ Sodium alginate in water
→ Methylcellulose in water
→ sodium carboxymethylcellulose in water.



Polymers at rest random arrangement water inbound

Polymer under flow alignment on long axes water is released

Fig. mechanistic explanation for the pseudoplastic flow

→ mathmatically expressed as-

$$\boxed{F^N = \eta' G}$$

$\eta' G$

Where,

N = Exponent (N≠1)
η' = Viscosity coefficient
G = Shear Strain.

③ Dilatant Flow

The system exhibits enhanced resistance to flow with increasing rate of shear.

- Those materials in which, viscosity increases when we increase shear stress.

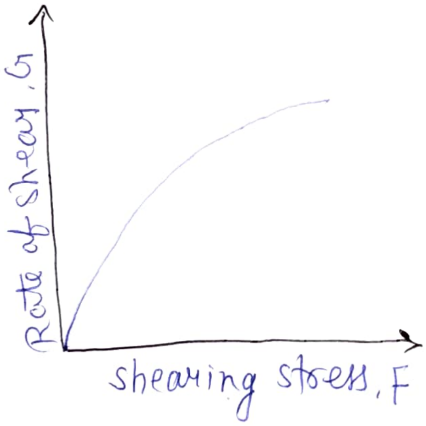
⇒ Dilatant materials are also often termed as shear thickening system

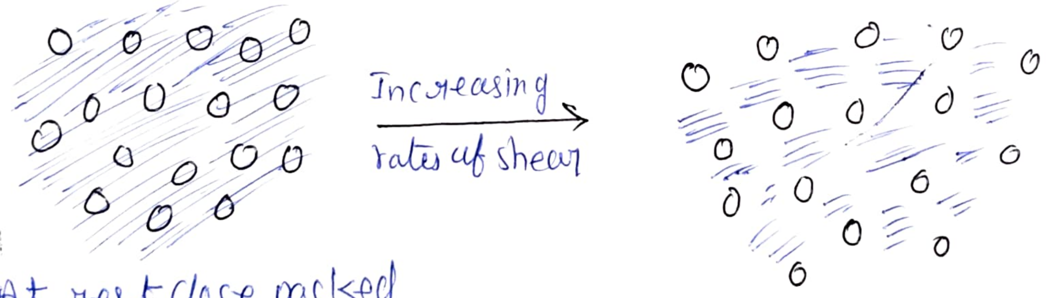
⇒ when the stress is removed, the system returns to its initial state of fluidity.

eg. suspensions containing high concentration of solids (>50%), deflocculated particles.

- suspension of starch in water.

Kaoline 12% or Zinc oxide 30% in water.





At rest close packed minimum void volume sufficient vehicle relatively low consistency

open packed high void volume insufficient vehicle relatively high consistency.

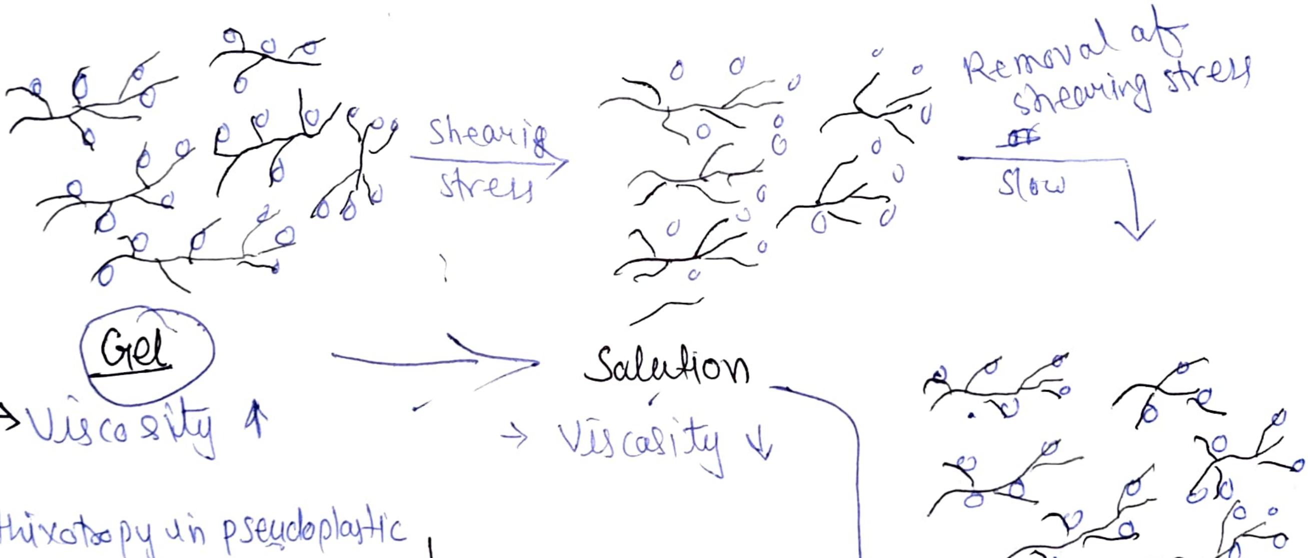
Ⓑ Time dependent
- Thixotropy
- Rheopexy

① **Thixotropy** :- Thixotropy is defined as an isothermal and comparatively slow recovery, on standing of a material, of a consistency lost through shearing.

⇒ this property exhibit by some non-newtonian pseudoplastic fluids because these fluids show change in viscosity when we apply shear on it.

Thixotropy < Thixo ⇒ stirring / shaking
Tropy ⇒ change

⇒ eg. Polymer (HPMC, CMC) in water (gel) etc.
(↳ hydropropyl methy cellulose)



→ thixotropy in pseudoplastic system.

⇒ Hysteresis loop – It is the up and down curve of thixotropy system.

⇒ Negative thixotropy :-

↳ also known as antithixotropy.

→ In this thixotropy, viscosity of system is increased on applying shearing stress and when we remove shearing stress it regain its viscosity.

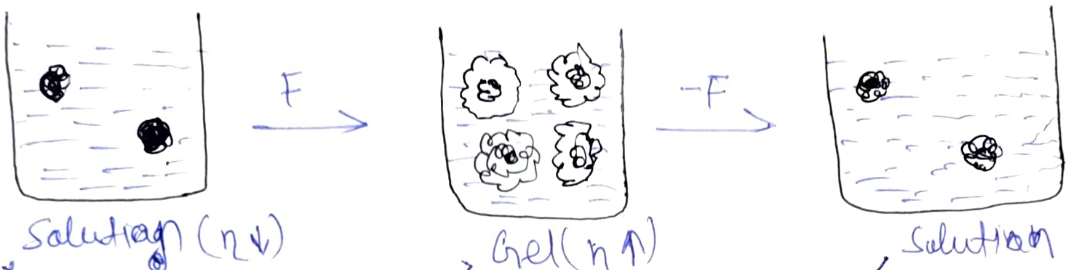
eg. Flocculated system (suspension containing low solid content)

→ Magnesia magma -

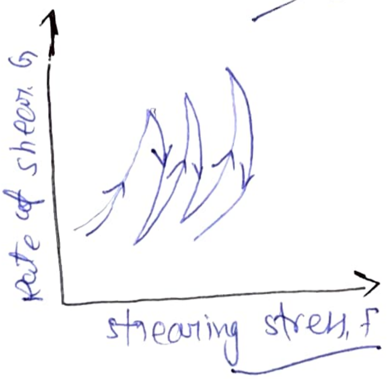
[Solution] $\xrightarrow[\text{stress}]{\text{Shearing}}$ [Gel] $\xrightarrow{\text{Removal of stress}}$ [Solution]

Viscosity(↓) → Viscosity(↑) → Viscosity(↓)

✓

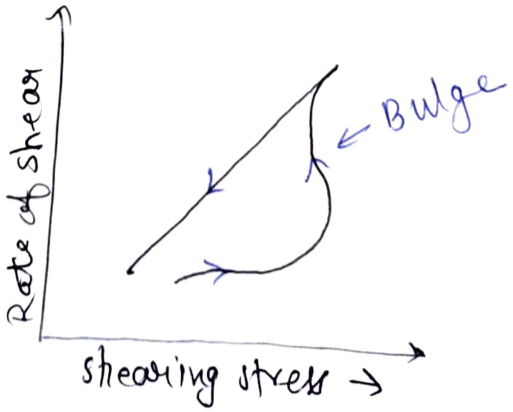


→ Negative thixotropy Rheogram.



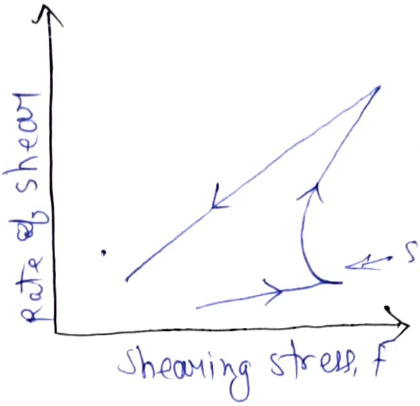
• **Bulges** :- substance which can swell in presence of water give a bulge

eg Bentonite gel (magma) 10-15 % w/v



⇒ **Spurs**:- In some highly structured thixotropy material, the bulged curve actually develop into spur eg. procain penicillin gel for injection in 2% carboxymethyl cellulose solution (cmc).

⇒ this value represents as (spur value) sharp point of structural breakdown at low shear rate



Thixotropy in formulation:-

A well formulated thixotropic suspension will not easily settle in the container and it will become fluid by shaking and easy to dispense.

⇒ Thixotropy is an important property in liquid pharmaceutical system.

⇒ the greater the thixotropy, the higher is the physical stability.

⇒ Rest → during storage suspension become gel & more stable

→ thixotropic properties eg → creams, ointments pouring of lotions from container etc.

eg. Procaine penicilline in water.

Determination of Viscosity :-

① Capillary viscometer
(ii) Falling ~~sphere~~ sphere viscometer
(iii) Rotational viscometer.

Viscometer

Single point
At a single rate of shear.
one point on the curve
Equipment:
Ostwald viscometer
Falling shere viscometer
Applications:
Newtonian fluid

multi point
several rates of shear
many points on the curve
Equipment:
Cup and bob } Rotational
Cone & plate } Viscometer
Applications:
non-Newtonian fluids
Newtonian fluids.

⇒ Several methods are available for the measurment of viscosity. A few of these are (as per BP)
Liquid paraffin → tube viscometer
Light liquid paraffin → tube viscometer
Dextran

~~Viscosit~~
Viscometer :- These are those devices or equipment, which is used to measure viscosity.

① ~~Cappi~~ Capillary Viscometer :-

Ostwald viscometer is mostly used in capillary viscometer.

→ Also known as U-tube viscometer.

⇒ It is mostly used for Newtonian fluids.

→ Apparatus :-

→ It consist of U- shaped glass tube.

→ Consist 2 bulb.

→ One section tube will be apply on tube 2.

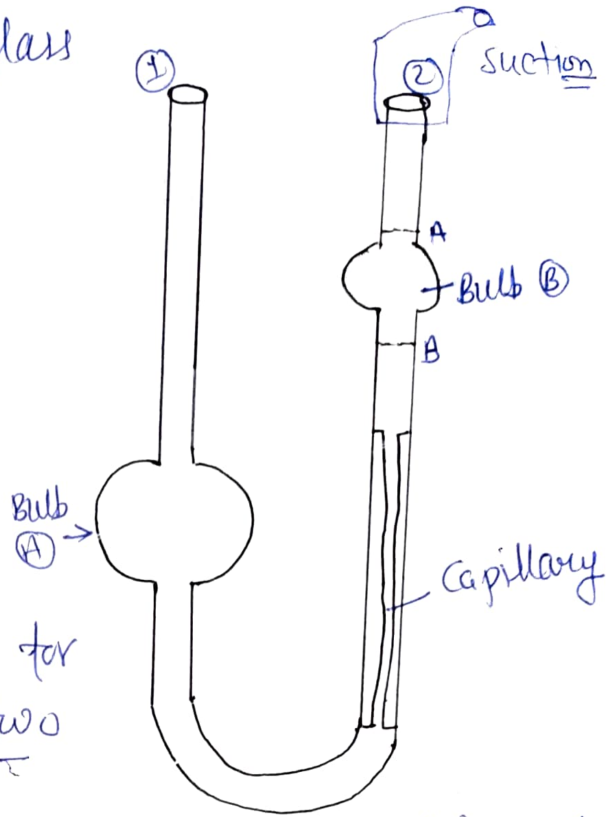


Fig. Capillary viscometer.

Principle :-

When a liquid flows by gravity, the time required for the liquid to pass between two marks (A & B) through a vertical capillary tube is determined. The time of flow of the liquid under test is compared with the time required for a liquid of known viscosity (usually water). The viscosity of the unknown liquid (η_1) can be determined using equation —

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

Where,

ρ_1 = density of unknown liquid (kg/m³)

t_1 = time of flow of unknown liquid, s

ρ_2 = density of known liquid, kg/m³

t_2 = time of flow of known liquid, s.

η_2 = viscosity of known liquid, Pa·s.

η_1 = viscosity of unknown liquid.

Method :-

⇒ Firstly viscometer is fixed to a stand in vertical position.

⇒ Now, take one fluid (standard fluid) which we known their viscosity and density.

⇒ Filled this in bulb A through tube 1.

⇒ Now suck this fluid through tube 2 ~~of~~ upto mark A ~~to~~ of the bulb 2.

⇒ Now, note the time taken to reach liquid at mark B ~~&~~ from A.

⇒ Note down all reading and now clean the viscometer.

⇒ Now, take another fluid (which we have ~~to~~ determine viscosity).

⇒ Now, do same as liquid and note down all reading and calculate using ~~the~~ above equation.

② Falling Sphere Viscometer :-

- Also called as Hoeppler Viscometer.

→ Based on the principle of stokes low.

$$\frac{(8\ h_8}{(\rho_s - \rho_8)\ 5t}$$

Apparatus:

- Consists of a glass tube which is filled by test viscous liquid.
- Tube is enclosed by a constant temperature jacket in which water is circulate around the tube.
- Also consist a glass/steel ball.

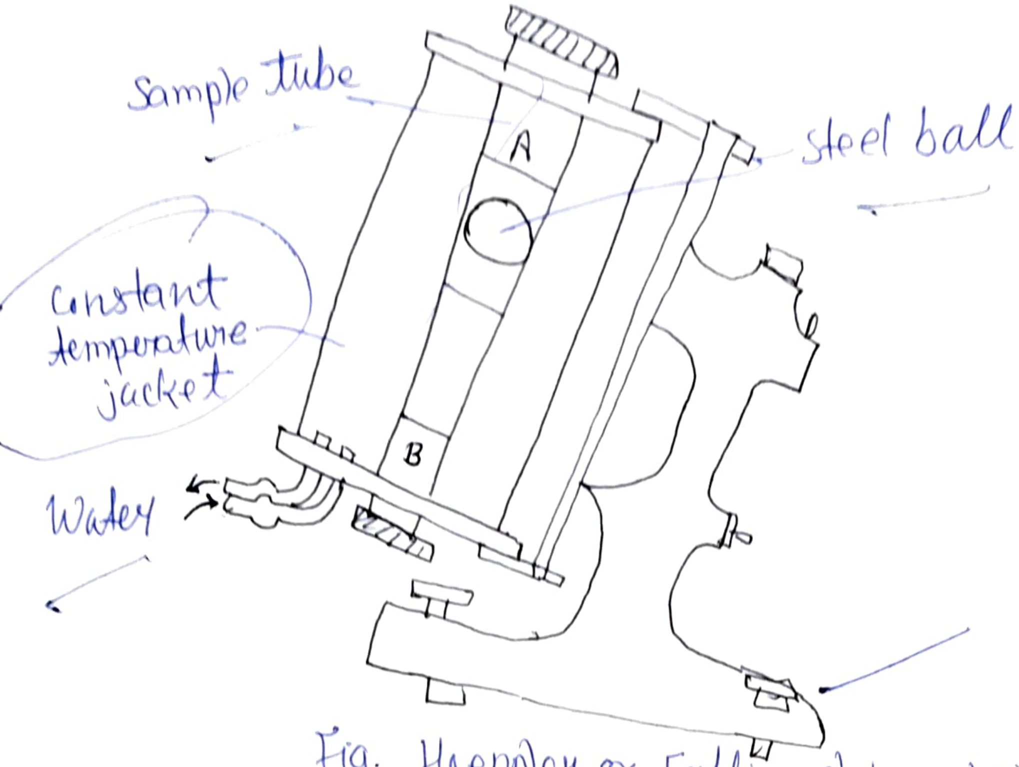


Fig. Hoeppler or Falling sphere Viscometer.

Method:

- Firstly fill the test liquid in ~~ey~~ tube.
- maintain temperature constant.
- Now, allow the ball to fall down and record that time.
- This process is repeated several times to obtain concurrent results.

⇒ The viscosity of Newtonian liquid is calculated from equation—

$$\boxed{\eta_1 = t\,(S_b - S_f)\,B}$$

Where,

t = time taken for the ball to fall b/w two points.

S_b = Specific gravity of the ball

S_f = specific gravity of test fluid.

B = Constant for a particular ball (N/m²)(Pa)

* For better results, select a ball which takes the not less than 30 seconds to fall between the two marks.

Rotational Viscometers

These viscometer are used for both Newtonian and Non Newtonian fluids.

→ It is of various type, we take most common viscometer for it.

→ Cone and Plate Viscometer:-

↳ Also known as absolute viscometer.

Apparatus -

- It consist of flat stationary plate and a wide angle rotating cone is placed centrally above it

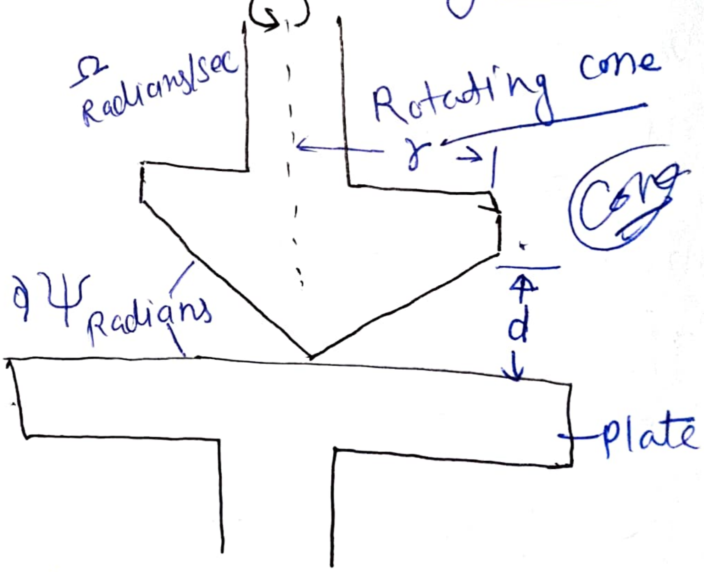


Fig. Principle of Cone & Plate viscometer

Method :-

- The sample is placed at centre of stationary plate and then it is raised into the position under the cone.
- Now, the sample is sheared in narrow gap between stationary plate and rotating cone.

☆ For better results, select a ball which takes not less than 30 seconds to fall between the two marks.

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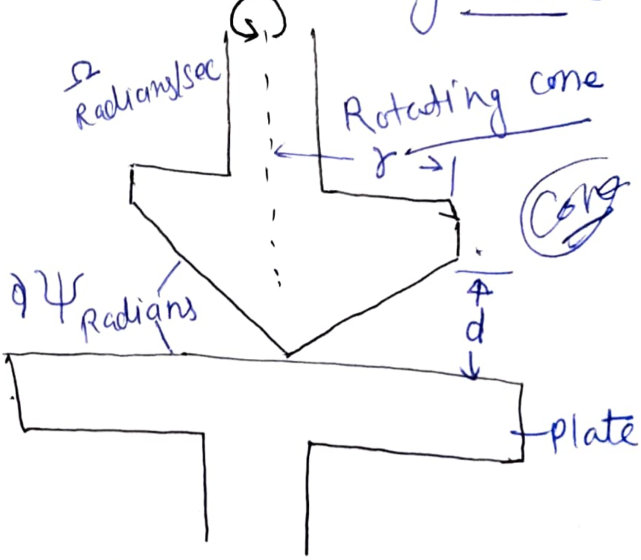


Fig. Principle of Cone & Plate viscometer

Method :-

- The sample is placed at centre of stationary plate and then it is raised into the position under the cone.
- Now, the sample is sheared in narrow gap between stationary plate and rotating cone.

→ Now, the rate of shear in RPM is increased or decreased.

→ Torque is produce on the cone which is measured-

Formula-

$$\boxed{\eta = C\frac{T}{v}}$$

Where,

η = viscosity of test liquid

C = Constant

T = Torque

v = speed of cone (RPM).

⇛ Deformation of Solids :- (Compaction)

It is defined as change in the size and shape of a solid.

Compaction:- Compaction of a powder is ~~steff~~ referred to a situation in which the powder is subjected to some level of mechanical force.

Compactibility ~~of~~ of a powder is defined as the ability of a powdered material to get compressed into a tablet of specified tensile strength.

Compression is a process of reduction in the bulk volume of the material as a result of displacement of the gas phase.

Compressibility of a powder is defined as the ability to decrease the volume of the powder when pressure is applied.

Consolidation; is an increase in the mechanical strength of bed of powder when subjected to rising compressive force resulting in particle-particle interactions.

Application:

⇛ The compaction effects and related forces are important in the manufacture of tablets.

⇛ It is helpful in the handling and filling of granules in hard gelatin capsule.

⇛ Essential for required bioavailability of drugs from a tablet, the effect of compressional pressure on the drug dissolution behaviour is essential.

Stress(σ) :- It is a force which we applied on solid to deform it.

"OR"

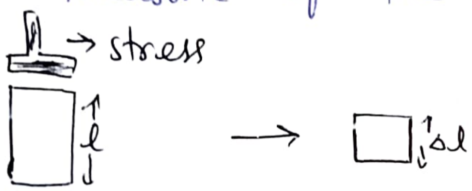
It is the ratio of the force (F) necessary to produce deformation to a change in the area, (ΔA)

$$\boxed{\text{Stress}(\sigma) = \frac{F}{\Delta A}}$$ ✓

- **Strain(z):** It is the deformation of solid which we get after applying shear stress.

"OR"

It is the measure of the amount of deformation.



then

$$\boxed{\text{Strain}(z) = \frac{\Delta l}{l}}$$ ✓

Types of Deformation :-

Basically the particle deformation are two types –

① Elastic deformation ✓

② Plastic deformation ✓

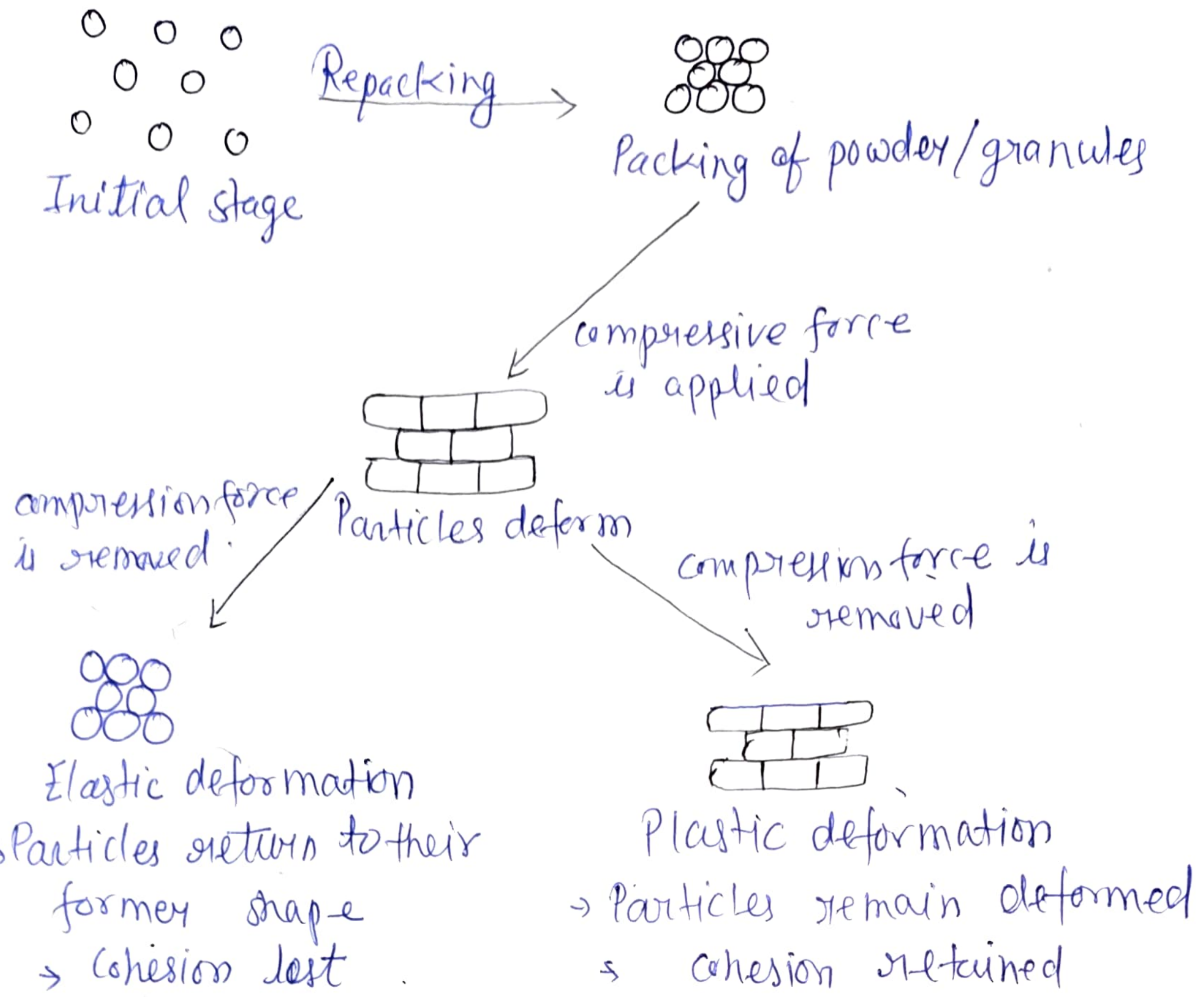


Fig: Deformation (Plastic & Elastic) of particles during compression.

① Elastic deformation:

It is a reversible process.

- when stress is applied, solid get deformed but the material return to its original shape when force is removed.

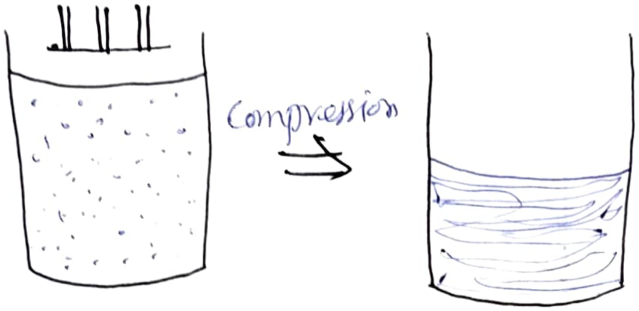
eg Rubber, metals, polymer, acetyl salicylic acid.

② Plastic deformation:- ~~It~~ is ~~irresible~~ irreversible process.

- when stress is applied, solid get deformed but the material does not return to its original shape when force is removed.

Heckle Equation:-

- It is most useful method for estimating the volume reduction under the compression pressure in pharmacy.



- It follow first order kinetics, where the pores in the powder are the reactant and the densification of the powder bed as the product.

Formula - $\boxed{\log \frac{1}{(1-D)} = KP + A}$

Where,

D = Relative density of powder
P = Pressure
K = Constant (for powder)
A = Constant (for machine)

- **Porosity** - $\boxed{E = \frac{V_p - V}{V_p}}$ $\varepsilon = 1 - \frac{V}{V_p}$

where,

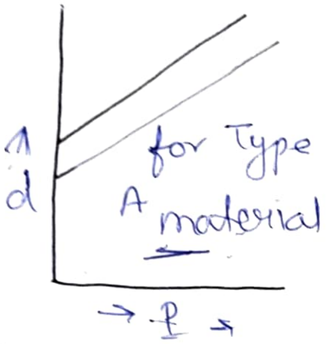
V_p = Volume at any applied load
V = Volume at theoretical zero porosity

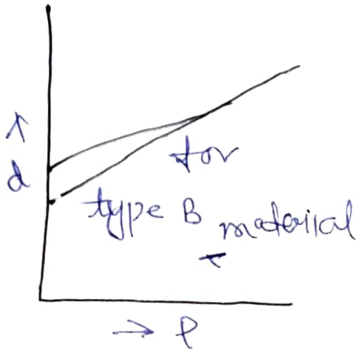
- used to check porosity.
- used for powder mixture.

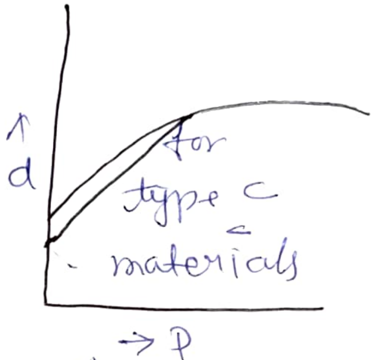
plots or curve

- **Heckel plots** - Density Vs Applied pressure

→ It can be affected by the time of compression, the degree of lubrication and the size of the die.







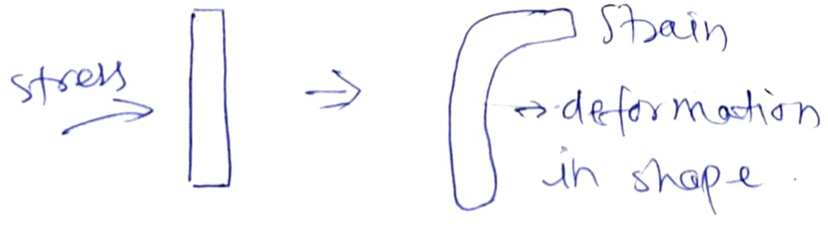
- Soft and readily undeep plastic deformation
  eg - sodium chloride
- Seen in harder material
  eg - Lactose
- Showing an initial steep linear region which become superimposed and flatten out as applied pressure.

Elastic Modulus

It is the ratio of stress to strain.

$$\text{Elastic modulus (Em)} = \frac{\text{stress}}{\text{strain}}$$

- The elastic modulus determines the amount of force (stress) required per unit deformation.

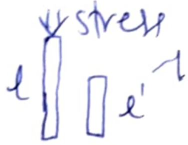


$$E_m = \frac{\text{Amount of force}}{\text{Change in shape (in angle)}}$$

- A material with large elastic modulus have less deformation.
- A material with small elastic modulus have more deformation.

Elastic Modulus

Young's Modulus
↳ Length



strain = l − l'

Bulk Modulus
↳ Area

strain = A − A'

Stress/Strain m.
↳ Angular

strain = θ − θ'