UNIT-2

Rheology

Rheo means to flow.

Rheology is the branch of science that deals with the deformation and flow of matter (solids & liquids)

Importance of Rheology

(1) Formulation of medicinal and cosmetic creams.

(2) Formulations of emulsions, suspensions, etc.

(3) Fluidity of solutions for injections.

(4) Squeezing of a paste from a tube.

(5) Passage of a liquid to syringe needle.

(6) In manufacturing of dosage forms.

(7) Syringibility of medicine, the pouring of liquids from containers, all depends on flow behavior of dosage forms.

Viscosity

→ Viscosity is the measure of internal friction of a fluid.

↓ A liquid flow in layers one above the other. And this friction occurs between these layers.
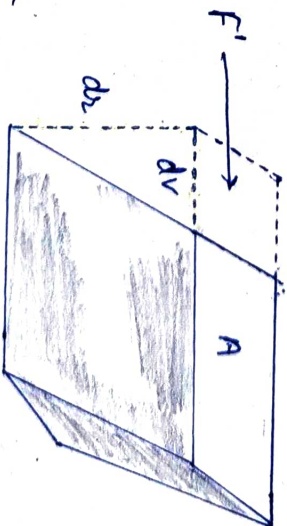
→ The greater the friction, the greater the amount of force required to cause the movement between the layers, resulting in the flow. This force applied is called shear.

Basic terminology

Shear stress (F):

It is the force applied per unit area to make liquid flow.

$$F = \frac{f'}{A}$$

Rate of shear (G) → It is the difference in velocities (dv) between two layers of liquids which are separated by distance (dr)

$$G = \frac{dv}{dr}$$

Newton's Law of Flow

Rate of shear is directly proportional to shear stress.

Shear stress ∝ Rate of shear

$$\frac{F'}{A} \propto \frac{dv}{dr} \Rightarrow \frac{F'}{A} = \eta \frac{dv}{dr}$$

$$[F = \eta G] \Rightarrow [\eta = \frac{F}{G}]$$

where, η = coefficient of viscosity.

F = shear stress

G = rate of shear

Thus,

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

Kinematic Viscosity

It is the viscosity of the liquid divided by its density (δ)

$$\text{Kinematic viscosity} = \frac{\eta}{\rho}$$

stokes and centistokes are the units of
(S)
kinematic viscosity.

Now, flow of liquids is of two types;

(1) Newtonian system of flow.
(2) Non-newtonian system of flow.

Newtonian System

Newtonian fluids are those which follows Newton's law of flow. Newtonian fluids show a linear relationship between shearing stress and rate of shear.

The graph shows that the fluid flows continuously without getting affected by the forces acting on it.
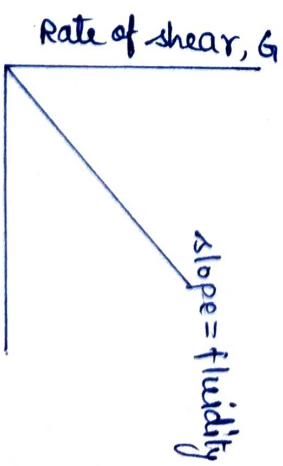
One of the best example of Newtonian fluids is water which flows continuously irrespective of being stirred or mixed at high speeds.

Other examples— chloroform, syrups, glycerine

Rate of shear, G

slope = fluidity

Shearing stress, F

Effect of temperature on viscosity

→ With increase in temperature, the system acquires thermal energy and eases the breakdown of cohesive forces between the molecules of the liquid. This decreases the viscosity of liquid.

$$\left[\eta \propto \frac{1}{T} \right] \Rightarrow \left[\eta \downarrow = T \uparrow \right]$$

→ But in gases, the viscosity increases with increase in temperature.

$$\left[\eta \propto T \right] \Rightarrow \left[T \uparrow = \eta \uparrow \right]$$

The relation between viscosity and temperature may be expressed as:

$$\left[\eta = A e^{E_V / RT} \right]$$

where, A = constant depending upon molecular weight and molar volume

E_V = Activation energy required to initiate the flow b/w the molecules.

Non-Newtonian Systems

A non-newtonian fluid is the one whose viscosity is variable according to the applied shear stress. They do not follow Newton's law of flow.

The relationship between 'F' and 'G' is not constant.

If a non-newtonian fluid is hit suddenly with a good amount of force, it behave more like a solid rather than a liquid. In case, if the force gently applied, e.g., on inserting finger slowly, the fluid remains a fluid.

Examples— starch in water, or sand.

Types of Non-Newtonian Flow

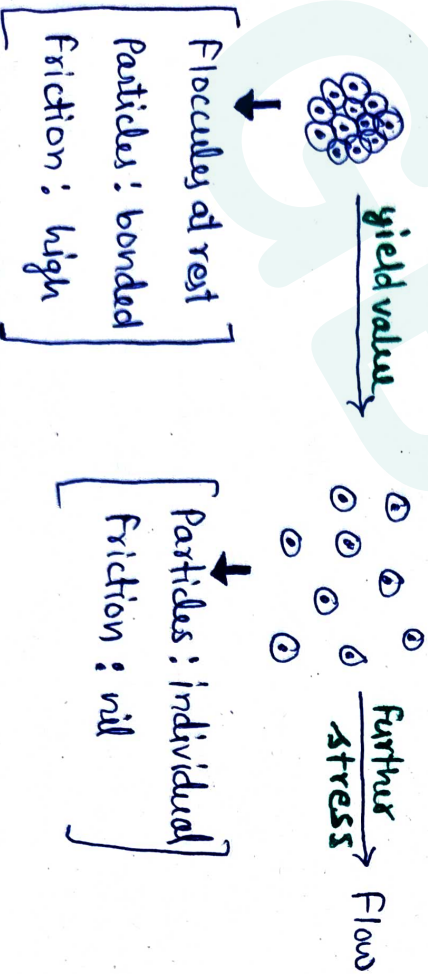Depending upon the pattern of consistency curves, there are of following three types:

(1) Plastic flow
(2) Pseudo-plastic flow
(3) Dilatant flow

Plastic Flow

In plastic flow, when the shear stress is applied, there is no change in the rate of shear initially, but only until shear stress reaches <u>yield value</u>.

Once the shear stress reaches above yield value, the plastic flow is considered similar to Newtonian flow.

<u>yield value</u> → It is the shear stress needed to break the contact (frictional forces) between the particles, so that they act individually.

yield value

Flocculers at rest
Particles: bonded
Friction: high

further stress → Flow

Particles: individual
Friction: nil

Mechanism

Particles aggregate to form flocculs when the system remains in a steady state.

shear stress equal to yield value is required to break the flocculs into individual particles.

And when the shear stress is increased further than yield value, flow starts.

Materials possessing plastic flow are generally known as Bingham bodies.

Bingham was a scientist who gave an equation to describe the quantitative behavior of these materials.

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

where, f = shear stress; f = yield value
G = Rate of shear
U = Plastic viscosity

Rate of shear, G

shear stress, F

slope = mobility

yield value
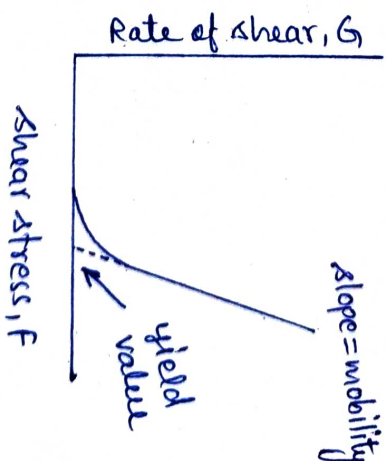
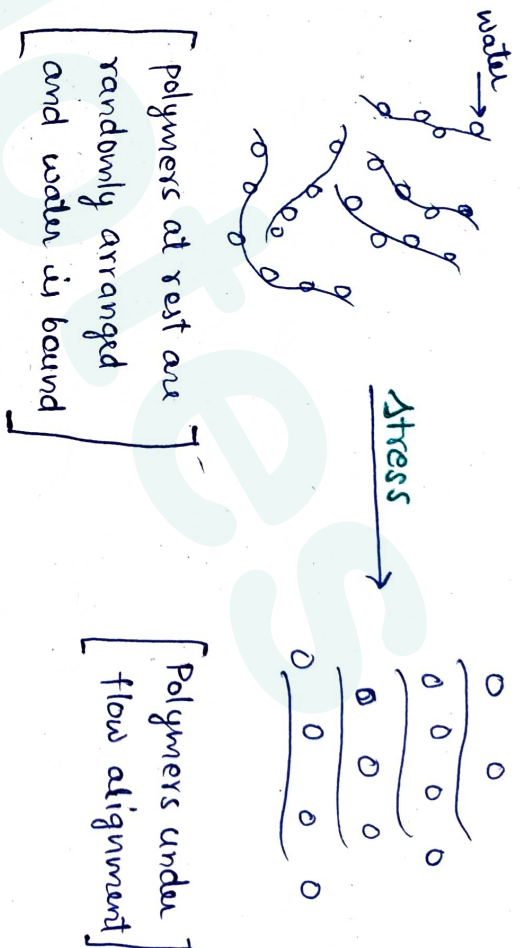Slope of rheogram is known as mobility. And, plastic viscosity (U) can be defined as the reciprocal of mobility.
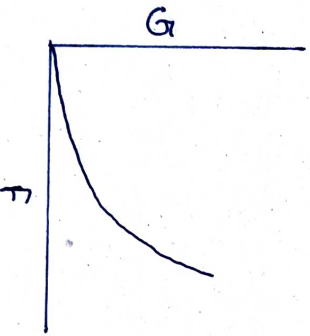
* Rheogram is a plot of shear rate (G) as a function of shear stress (F). Rheogram is also known as consistency curve, or flow curve.

Pseudo-Plastic Flow

For a pseudo-plastic flow, the consistency curve starts from the origin. On increasing the shear stress, the rate of shear increases but results in a non-linear curve. Hence, a single value is not sufficient to describe the viscosity.

Some examples of pseudo-plastic flow are:
(1) Sodium alginate in water.
(2) Tragacanth in water.
(3) Sodium cmc in water.
(4) Methylcellulose in water.
(5) Acacia in water.
(6) Ethyl cellulose in water.

(graph: G on vertical axis, F on horizontal axis)

Polymers at rest are randomly arranged and water is bound

water →

↓ Stress

The following formula describes the curve of pseudo-plastic flow.

$$F^N = \eta' G$$

where, N = number given to exponent
η' = viscosity coefficient.

N remains more than 1 in case of pseudo-plastic fluids. The value of N increases when the flow of material becomes non-Newtonian.

Polymers under flow alignment

Dilatant Flow

In dilatant flow, the viscosity increases with increase in shear stress. And when the stress is removed, a dilatant system returns to its original state of fluidity.
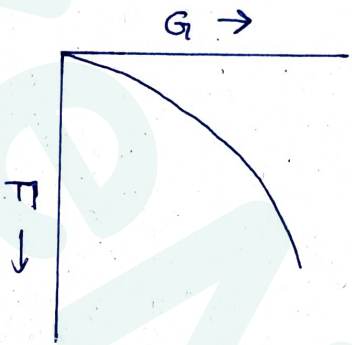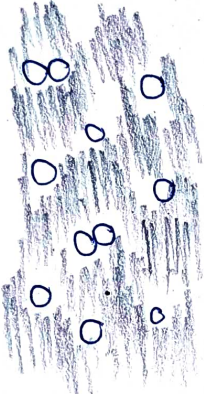
Examples:

(1) Suspension of starch dissolved in water.

(2) Suspensions having high concentration of solids (>50%) consisting of deflocculated particles.

(3) Zinc oxide (30%) in water, 12% kaolin in water.
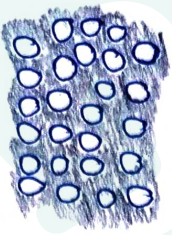
Increase shear
↓

close-packed particles
minimum void volume
sufficient vehicle
low consistency

open-packed (dilated)
increased void volume
insufficient vehicle
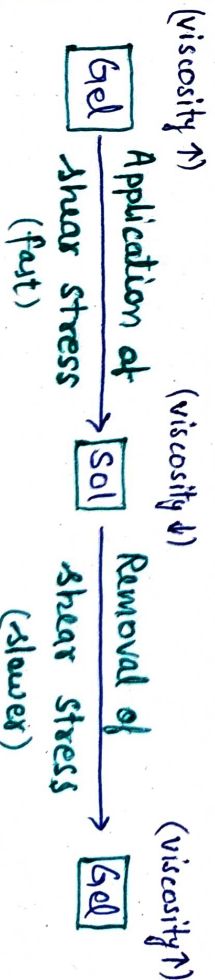high consistency

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Thixotropy

→ Thixotropy can be defined as the isothermal recovery of a system whose consistency is lost by applying a shear stress. But, this process is relatively slower than the change.
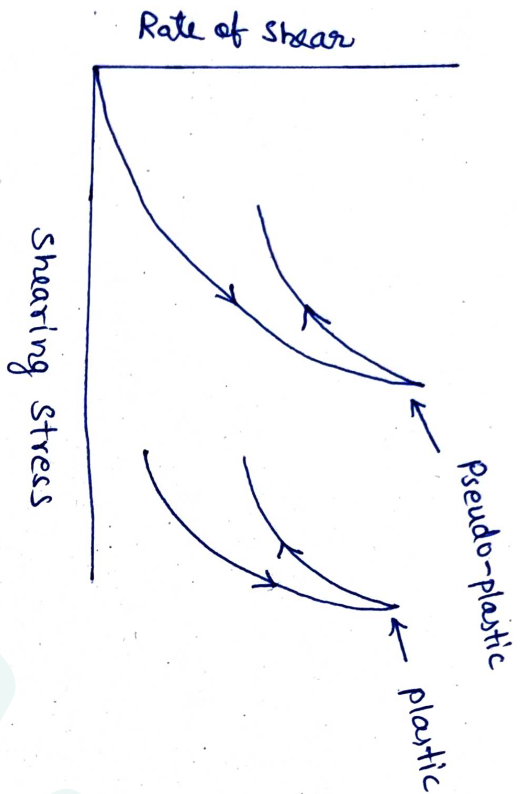
This whole process is isothermal (same temperature throughout).

→ Thixotropy is shown by non-Newtonian fluids (plastic, pseudo-plastic and dilatant systems).

1) Thixotropy in Plastic and Pseudo-Plastic Systems

At any given temperature, increasing the shear stress gradually decreases the viscosity of these systems. When this shearing stress is removed, systems re-gain their viscosity after a certain time-lag. Example,

Gel (viscosity ↑) → Application of shear stress (fast) → Sol (viscosity ↓)

Sol → Removal of shear stress (slower) → Gel (viscosity ↑)

A rheogram for such systems give a hysteresis loop. Both the curves do not superimpose each other.

Examples -

(1) Plastic - Bentonite gel, petrolatum

(2) Pseudo-plastic - dispersion of synthetic suspending agents.

(2) Thixotropy in Dilatant Systems

At any given temperature, increasing the shear stress increase the viscosity of dilatant systems. However, they re-gain the viscosity when the shearing stress is removed.

Rate of shear
Shearing Stress

← Pseudo-plastic
← Plastic
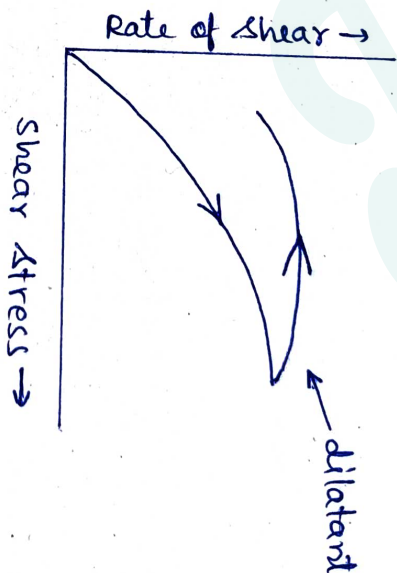
Anti-thixotropy

This is also known as negative thixotropy. In anti-thixotropy, there is an increase in viscosity on applying shear stress but re-gains its viscosity after the shear stress is removed. Unlike thixotropy, the down-curve on rheogram shows an increase in consistency rather than decrease.

Rate of shear →
Shear stress →
← dilatant

(viscosity ↓)
| Sol |
Application of Shear stress

(viscosity ↑)
| Gel |
Removal of Shear stress

(viscosity ↓)
| Sol |

e.g:- when a flocculated system which contains large number of deflocculated particles and less floccule, is applied by shear stress, the number of flocculs increases, increasing the viscosity. At regains the viscosity after removal of stress.
Example- Magnasia Magma
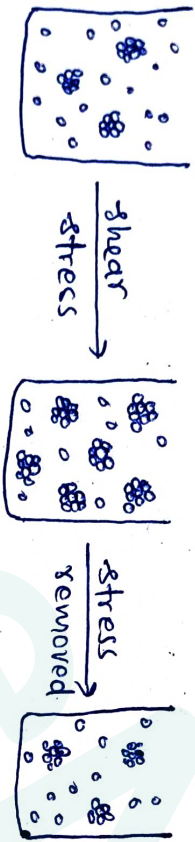
The viscosity obtained on the down-curve at any given shear stress is greater than that one obtained on the up-curve.

Rate of shear, G

Shear stress, F

→ Thixotropy in Formulation

→ Thixotropy is a desirable property in liquid pharmaceutical systems that ideally should have a high consistency in the container & spread easily

→ For example, a thixotropic suspension which is well-formulated will not easily settle down in the container, will become fluid when shaken, and will maintain its stability for a longer time

→ Thixotropic properties maintain stability in formulations such as emulsions, creams, lotions, parenteral suspensions, and ointments.

Determination of Viscosity

Measurement of fluid viscosity is done by an instrument called viscometer.

Following types of viscometers are used:
(1) Capillary viscometers
(2) Falling sphere viscometer
(3) Rotational viscometer

Capillary Viscometer

The low viscosity of Newtonian fluids can be accurately measured by capillary viscometers. It is also known as U-tube viscometer. We will understand the working of capillary viscometer by ostwald's U-tube viscometer.

Procedure

(1) Through the left arm, the liquid is introduced into the viscometer till it reaches the level 'A'.

(2) The viscometer is fixed at a desired temperature.

(3) The volume of sample is adjusted and the liquid is blown or sucked into the right arm till it reaches the just above the 'B' mark.

(4) Lastly, the pressure or suction is released and time taken by the liquid to fall from mark 'B' to 'C' is noted.

A
B
C
Capillary tube
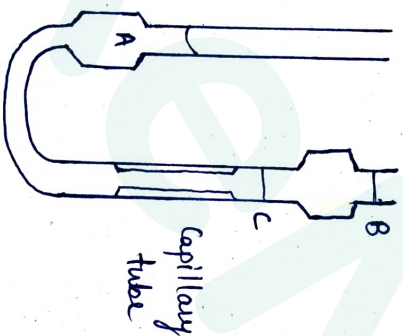
Calculation

The experiment is first conducted with water and later with the test fluid (for which we have to calculate viscosity), to determine the relative viscosity with respect to water.

$$\text{Relative viscosity} \Rightarrow \frac{n_1}{n_2} = \frac{\rho_1 t_1}{\rho_2 t_2}$$

where,

t_1 = time required by test liquid (unknown)

t_2 = time required by water (known)

ρ_1 = density of unknown liquid.

ρ_2 = density of water

n_1 = viscosity of unknown liquid

n_2 = viscosity of water.

The absolute viscosity of the test liquid can be calculated as:

Absolute viscosity = Relative viscosity × Absolute viscosity of water

Falling Sphere Viscometer

This viscometer is suitable for Newtonian systems. Stokes law is the basis for falling sphere viscometer.

Stokes law states that :- when a body falls in viscous media, it experiences a resistance which oppose the motion of fluid.

The viscometer is Hoeppler falling sphere viscometer.

Working

→ Falling sphere (or ball) viscometer consists of a glass or steel ball that rolls down in a vertical glass tube. This tube contains sample liquid at a known constant temperature.

→ The viscosity of the liquid sample is inversely proportional to the rate at which a ball falls.

→ The temperature of the tube is in equilibrium with the water present in the surrounding jacket.

→ The jacket and the tube are then turned upside-down which sets the ball at the top of the inner glass tube. The time required by the ball to fall between the two points is then measured repeatedly for several times.

calculation formula ⇒

$$\eta = t\,(S_b - S_f)\,B$$

where,

t = time (sec) for ball to fall b/w two points

S_b = specific gravity of ball

S_f = specific gravity of the fluid ⎤ at a particular temperature

B = constant for a particular ball

Rotational Viscometer

These are used for both, Newtonian as well as Non-Newtonian systems.

Rotational viscometers works on the principle that the torque required to turn an object in a fluid changes according to the viscosity of that fluid, cone and plate viscometer is one of the most commonly used rotational viscometers.

Rotating cone

Sample

stationary plate

radian/sec

d
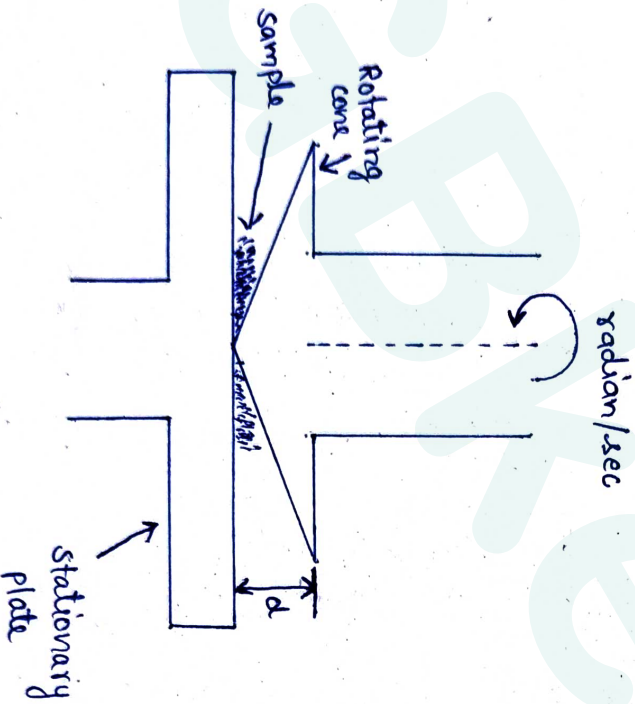
Working

→ It consists of a smooth plate and cone.

→ The sample is placed at the centre of the plate.

→ The sample is present between the narrow gap of plate and cone. The cone is rotated.

→ The torque transmitted through the sample to cone is measured, or the torque required to turn the cone is measured.

Calculation

$$\eta = k \frac{\tau}{V}$$

where,

η = viscosity of liquid

τ = torque

V = rpm

k = constant.

Deformation of Solids

Any change in the shape and size of a material is called deformation. To bring any deformation in a solid's size and shape, application of an external force is required.

The deformations in solids are of 2 types:
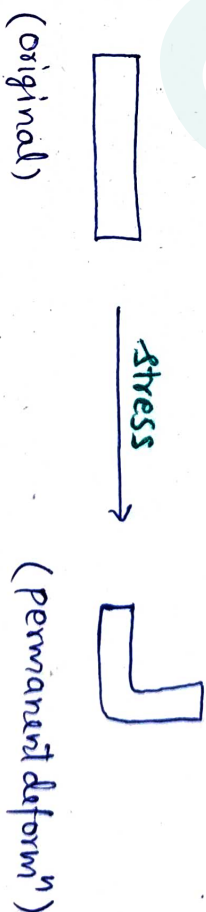(1) Elastic deformation   (2) Plastic deformation

Elastic Deformation

When the removal of net force allows a body to regain its original form, it is called elastic deformation. e.g. stretching of a spring.

Therefore, it is reversible.

[original] shape   external force   force removed   [Deformed] shape
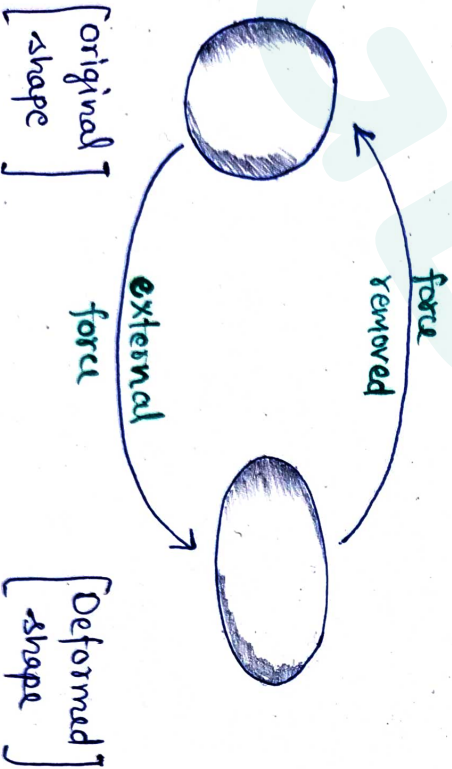
Plastic Deformation

→ It is irreversible

→ Object when applied with force initially undergoes elastic deformation which is called its elastic limit. Beyond elastic limit, it is deformed permanently (exhibits plastic behavior).

(Original)

[ ] ⟶ stress ⟶ [_] (Permanent deform")

Stress & Strain

Stress is the measure of force required to cause deformation.

$$Stress = \frac{Force}{Area} \Rightarrow \frac{P}{A}$$

A strain is the measure of the degree of deformation.

$$strain = \frac{Change\ in\ length}{Original\ length} = \frac{\Delta L}{L}$$

The ratio of stress to strain is known as elastic modulus.

Elastic Modulus (Young's Modulus)

The elastic modulus is the measure of the stiffness of a material. In other words, it is a measure of how easily any material can bend or be stretched.

$$\text{Elastic modulus} = \frac{\text{stress}}{\text{strain}}$$

→ A low elastic modulus of a material means, it can be easily deformed under an applied stress. e.g. rubber band

→ Hooke's law describes the stress-strain relationship for elastic deformation.

$$\boxed{\sigma = E \cdot \varepsilon}$$

where,

σ = Applied stress

E = Young's Modulus of Elasticity

ε = strain $\left[\varepsilon = (l - l_0) \, l_0 \right]$

l_0 = original length

l = stretched length

Applications of Elastic Modulus

→ To calculate how much a material will stretch and also how much potential energy will be stored.

→ to determine how a given material will respond to stress.

→ Elastic Modulus is used to characterise biological materials like cartilage and bone.

Heckel Equation

The Heckel equation is the most useful method for estimating the volume reduction under the applied compression pressure.

Heckel measured that decline in the voids (powder) follows the first order kinetics when a powder is compressed, it will reduce in volume. Heckel equation is used to estimate that reduction of volume.

The Heckel equation is expressed as;

$$\ln\left[\frac{1}{1-D}\right] = KP + A$$

where,

D = relative density of a powder

P = Applied pressure

constant K = measure of plasticity of a compressed material (slope)

constant A = related to particle-re-arrangement and fragmentation (intercept)

Types of Materials on basis of Heckel plots

| Type-A | Type-B | Type-C |

Type-A

Soft materials,
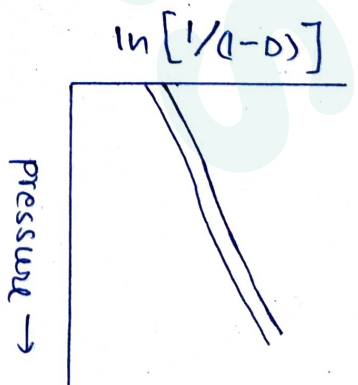Readily
undergo
plastic
deformation

Type-B

Harder,
first brittle
fracture
then plastic
flow

Type-C

Rearrangement
stage is
absent,
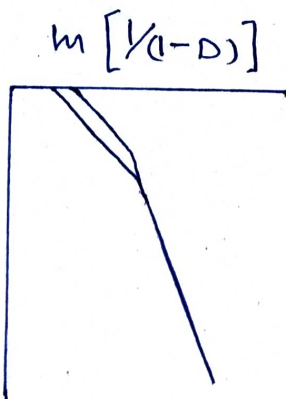densification
(density ↑)
is due to plastic
deformation.

Type-A Materials

→ linear relationship with plots remaining parallel

→ indicative of plastic deformation

→ e.g. sodium chloride

Type-B Materials

→ initial curved followed by straight line

→ indicate that particles are fragmenting at early stages of the compression.

→ undergo fragmentation to provide denser packing. e.g. lactose

Type-C Materials

→ initially steep curve

→ no compaction after a point

→ e.g. starch