Rheology

- https://www.youtube.com/watch?v=Mq8RA01RMTw&index=6&list=LLuWXeHsDF17q3DX0vbmQmuA
- https://www.youtube.com/watch?v=cg616gnQlxk

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Definitions

- Rheology : is the study of Flow (liquids and semisolids)
- Viscosity: An Expression to describe the Resistance of fluids to flow(High viscosity=> high resistance to flow)

Flow:

Newtonian

Non Newtonian

Importance of rheology study

- Manufacturers of medicinal and cosmetic creams, pastes,lotions….etc must be capable of producing products with acceptable consistency and smoothness and reproducing these qualities each time a new batch is prepared.
- Rheology is involved in the mixing and flow of materials, their packaging into containers, and their removal prior to use, whether this is achieved by pouring from a bottle, extrusion from a tube, or passage through a syringe needle

Importance of rheology study

- can affect its patient acceptability, physical stability, and even biologic availability. For example, viscosity has been shown to affect absorption rates of drugs from the gastrointestinal tract.
- Rheologic properties of a pharmaceutical system can influence the selection of processing equipment used in its manufacture

Newtonian Flow

Isaac Newton

- Newton was one from the first scientists to study viscosity
- He recognized that the higher the viscosity of a liquid, the greater is the force per unit area (*shearing stress) required to produce a certain* rate of shear

NEWTONIAN'S Law OF FLOW

- Let us consider a block of liquid consisting of parallel plates of molecules as shown in the figure. (like a deck of cards)

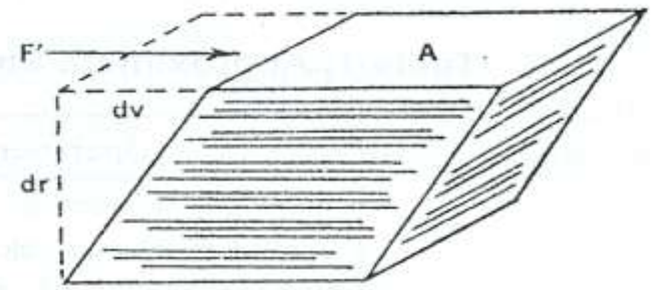
- The bottom layer is considered to be fixed in place.

- If the top plane of liquid is moved at constant velocity, each lower layer will move with a velocity directly proportional to its distance from the bottom layer

dv: Difference in velocity between two planes

dr: Extremely small distance between two planes

F`: Force A:Area

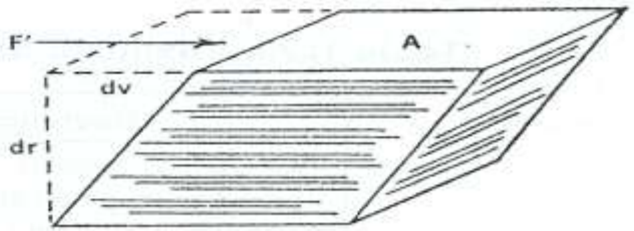


Representation of flow of liquid

Representation of shearing force acting on a block of material dv: Difference in velocity between two planes

dr: Extremely small distance between two planes

F`: Force A:Area



Representation of flow of liquid

- dv/dr : is called Shear Rate(Velocity gradient): Difference of velocity(dv) between two planes of liquid separated by extremely small distance (dr)
- Shear Rate= G=dv/dr (change in speed related to change in distance) (1/s)

- Shearing Stress: Force per Unit area=F=(F`/A)
- What is the Relation Between F`A and dv/dr
- F=F`/A=(Coefficient) x dv/dr
- This Cofficient(η) is named **Viscosity**

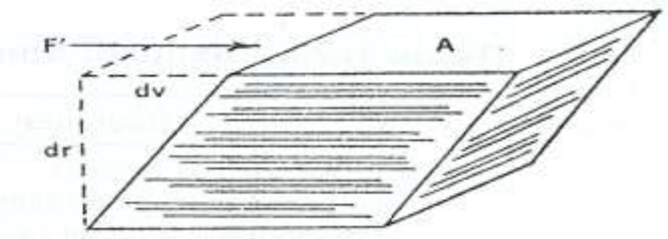
$$\frac{F'}{A} = \eta \frac{dv}{dr}$$

dv: Difference in velocity between two planes

dr: Extremely small distance between two planes

F`: Force A:Area

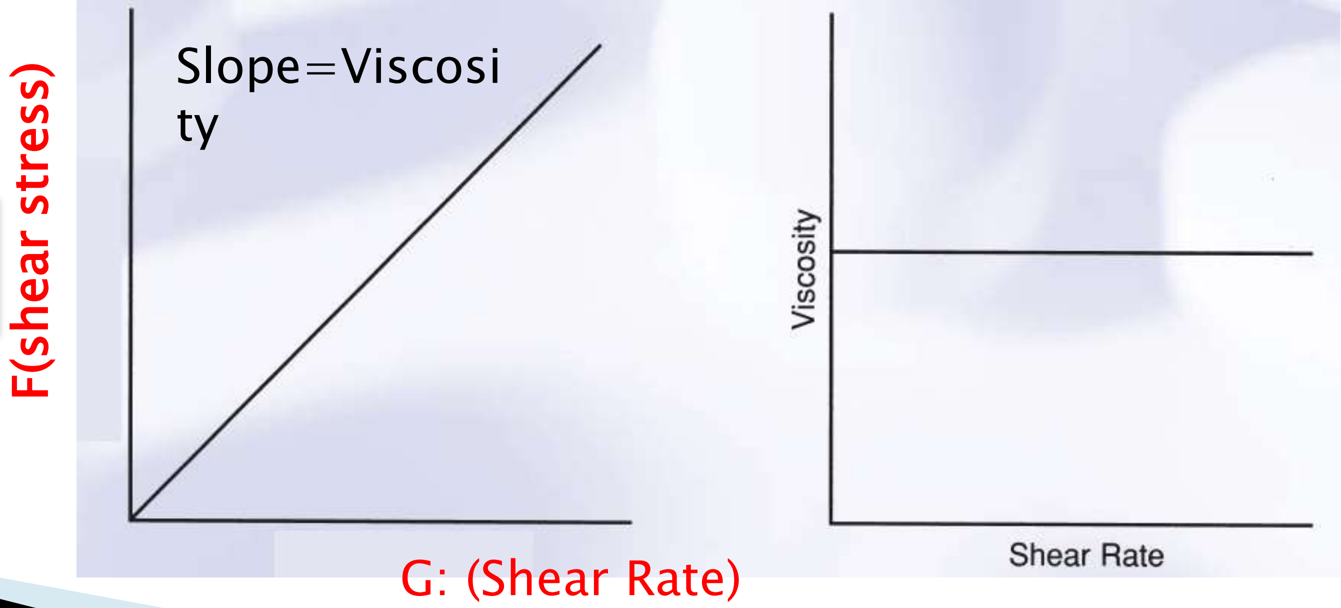
$$F=\frac{F'}{A}=\eta\frac{dv}{dr}$$



Representation of flow of liquid

- dv/dr=G: Shear Rate
- F: Shear Stress= F`/A
- **η= (F'/A)/(dv/dr)= F/G**

Newtonian Flow



Units of Viscosity

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

Poise: **The unit of viscosity is the *poise*,**

Poise definition: **the shearing force required to produce a velocity of 1 cm per second between two parallel planes of liquid, each 1 cm^2 in area and separated by a distance of 1 cm.**

- dyne sec/cm^2 or **g/(cm.s)**
- **Generaly cP: centipoise is used**

$$\eta = \frac{F' dr}{A\, dv} = \frac{\text{dynes} \times \text{cm}}{\text{cm}^2 \times \text{cm/sec}} = \frac{\text{dyne sec}}{\text{cm}^2}$$

$$\frac{\text{dyne sec}}{\text{cm}^2} = \frac{\text{g} \times \text{cm/sec}^2 \times \text{sec}}{\text{cm}^2} = \frac{\text{g}}{\text{cm sec}}$$

- **η : Viscosity, absolute viscosity, dynamic viscosity**
- **Poise**

Fluidity= 1/ **η**

Newtonian Viscosities

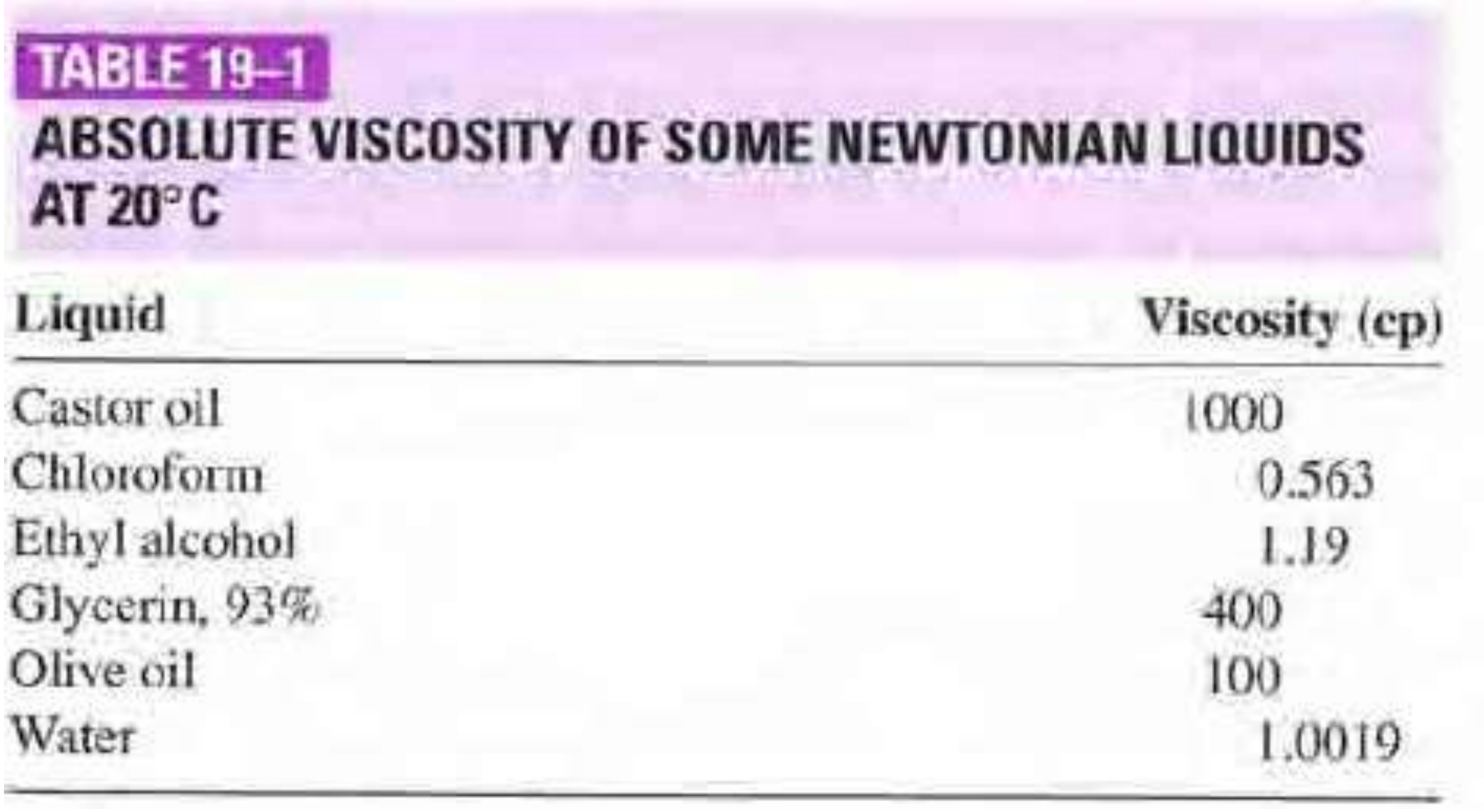


TABLE 19–1

ABSOLUTE VISCOSITY OF SOME NEWTONIAN LIQUIDS AT 20°C

Liquid	Viscosity (cp)
Castor oil	1000
Chloroform	0.563
Ethyl alcohol	1.19
Glycerin, 93%	400
Olive oil	100
Water	1.0019

Kinematic Viscosity

- The official compendia, the USP and NF, use kinematic viscosity, the absolute viscosity divided by the density of the liquid, as follows:
- Kinematic viscosity = η/ρ *(unit Stokes/centistokes)*
- *Stokes* (cm^2/s)

One stoke is equivalent to one poise divided by the density of the fluid in g/cm^3

Relative Viscosity

- Water is used as a standard for Newtonian liquid viscosity
- Relative viscosity= $\eta_{rel} = \dfrac{\text{Viscosity of Liquid}}{\text{Viscosity of water}}$
- At certain temperature

Questions

- Acetone viscosity was found to be 0.313 cp at 25°C. Its density at 25°C is 0.788 g/cm3.
- What is the kinematic viscosity of acetone at 25°C?
- b. Water viscosity at 25°C is 0.8904 cp. What is the viscosity of acetone relative to that of water (relative viscosity, ηrel) at 25°C?

A) Kinematic viscosity

- = 0.313 cp ÷ 0.788 g/cm3
- = 0.397 centipoise/(g/cm3), or 0.397 cS

B) **Relative Viscosity**

ηrel(acetone) = 0.313 cp/0.8904 cp = 0.352 (Units???).

Choice of Viscometer

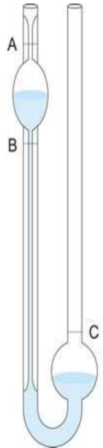
- Successful determination and evaluation of rheologic properties of any particular system depend, in large part, on choosing the correct instrumental method (Newtonian/non-newtonian)
- Because shear rate in a Newtonian system is
- directly proportional to shearing stress, instruments that operate at a single shear rate can be used.
- These —single-point instruments provide a single point on the rheogram; extrapolation of a line through this point to the origin will result in a complete rheogram

Choice of visicometer

- if the system is non-Newtonian, a single-point determination is virtually useless in characterizing its flow properties. It is therefore essential that, with non-Newtonian systems, the instrument can operate at a variety of shear rates.
- Single point viscometer: capillary, falling-sphere (single shear rate)”Newtonian”
- (multipoint, rotational instruments) can be used with both Newtonian and non-Newtonian systems cup-and-bob, and cone-and-plate viscometers.

Capillary viscometer

- *Principle :* measuring the time required for the liquid to pass between two marks as it flows by gravity through a vertical capillary tube known as an *Ostwald viscometer*
- The time of flow of the liquid under test is compared with the time required for a liquid of known viscosity (usually water) to pass between the two marks

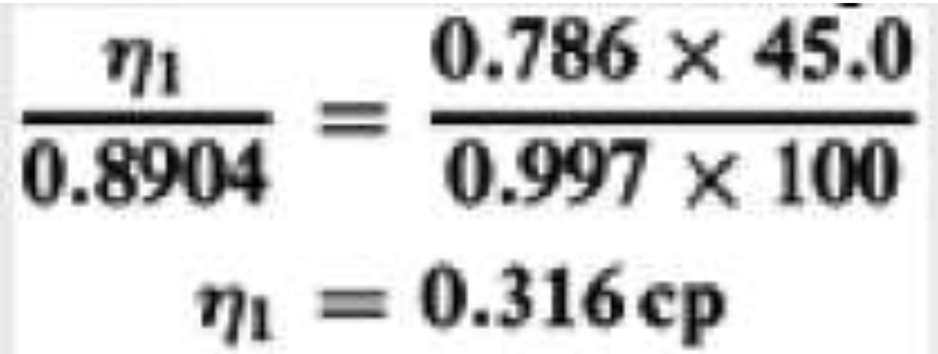


- If η1 and η2 are the viscosities of the unknown and the standard liquids, respectively, $\rho_1$and ρ_2 are the respective densities of the liquids
- and *t1 and t2 are the* ρ*respective* flow times in seconds
- the absolute viscosity of the unknown liquid, η1, is determined by substituting the
- experimental values in the equation

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

- **Viscosity of Acetone**
- Consider the viscosity measurement of acetone discussed Assume that the time required for acetone to flow between the two marks on the capillary viscometer was 45 sec and for water the time was 100 sec, at 25°C. The density of acetone is 0.786 g/cm3 and that of water is 0.997 g/cm3 at 25°C. The viscosity of water is 0.8904 cp at this temperature.
- The viscosity of acetone at 25°C how much

Solution



$$\frac{\eta_1}{0.8904} = \frac{0.786 \times 45.0}{0.997 \times 100}$$

$$\eta_1 = 0.316\,\text{cp}$$

Poiseuille's Law

- Trying to find what factors affects the flow of fluid through pipes he isolated the following factors
- 1- Pressure difference between the heads of capillary (bigger the pressure difference the faster the flow)
- 2- Length of pipe
- 3- the radius of pipe(more liquid will flow from wider pipe)
- 4- the viscosity coefficient (water flows more easily than glycerine)

Poiseuille's Law

$$\frac{dV}{dt} = \frac{\Delta p \, \pi R^4}{8 \eta L}$$

- dv/dt : Flow rate (Volumetric)”cm^3/s”
- $\triangle p$: pressure head difference between pipe ends (dyne/cm2)”Force/unit area”
- R (r): pipe radius
- η: viscosity
- L: pipe length

$$\eta = \frac{\pi r^4 t \Delta P}{8 l V}$$

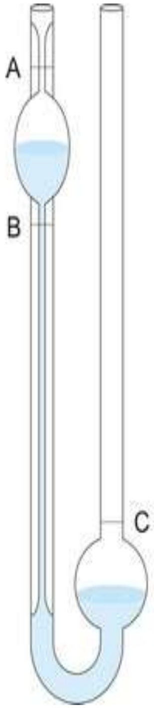
$$\eta = K t \Delta P$$

$$\frac{dV}{dt} = \frac{\Delta p \, \pi R^4}{8 \eta L} \qquad \eta = \frac{\pi r^4 t \Delta P}{8 l V} \qquad \eta = K t \Delta P$$

- The pressure head *ΔP depends on mass ρ of the liquid being measured, the acceleration of* gravity, and the difference in heights of liquid levels in the two arms of the viscometer
- Acceleration of gravity is a constant, however, and if the levels in the capillary are kept constant for all liquids, these terms can be incorporated in the constant and the viscosities of the unknown and the standard liquids can be written as

$$\eta_1 = K' t_1 \rho_1 \qquad \eta_2 = K' t_2 \rho_2$$

- The viscosity of Newtonian materials can be easily determined using a capillary viscometer, such as the Ostwald pipet, and the following relationship:
- $\eta = Kt\rho$
- Where η' is viscosity,
- k : is a coefficient, including such factors as the radius and length of the capillary, volume of the liquid flowing,,
- t is time, and
- ρ is density of the material.



Falling-Sphere Viscometer

- a glass or steel ball rolls down an almost vertical glass tube containing the test liquid at a known constant temperature
- The rate at which a ball of a particular density and diameter falls is an inverse function of the viscosity of the sample

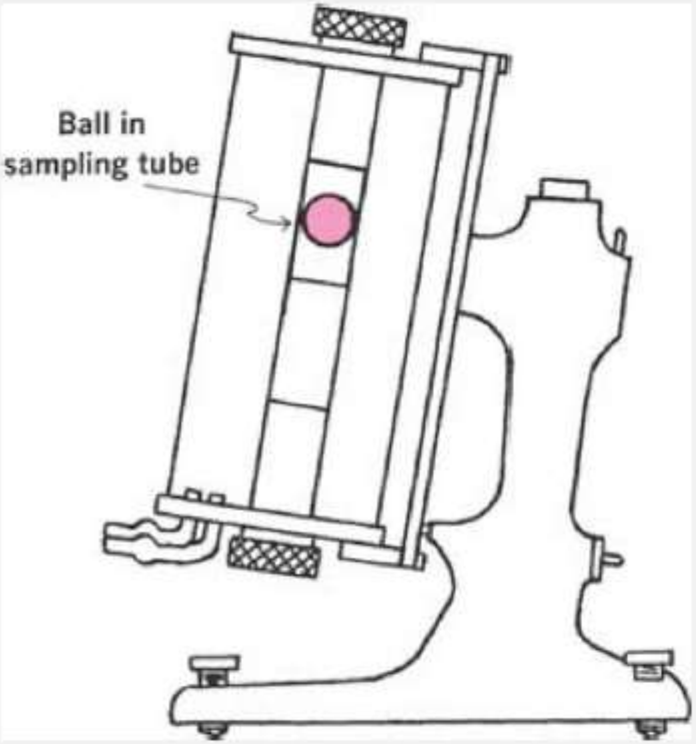


Fig. 19-13. Hoeppler falling-ball viscometer.

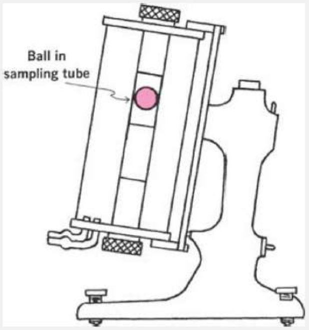


Fig. 19-13. Hoeppler falling-ball viscometer.

- The sample and ball are placed in the inner glass tube and allowed to reach temperature equilibrium with the water in the surrounding constant temperature jacket
- The tube and jacket are then inverted, which effectively places the ball at the top of the inner glass tube. The time for the ball to fall between two marks is accurately measured andrepeated several times

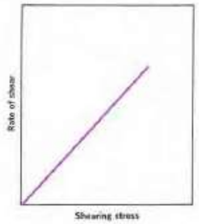
- The viscosity of a Newtonian liquid is then calculated from

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

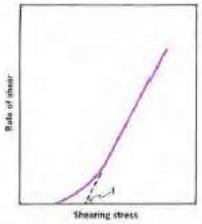
- *t is the time interval in seconds for the ball to fall between the two points*
- *Sb and Sf are the* specific gravities of the ball and fluid, respectively, at the temperature being used.
- *B is a constant for a* particular ball and is supplied by the manufacturer (material diameter)
- For best results, a ball should be used such that *t is not less than 30 sec*

Non-Newtonian Systems

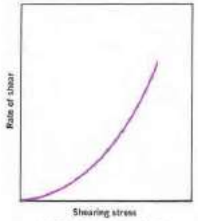
- The majority of fluid pharmaceutical products are not simple liquids and do not follow Newton's law of flow.
- Non-Newtonian behavior is generally exhibited by liquid and solid heterogeneous dispersions, emulsions, liquid suspensions, and ointments.



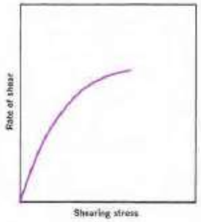
(a) Newtonian flow



(b) Simple plastic flow

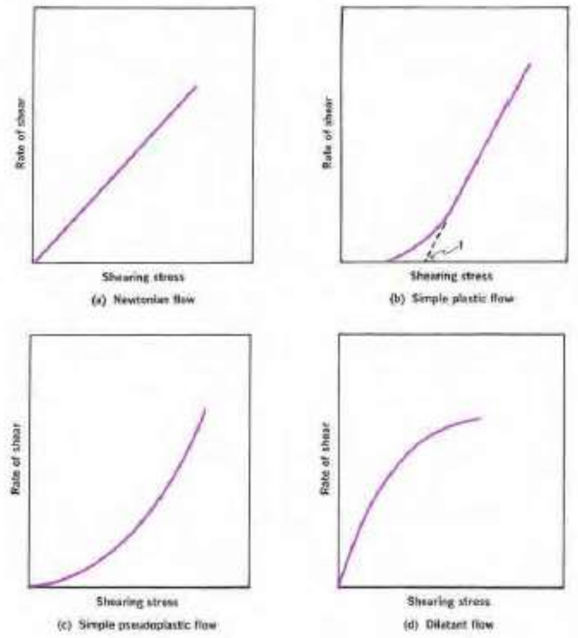


(c) Simple pseudoplastic flow



(d) Dilatant flow

Non-Newtonian flow



(a) Newtonian flow

(b) Simple plastic flow

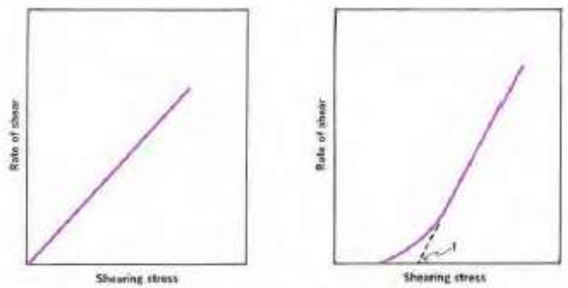
(c) Simple pseudoplastic flow

(d) Dilatant flow

- Non-Newtonian substances are those that fail to follow Newton's equation of flow.
- Non-Newtonian flow is characterized by a change in viscosity characteristics with increasing shear rates.

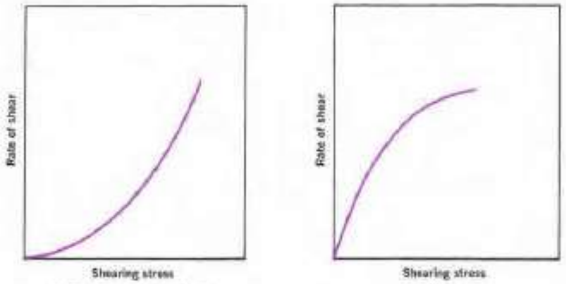
- There are three general types of non-Newtonian materials:

1. Plastic Flow
2. Pseudoplastic Flow
3. dilatant. Flow



(a) Newtonian flow

(b) Simple plastic flow



(c) Simple pseudoplastic flow

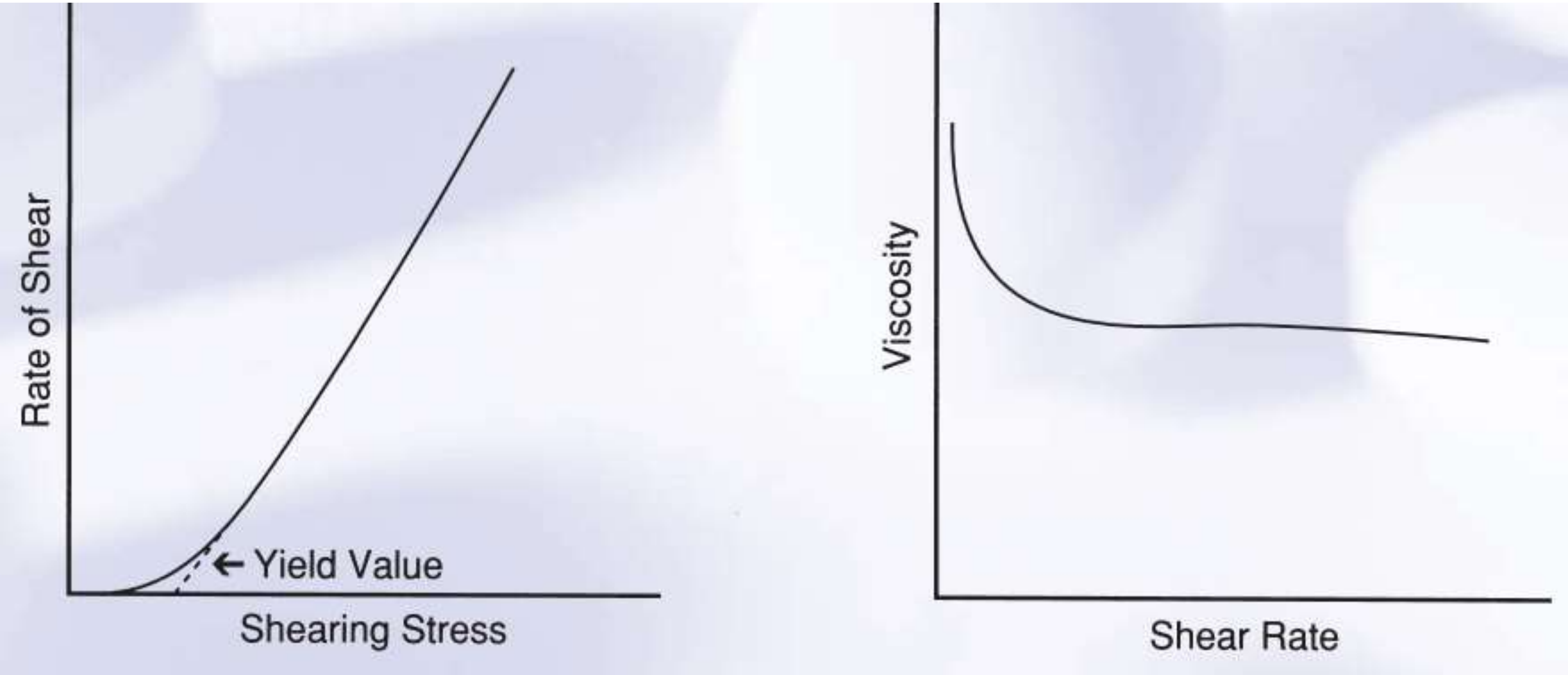
(d) Dilatant flow

Plastic flow

- Substances that exhibit plastic flow are called *Bingham bodies*.
- A Bingham body does not begin to flow until a shearing stress corresponding to the yield value is exceeded.
- Plastic flow does not begin until a shearing stress corresponding to a certain yield value is exceeded.
- The flow curve intersects the shearing stress axis and does not pass through the origin.
- After yield value With increasing shearing stress, the rate of shear increases; consequently, these materials are also called shear-thinning systems.

- The materials are elastic below the yield value.

Plastic flow

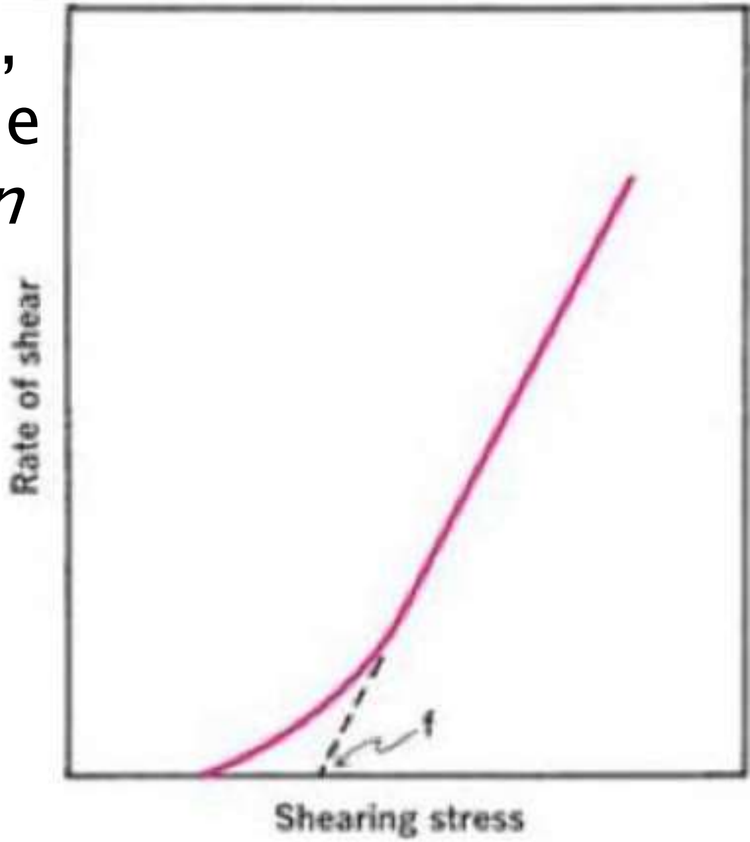


*i.e. (*Tomatoes Sauce, Honey , Flocculated particles in a concentrated suspensions usually show plastic flow) Plastic viscosisity

- The slope of the rheogram is termed the *mobility, analogous to fluidity in Newtonian* systems, and its reciprocal is known as the *plastic viscosity, U. The equation describing plastic flow is*

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

- *f is the yield value, or intercept, on the shear stress axis in dynes/cm2,*
- *and F and G are (Shear stress and shear rate)*



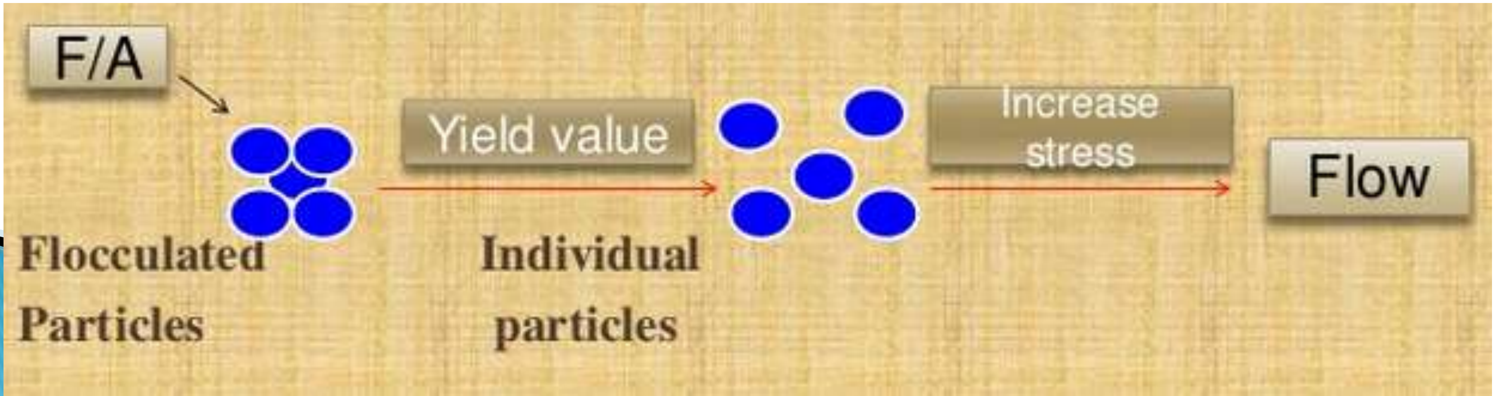
(b) Simple plastic flow

- A plastic material was found to have a yield value of 5200 dynes/cm2. At shearing stresses above the yield value, *F was found to increase linearly with G. If the rate of shear was 150* sec–1 when *F was 8000 dynes/cm2, calculate U, the plastic viscosity of the sample.*

$$\begin{aligned} U &= (8000 - 5200)/150 \\ &= 2800/150 \\ &= 18.67 \text{ poise} \end{aligned}$$

Plastic Flow

- Plastic flow is associated with the presence of flocculated particles in concentrated suspensions
- A yield value exists because of the contacts between adjacent particles (brought about by van der Waals forces), which must be broken down before flow can occur
- Consequently, the yield value is an indication of force of flocculation
- The more flocculated the suspension, the higher will be the yield value.
- Frictional forces between moving particles can also contribute to yield value

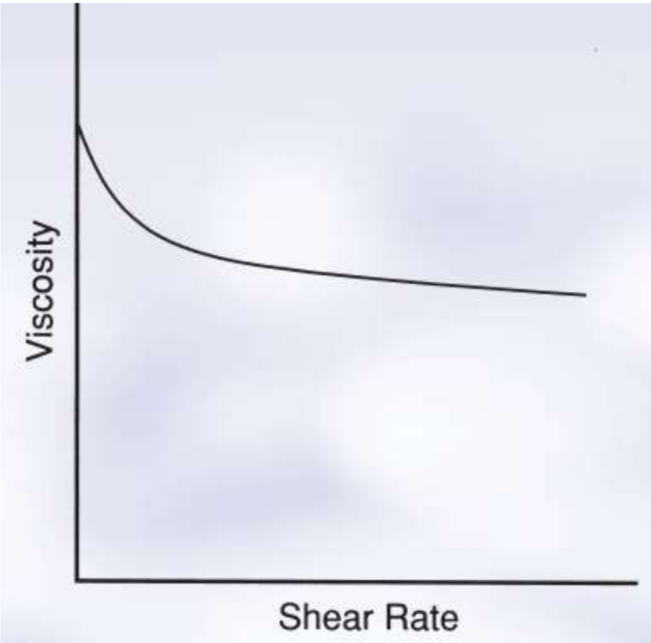


Pseudoplastic flow

- *Pseudoplastic* substances begin flow when a shearing stress is applied; therefore, they exhibit no yield value.

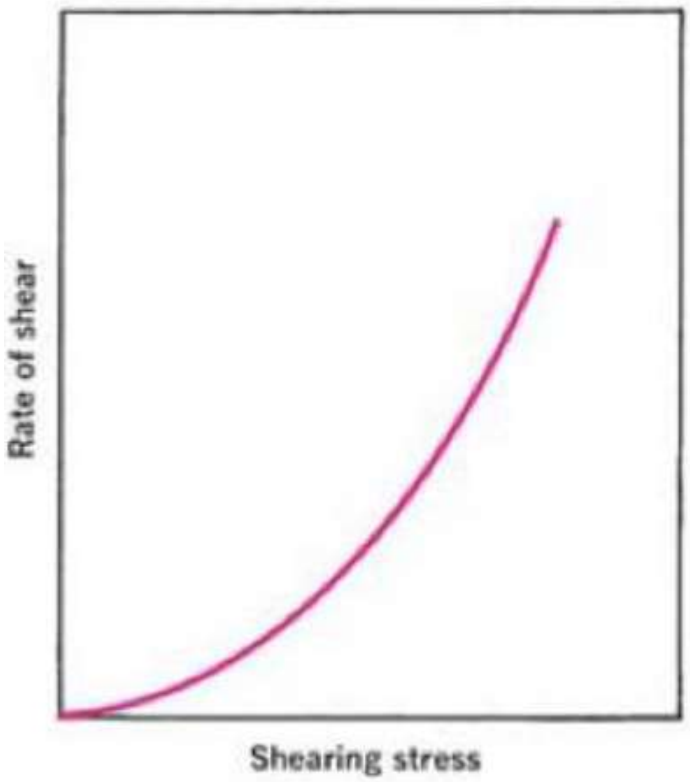
- With increasing shearing stress, the rate of shear increases; consequently, these materials are also called shear-thinning systems.
- **Shear thinning** is a term used in rheology to describe non-Newtonian fluids which have decreased viscosity when subjected to **shear** stress

- It is postulated that this occurs as the molecules, primarily polymers, align themselves along the long axis and slip or slide past each other.

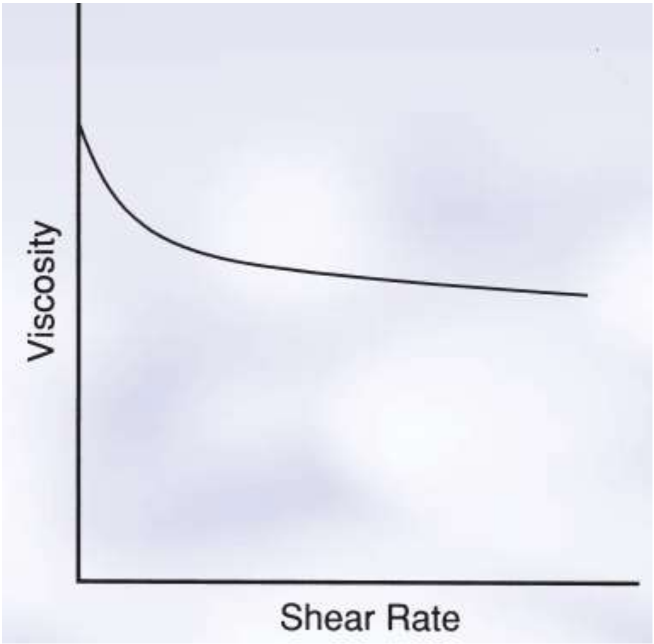


- With increased agitation, the polymers align themselves in the direction of flow → *internal resistance ↓* → *viscosity ↓*

Pseudoplastic flow



(c) Simple pseudoplastic flow



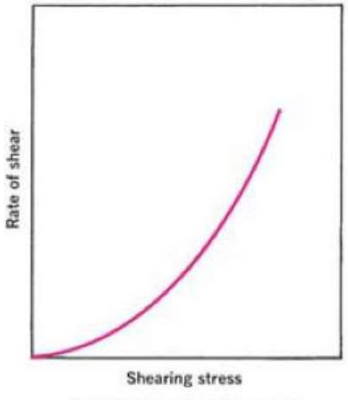
A large number of pharmaceutical products, including natural and synthetic gums, e.g. liquid dispersions of tragacanth, sodium alginate, methyl cellulose, and Na-carboxymethylcellulose show pseudoplastic flow

- no yield value as there is in a plastic system
- the consistency curve for a pseudoplastic material begins at the origin
- Furthermore, because no part of the curve is linear, the viscosity of a pseudoplastic material cannot be expressed by any single value
- The most satisfactory representation for a pseudoplastic material, however, is probably a graphic plot of the entire consistency curve.

Rheogram

Rheograms

- A *rheogram is a plot of shear rate, G, as a function of shear stress, F. Rheograms are also* known as consistency curves or flow curves
- The rheologic properties of a given material are most completely described by its unique rheogram



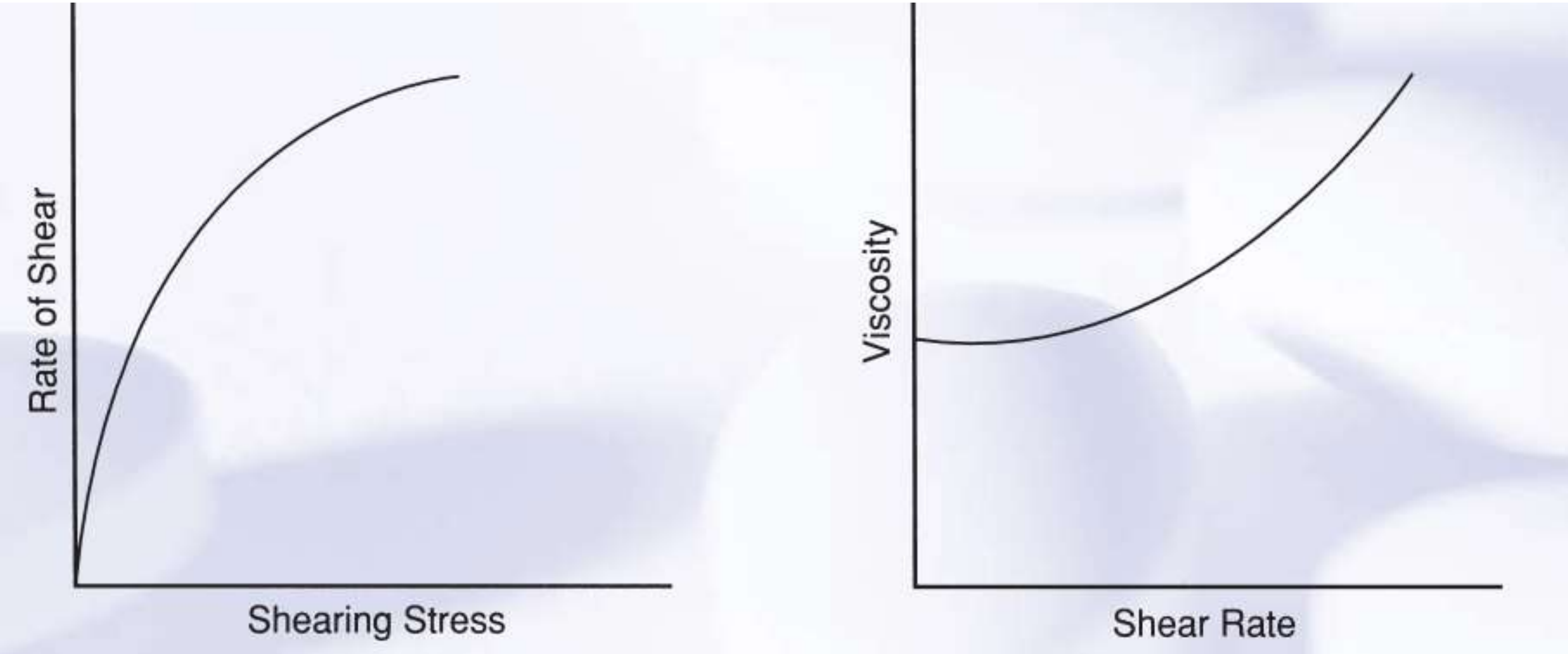
(c) Simple pseudoplastic flow

- Pseudoplastic flow is typically exhibited by polymers in solution
- The viscosity of a pseudoplastic substance decreases with increasing rate of shear
- As shearing stress is increased, normally disarranged molecules begin to align their long axes in the direction of flow. This orientation reduces internal resistance of the material and allows a greater rate of shear at each successive shearing stress.

Dilatant flow

- *Dilatant* materials are those that have an increase in viscosity with increasing shear rate.
- These are also called shear-thickening systems.
- When stress is removed, a dilatant system returns to its original state of fluidity.
- Dilatant systems are usually characterized by having a high percentage of **solids in the formulation. 50% or more**

Dilatant flow



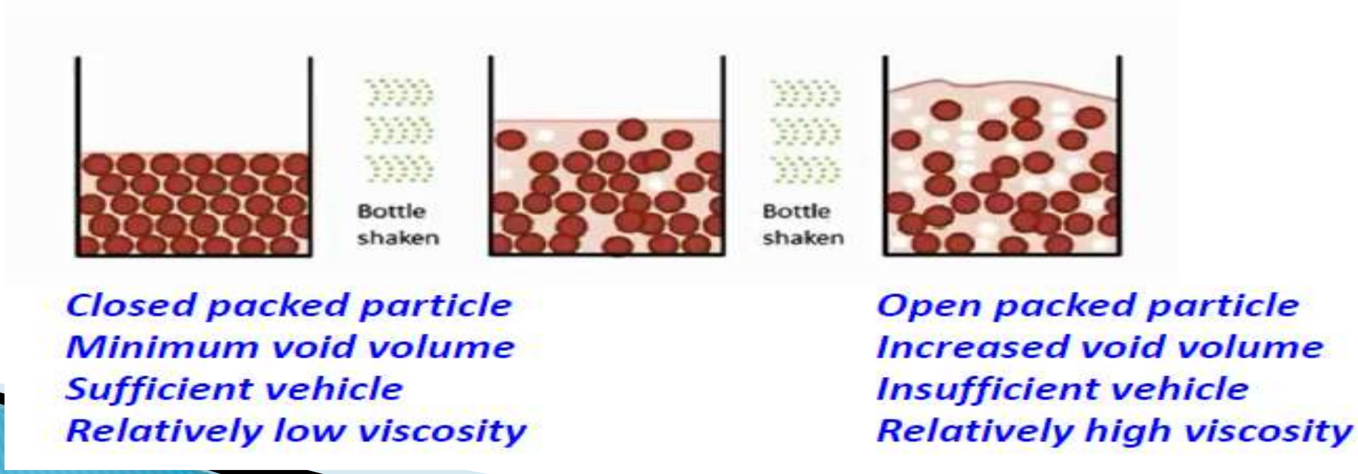
- Substances possessing dilatant flow properties are suspensions containing a high concentration (about 50 percent or greater) of small, deflocculated particles.

Dilatant flow

- Opposite to Pseudoplastic flow **(shear–thickening system) – Increased viscosity with increased shear stress – Apparent viscosity is 1/slope at any point along the curve.**
- Systems are called dilatant because they also increase in volume with agitation

Dilatant behavior may be explained as follows:

- At rest, the particles are closely packed with the minimum interparticle volume, or voids (empty space).
- The amount of vehicle in the suspension is sufficient, however, to fill this volume and permits the particles to move
- As the shear stress is increased, the bulk of the system expands or dilates .
- The amount of vehicle , becomes insufficient to fill the increased voids .
- Accordingly, the resistance to flow increases because the particles are no longer completely wetted or lubricated by the vehicle.
- Thus, the suspension will set up as a firm paste



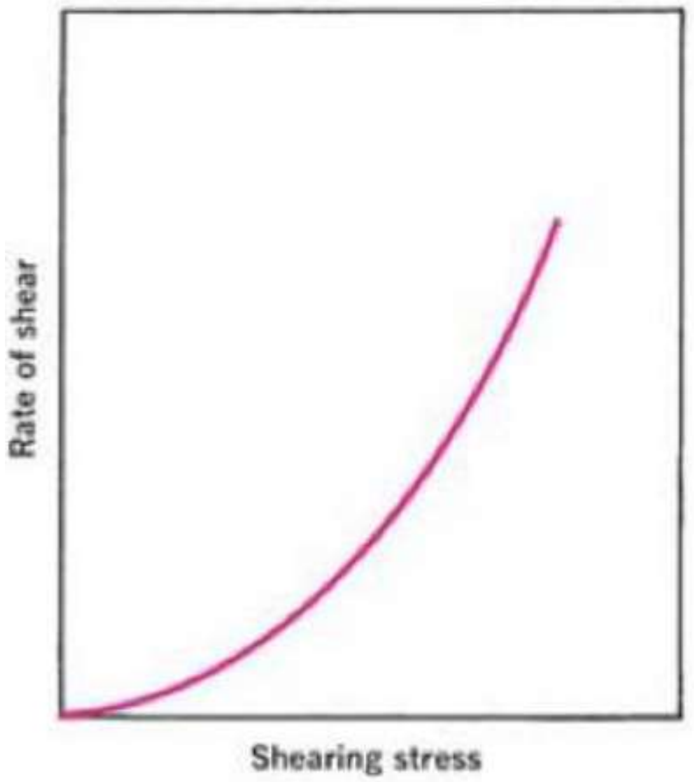
- processing of dispersions containing solid particles is facilitated by the use of high-speed mixers, blenders, or mills.
- Although this is advantageous with all other rheologic systems, dilatant materials may solidify under these conditions of high shear, thereby overloading and damagingprocessing equipment.

Non Newtonian viscosity

The viscosity of non-Newtonian materials is determined using a viscometer capable of producing differing shear rates, measuring the shear stress, and plotting the results

Thixotropy

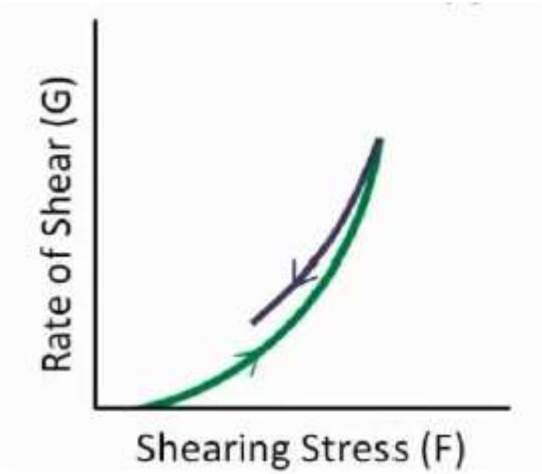
- several types of behavior are observed when rate of shear is progressively increased and plotted against resulting shear stress
- It may have been assumed that if the rate of shear were reduced once the desired maximum had been reached, the downcurve would be identical with, and superimposable on, the upcurve
- this is true for Newtonian systems, the downcurve for non-Newtonian systems can be displaced relative to the upcurve



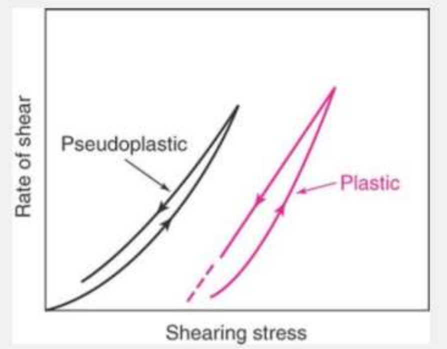
(c) Simple pseudoplastic flow

Thixotropy

- When left to rest, Newtonian systems will revert back to their original form. That is, they have identical downward curves.
- ▪When left to rest, non-Newtonian systems do **slowly revert back to something close to their original form, BUT they do not have identical downward curves.**



Thixotropy



- With shear-thinning systems (i.e., pseudoplastic), the downcurve is frequently displaced to the left of the upcurve
- showing that the material has a lower consistency at any one rate of shear on the downcurve than it had on the upcurve
- This indicates a breakdown of structure (and hence shear thinning) that does not reform immediately when stress is removed or reduced
- This phenomenon, known as *thixotropy*

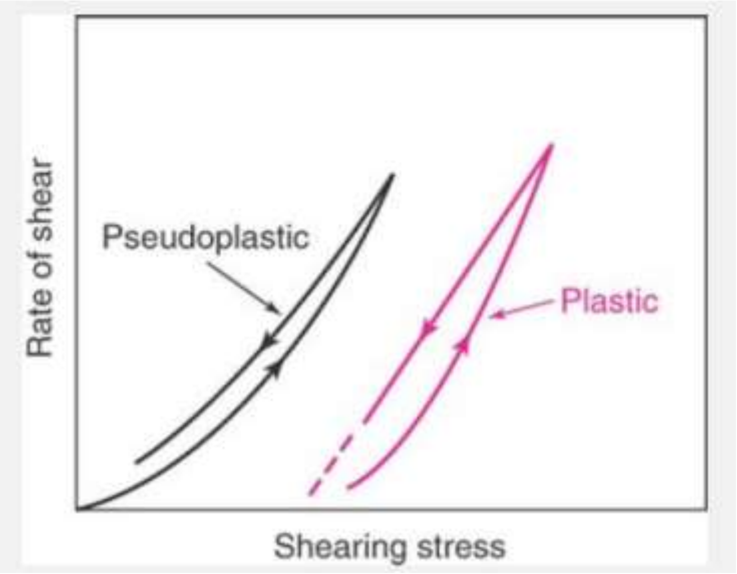
Thixotropy, may be defined as:

an isothermal and comparatively slow recovery, on standing of a material, of a consistency lost through shearing.

In other words

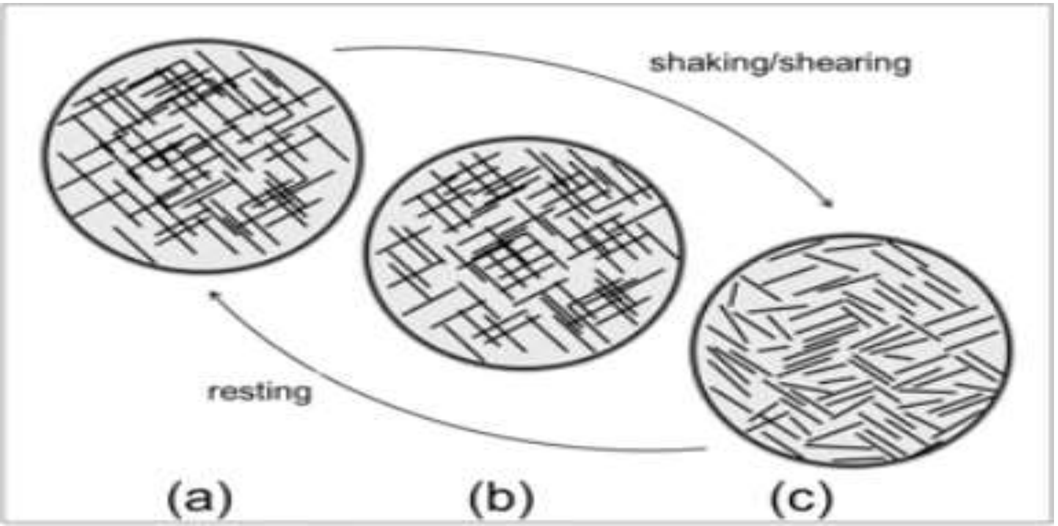
Systems that shows shear thinning when increasing share rate and then they take a fixed time to return to a more viscous state**.** (a time-dependent shear thinning)

- thixotropy can be applied only to shear-thinning systems.
  (Plastic , and pseudoplastic flow)

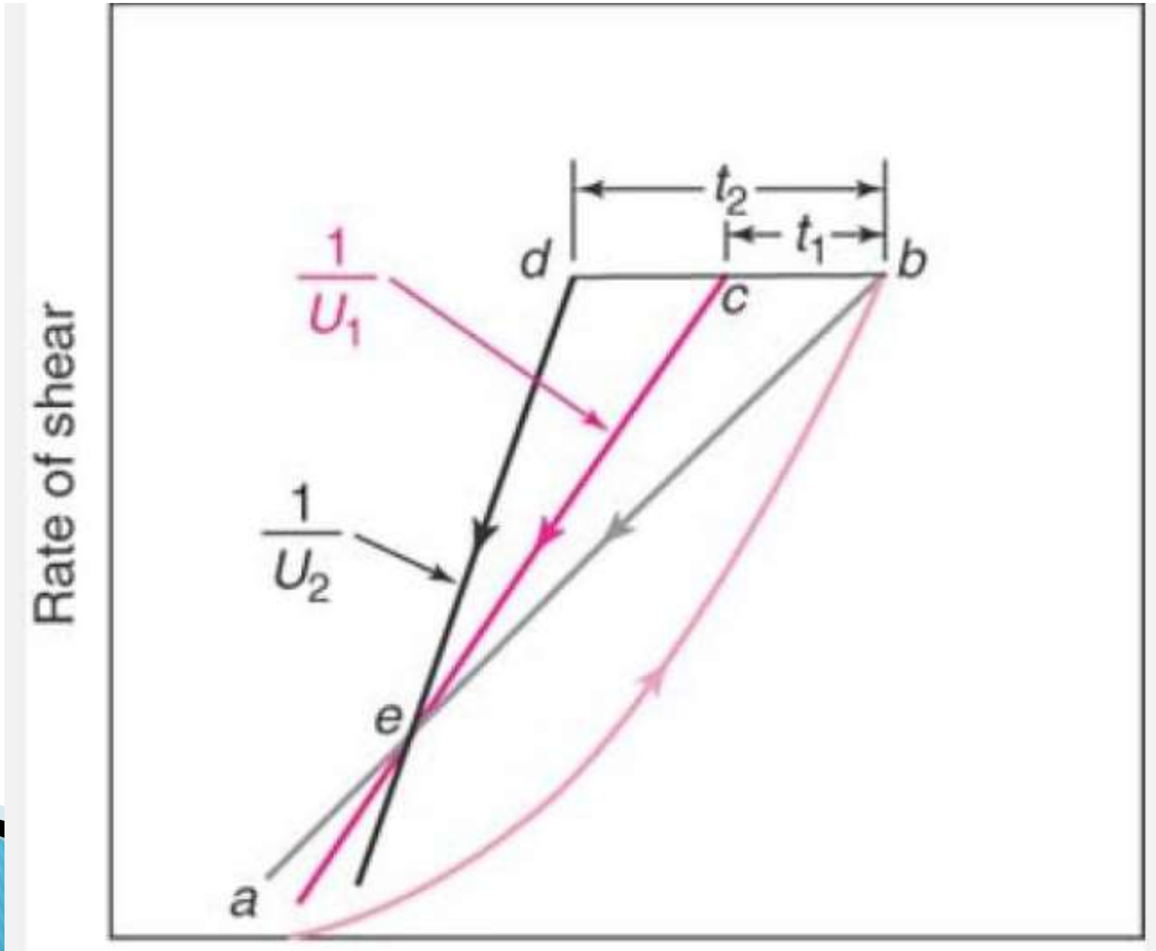


- Thixotropic systems usually contain asymmetric particles that, through numerous points of contact, set up a loose three dimensional network throughout the sample.
- At rest, this structure have some degree of rigidity on the system, and it resembles a gel.
- As shear is applied and flow starts, this structure begins to break down as points of contact are disrupted and particles become aligned
- The material undergoesa gel-to-sol transformation and exhibits shear thinning

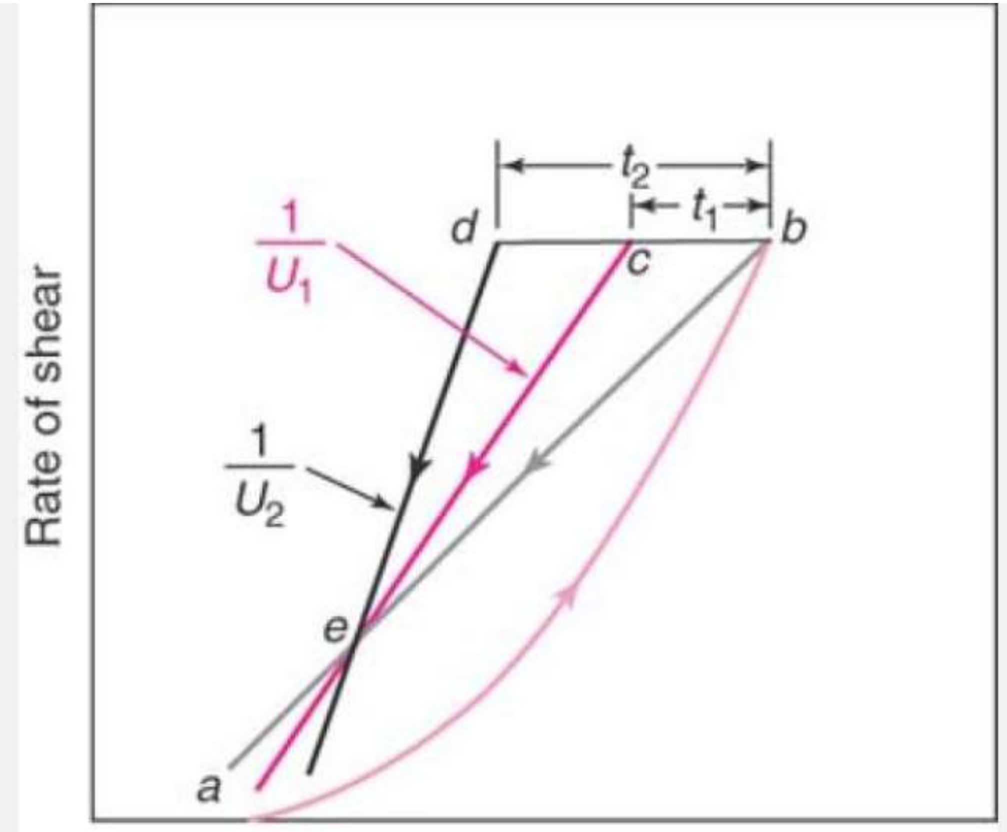
- On removal of stress, the structure starts to reform. This process is not instantaneous; rather, it is a progressive restoration of consistency as asymmetric particles come into contact with one another by undergoing random Brownian movement



- Rheograms obtained with thixotropic materials are therefore highly dependent on the rate at which shear is increased or decreased and the length of time a sample is subjected to any one rate of shear.

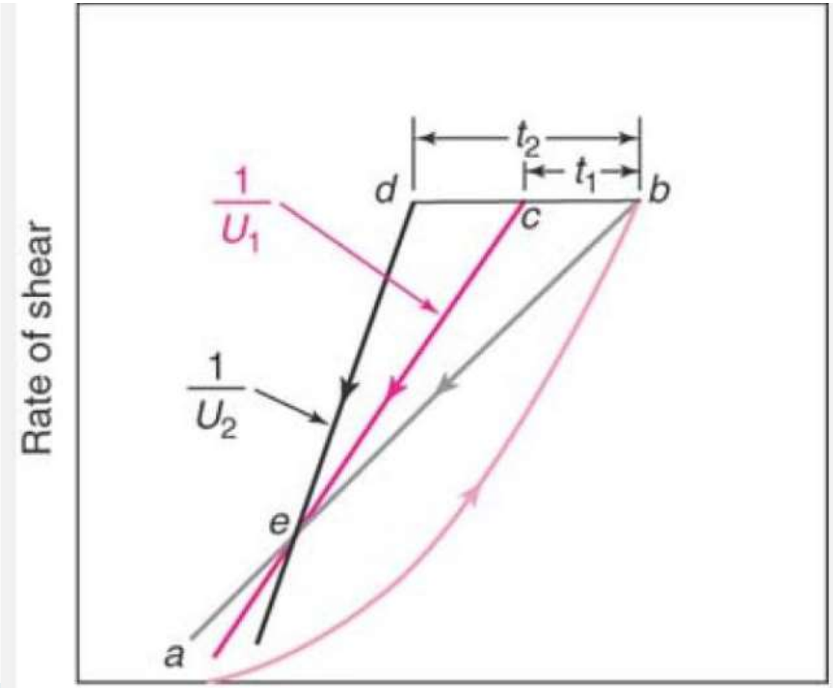


- suppose that in Figure the shear rate of a thixotropic material is increased in a constant manner from point *a to point b and is then decreased at the same rate back to e.*
- Typically, this would result in the so-called *hysteresis loop abe.*

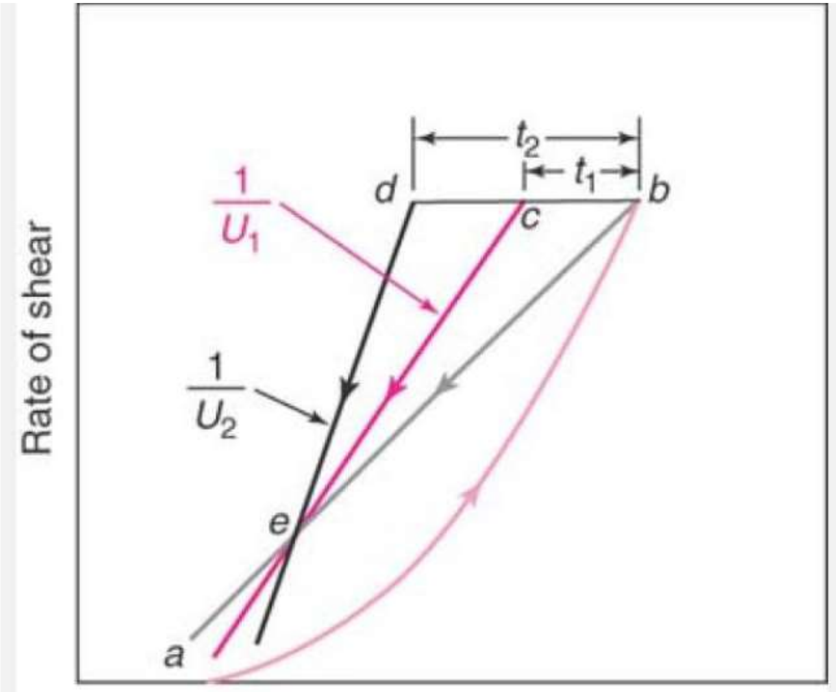


- If, however, the sample was taken to point *b and the shear rate held constant for a certain period of time (say, t1 seconds), shearing stress,* and hence consistency, would decrease to an extent depending on time of shear, rate of shear, and degree of structure in the sample. Decreasing the shear rate would then result in the *hysteresis loop abce*

If the sample had been held at the same rate of shear for *t2seconds, the loop abcde*



- Therefore, the rheogram of a thixotropic material is not unique but depends on the approach used in obtaining the rheogram



Degree of Hysteresis

- The difference between the upward and downward curve in thixotropic systems is known as the **degree of hysteresis – As products with high molecular weight take longer to recover, their degree of hysteresis will be larger than systems with low molecular weight particles**
- **A thixotropic agent such as microcrystalline cellulose is incorporated into the suspensions or emulsions to give a high viscosity.**

Negative Thixotropy (or *antithixotropy*)

- increase rather than a decrease inconsistency on the downcurve. This increase in thickness or resistance to flow with increased time of shear

magnesia magma

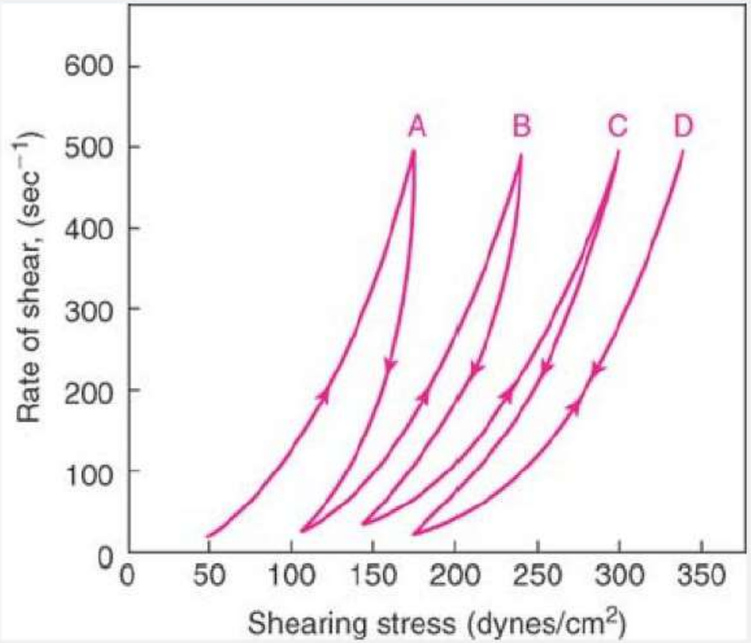


Fig. 19-9. Rheogram of magnesia magma showing antithixotropic behavior. The material is sheared at repeated increasing and then decreasing rates of shear. At stage *D*, further cycling no longer increased the consistency, and the upcurves and downcurves coincided. (From C. W. Chong, S. P. Eriksen, and J. W. Swintosky, J. Am. Pharm. Assoc. Sci. Ed. **49,** 547, 1960. With permission.)

Negative thixoptropy

- Antithixotropy or negative thixotropy should not be confused with dilatancy Dilatant systems are deflocculated and ordinarily contain greater than 50% by volume of solid dispersed phase,
- whereas antithixotropic systems have low solids content (1%–10%) and are flocculated
- It is believed that antithixotropy results from an increased collision frequency of dispersed particles or polymer molecules in suspension, resulting in increased interparticle bonding with time

.

Negative Thixotropy

- This changes an original state consisting of a large number of individual particles and small floccules to an eventual equilibrium state consisting of a small number of relatively large floccules.
- At rest, the large floccules break up and gradually return to the original state of small floccules and individual particles.

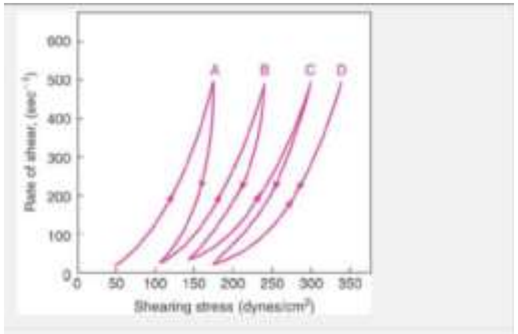


Fig. 19-9. Rheogram of magnesia magma showing antithixotropic behavior. The material is sheared at repeated increasing and then decreasing rates of shear. At stage *D*, further cycling no longer increased the consistency, and the upcurves and downcurves coincided. (From C. W. Chong, S. P. Eriksen, and J. W. Swintosky, *J. Am. Pharm. Assoc. Sci. Ed.* **49**, 547, 1960. With permission.)

Thixotropy in Formulation

- Thixotropy is a desirable property in liquid pharmaceutical systems that ideally should have a high consistency in the container, yet pour or spread easily
- For example, a well-formulated thixotropic suspension will not settle out readily in the container, will become fluid on shaking, and will remain long enough for a dose to be dispensed. Finally, it will regain consistency rapidly enough so as to maintain the particles in a suspended state.

Thixotropy in Formulation

- A similar pattern of behavior is desirable with emulsions, lotions, creams, ointments, and parenteral suspensions to be used for intramuscular depot therapy.

- Concentrated parenteral suspensions containing from 40% to 70% w/v of procaine penicillin G in water were found to have a high inherent thixotropy and were shear thinning
- Consequently, breakdown of the structure occurred when the suspension was caused to pass through the hypodermic needle.
- Consistency was then recovered as rheologic structure reformed. This led to formation of a depot of drug at the site of intramuscular injection where drug was
- slowly removed and made available to the body.

Non Newtonian Visicometer

- single-point instruments can lead to erroneous results if used to evaluate non-Newtonian systems because flow properties could vary significantly despite identical measured viscosities.
- All viscometers can be used to determine Newtonian viscosities
- cup-and-bob, and cone-and-plate viscometers (multipoint, rotational instruments)
- Measure viscosity, yield value, thixotropy

Cup-and-Bob Viscometer

- In cup-and-bob viscometers, the sample is sheared in the space between the outer wall of a bob and the inner wall of a cup into which the bob fits.
- The various instruments available differ mainly in whether the torque results from rotation of the cup or of the bob
- the *Couette type of viscometer, the cup is rotated*
- The *Searle type of viscometer uses a stationary cup* and a rotating bob.

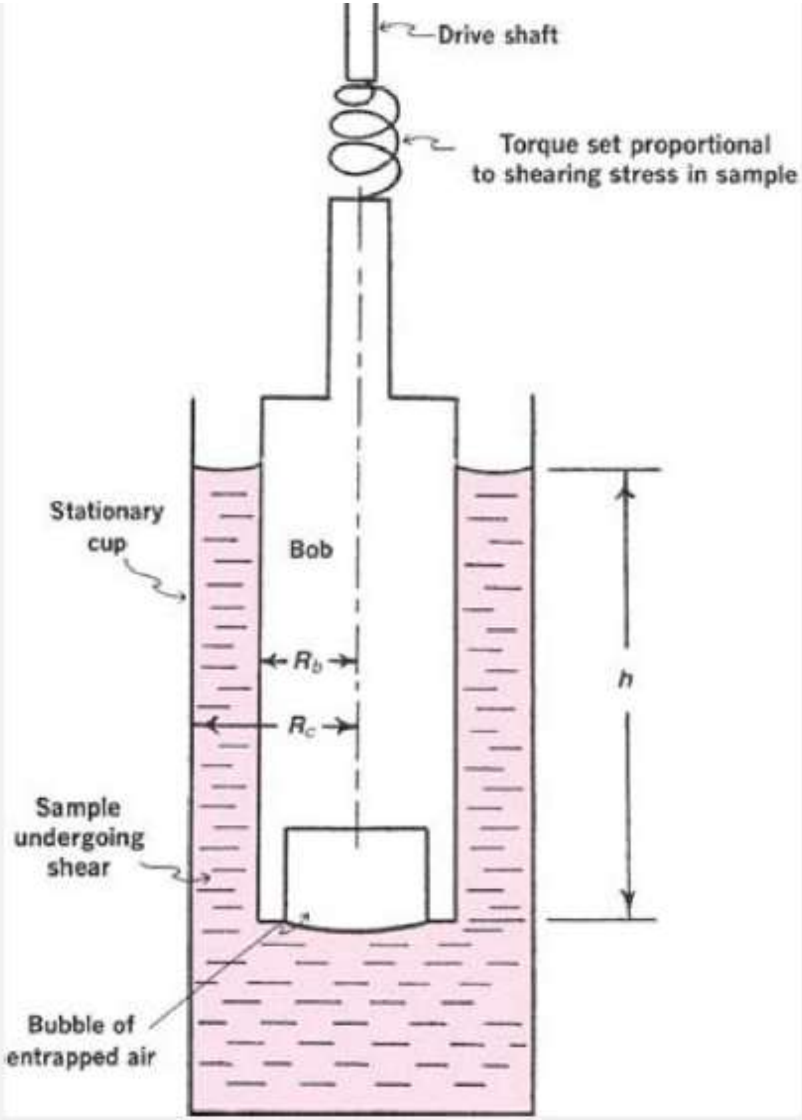


Fig. 19-14. Principle of rotational cup-and-bob viscometer (Searle type). See text for explanation.

- **Torque: Rotational force (*Torque* is a measure of how much a force acting on an object causes that object to rotate.)**
- the angular velocity of a particle is measured around or relative to a point, called the origin in radians/sec produced by *T*, the torque in dynes cm.

$$\Omega = \frac{1}{\eta}\frac{T}{4\pi h}\left(\frac{1}{R_b^2} - \frac{1}{R_c^2}\right)$$

- Equation for rotational visicometer
- Ω is the angular velocity in radians/sec produced by *T*, the torque in dynes cm.
- *h*, : The depth to which the bob is immersed in the liquids is and R_b and R_c are the radii of the bob and cup,

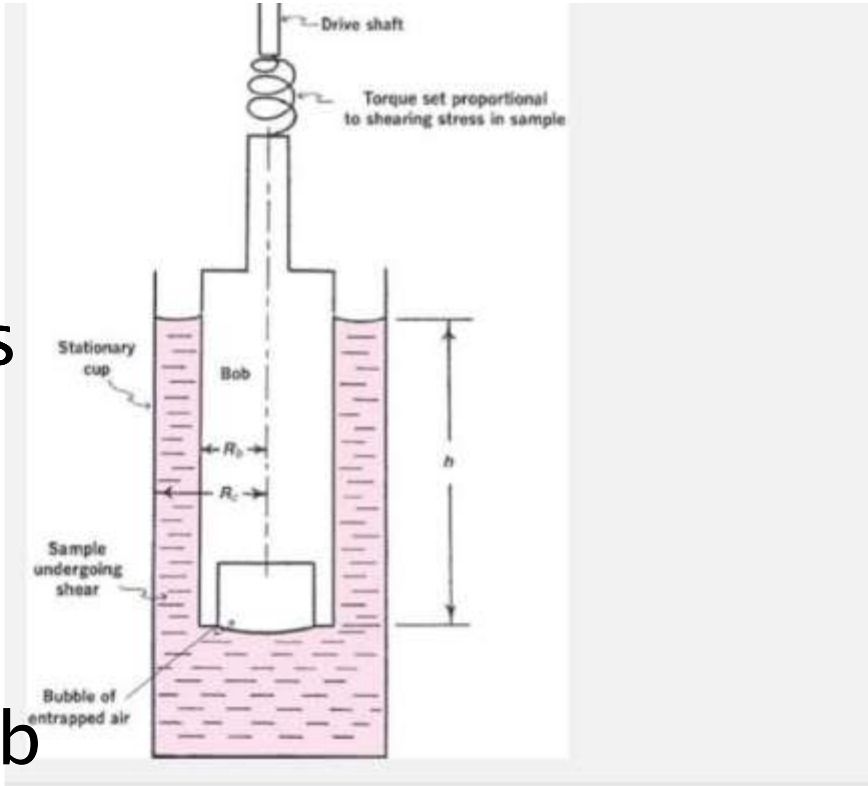


Fig. 19-14. Principle of rotational cup-and-bob viscometer (Searle type). See text for explanation.

$$\Omega = \frac{1}{\eta}\frac{T}{4\pi h}\left(\frac{1}{R_b^2} - \frac{1}{R_c^2}\right)$$

$$\eta = K_v\frac{T}{\Omega}$$

Ω is the angular velocity in radians/sec produced by *T*, the torque in dynes cm.

h, : The depth to which the bob is immersed in the liquids is and R_b and R_c are the radii of the bob and cup,

Kv: instrument constant

Brookfield viscometer(digital)

- The Brookfield viscometer is a rotational viscometer of the Searle type that is popular in the qualitycontrol laboratories of pharmaceutical manufacturers.
- A number of spindles (bobs) of various
- geometries, including cylinders, t-bars, and a cone-plate configuration, are available to provide scientific rheologic data for Newtonian and non-Newtonian liquids

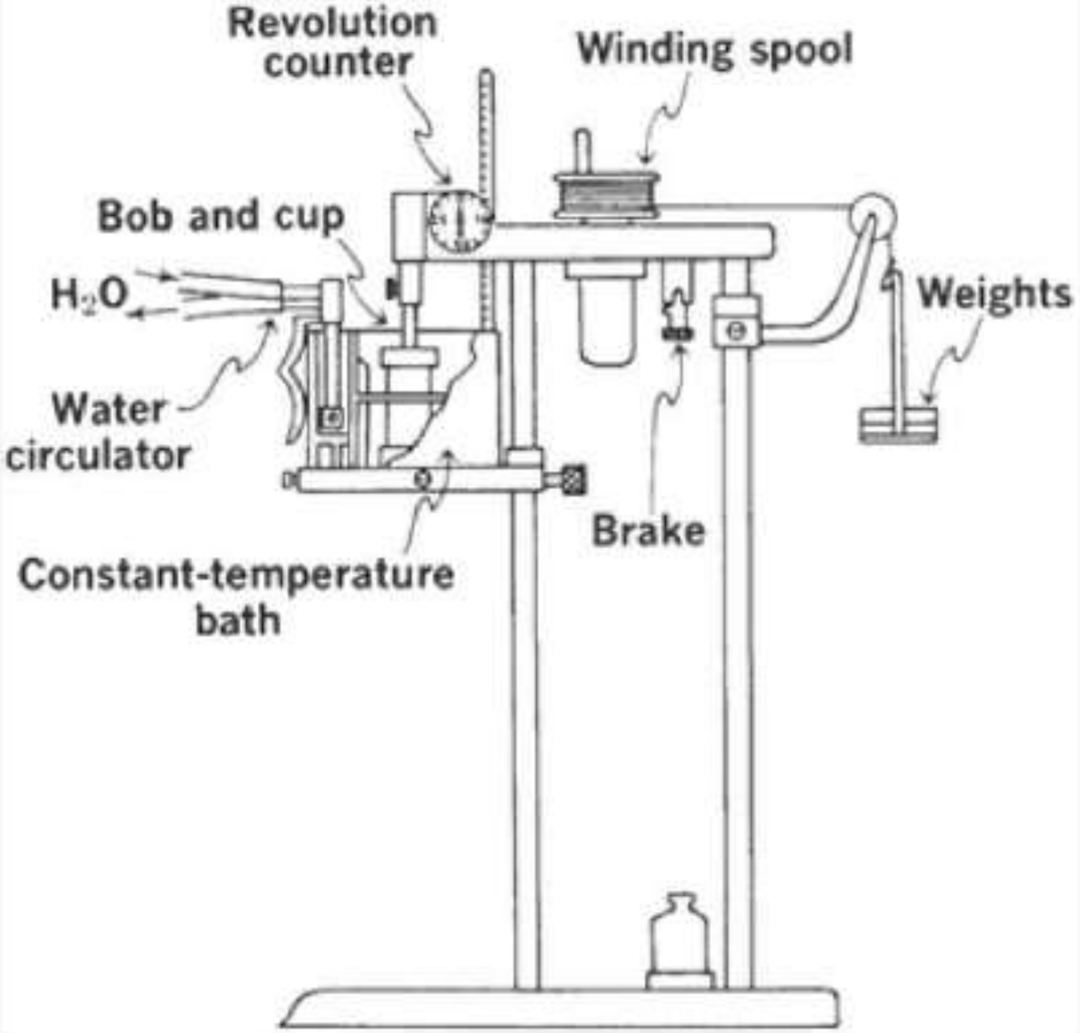


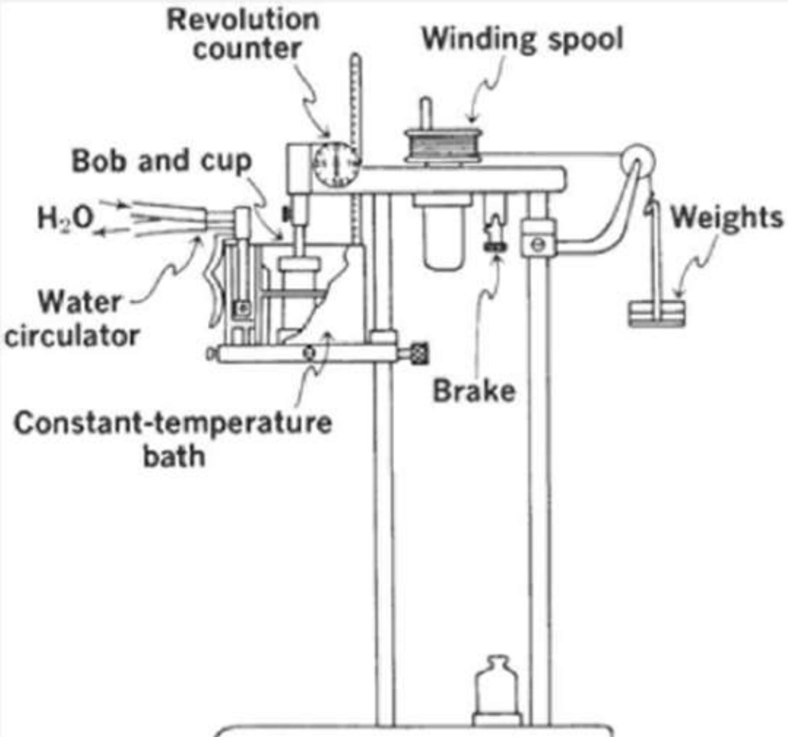
Fig. 19-16. Stormer viscometer. The falling weights cause the bob to rotate in the stationary cup. The velocity of the bob is obtained by means of a stopwatch and the

$$\eta = K_v \frac{T}{\Omega}$$

- Ω is a function of *v, the* rpm generated by the weight, *w, in grams, which is proportional to T.(torque)*
- *Equation* ***can then be***written as

$$\eta = K_v \frac{w}{v}$$

The constant *Kv can be determined by analyzing an oil of known viscosity in the instrument; reference*
oils for this purpose are obtained from the National Bureau of Standards.



- The Searle type of viscometer uses a stationary cup and a rotating bob
- The rate of shear, *G*, is selected manually or programmed for automatic plotting of upcurves and downcurves. Its value in sec–1 is proportional to the speed of the bob shaft,

https://www.youtube.com/watch?v=ONoV98kMkYA

Viscoelasticity

- All viscous liquids deform continuously under the influence of an applied stress – They exhibit viscous behavior.
- Solids deform under an applied stress, but soon reach a position of equilibrium, in which further deformation ceases. If the stress is removed they recover their original shape – They exhibit elastic behavior

Viscoelasticity

- Viscoelasticity is the property of a substance of exhibiting both elastic and viscous behavior,
- Elasticity is the tendency of solid materials to return to their original shape after forces are applied and removed from them.
- Viscosity is the resistance to flow (High or low viscosity)
- Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation

- Visicoelastic material They stretch (elastic) and they flow (viscous)
- A semisolid is considered to demonstrate both solid and liquid characteristics. (vsicoelastic)
- Many of the systems studied in pharmacy belong to this class, examples being creams, lotions, ointments, suppositories, suspensions, emulsifying, and suspending agents
- Importance study deformation under continuous stress like gravity

Modeling viscoelasticity

- Maxwell Unit (model)
- An elastic solid is modeled by the movement of a Hooke spring
- viscous fluid as movement of a piston in a cylinder (or *dashpot, as it is called) filled with a liquid*
- The behavior of a semisolid as a viscoelastic body can therefore be described by the combination of the dashpot and spring

Spring elastic, dashpot viscous
Maxwell : Viscoelastic model

https://www.youtube.com/watch?v=ZVK1qVkXfC4

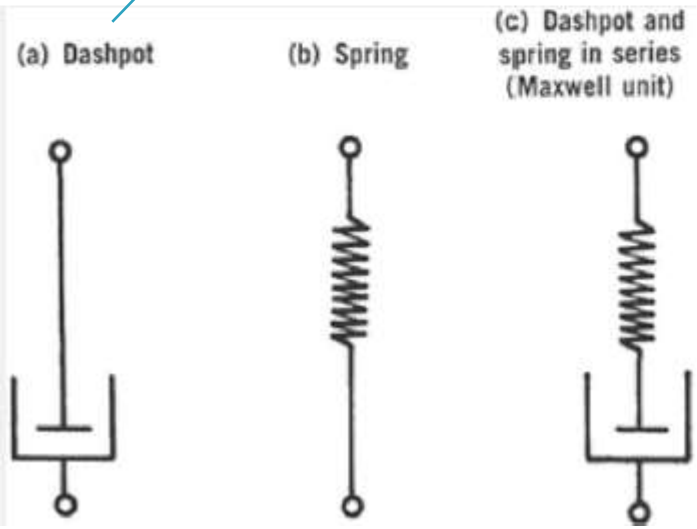
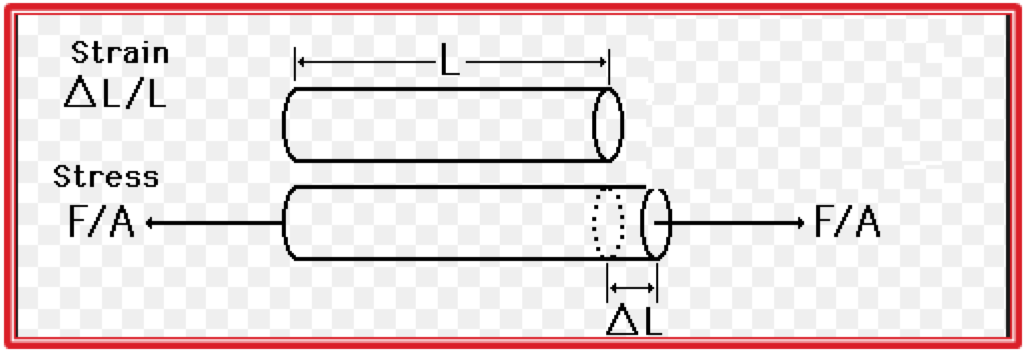


Fig. 19-20. Mechanical representation of a viscoelastic material using a dashpot and spring. The dashpot and spring in series is called a*Maxwell element* or *unit.*

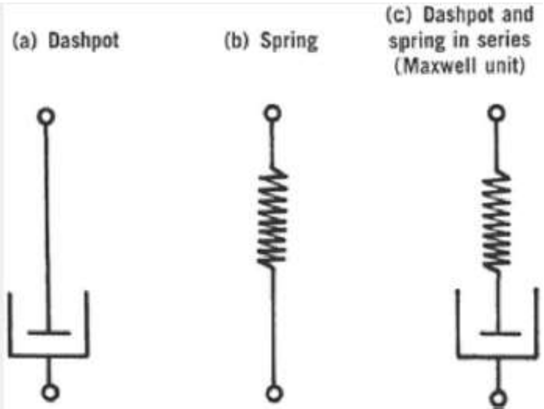
Strain

- As force is applied to elastic material of length L it deforms by △L along the axis of force
- △L/L (strain or deformation is the dimensionless)



Maxwell Model

- As a constant stress is applied to the Maxwell unit, there is a strain on the material that can be thought of as a displacement of the spring. The applied stress can be thought of as also producing a movement of the piston in the dashpot due to viscous flow. Removal of the stress leads to complete recovery of the spring, but the viscous flow shows no recovery, that is, no tendency to return to its original state



Voigt unit(Model)

- the spring and the dashpot are attached in parallel rather than in series, the drag of the viscous fluid in the dashpot simultaneously influences the extension and compression of the spring that characterizes the solid nature of the material,.

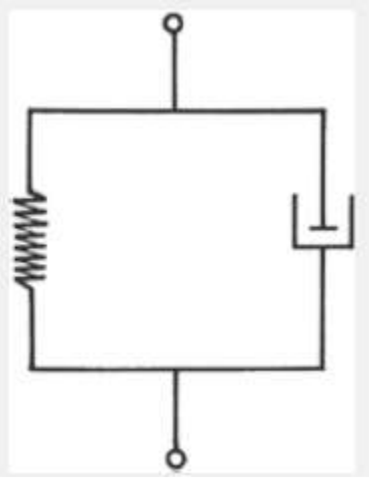
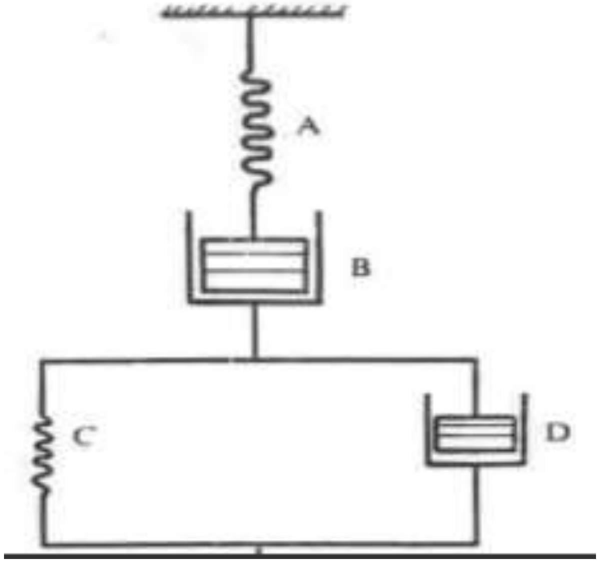


Fig. 19-21. Spring and dashpot combined in parallel as a mechanical model of a viscoelastic material, known as a *Voigt element*.

Combined model

- The Maxwell and Voigt mechanical models representing viscoelastic behavior in two different ways can be combined into a generalized model to incorporate all possibilities of flow and deformation of non-Newtonian materials

https://www.youtube.com/watch?v=q9emsMcG8cc&list=PLA75LXJ5d6KM2XUO-UvDNSxUwxb_rMgbl



- Fluid viscosity

$$\eta = F/G$$

- shear stress, *F, and shear rate, G*
- A solid material, on the other hand, is not characterized by flow but rather by elasticity,
- Elastic Modulus

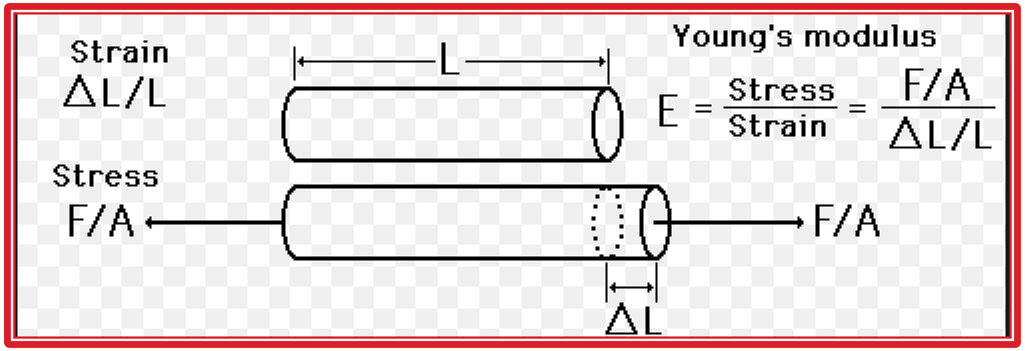
$$E = F/\gamma$$

- *E is the elastic modulus (dyne/cm2), F is the stress (dyne/cm2), and γ is the strain*
- *E: ratio of stress (force per unit area) along an axis to strain (ratio of deformation over initial length) along that axis"*

Elastic modulous(Elasticity)

$$E = F/\gamma$$

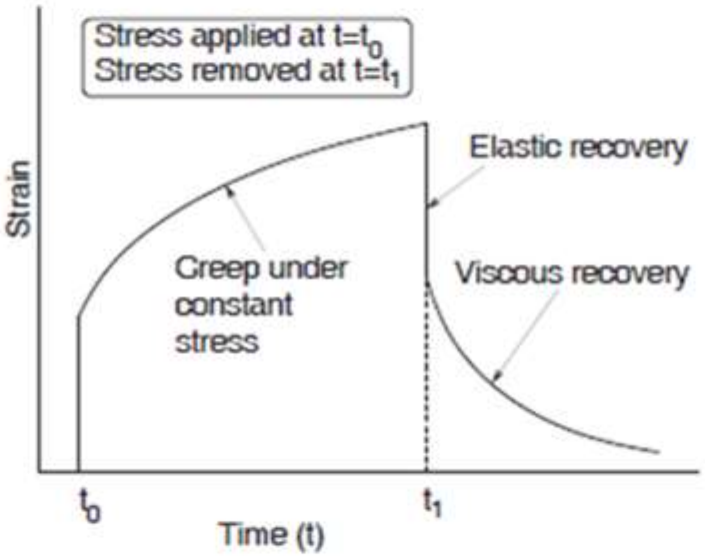
Units :dyne/cm^2



As force is applied to elastic material of length L it deforms by $\triangle$L along the axis of force
$\triangle$L/L (strain or deformation is the dimensionless)

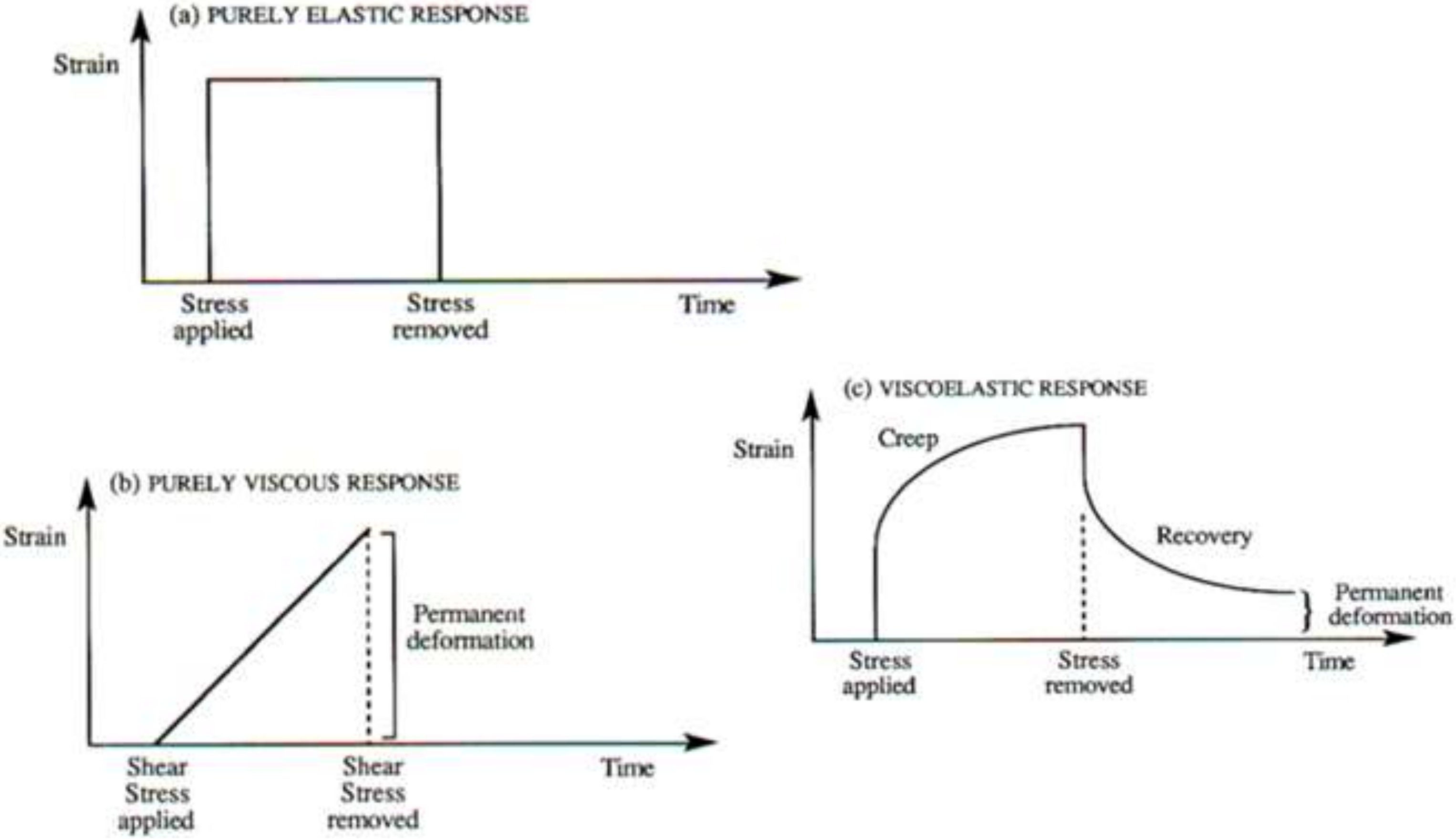
Creep :

- Slow deformation of material under constant pressure



When subjected to a constant stress, viscoelastic materials experience a time-dependent increase in strain.
 This phenomenon is known as viscoelastic creep.
When the stress is maintained for a shorter time period, the material undergoes an initial strain until a time , after which the strain immediately decreases (discontinuity) then gradually decreases at times $t>t1$ to a residual strain.

the tendency of a solid material to move slowly or deform permanently under the influence of mechanical stresses. It can occur as a result of long-term exposure to high levels of stress that are still below the yield strength of the material.


(a) PURELY ELASTIC RESPONSE
Strain
Stress applied
Stress removed
Time
(b) PURELY VISCOUS RESPONSE
Strain
Permanent deformation
Shear Stress applied
Shear Stress removed
Time
(c) VISCOELASTIC RESPONSE
Strain
Creep
Recovery
Permanent deformation
Stress applied
Stress removed
Time

- The compliance (strain or derformation per force in a determined unit area) of a viscoelastic material as a function of time
- *Can be measured by a creep viscometer*

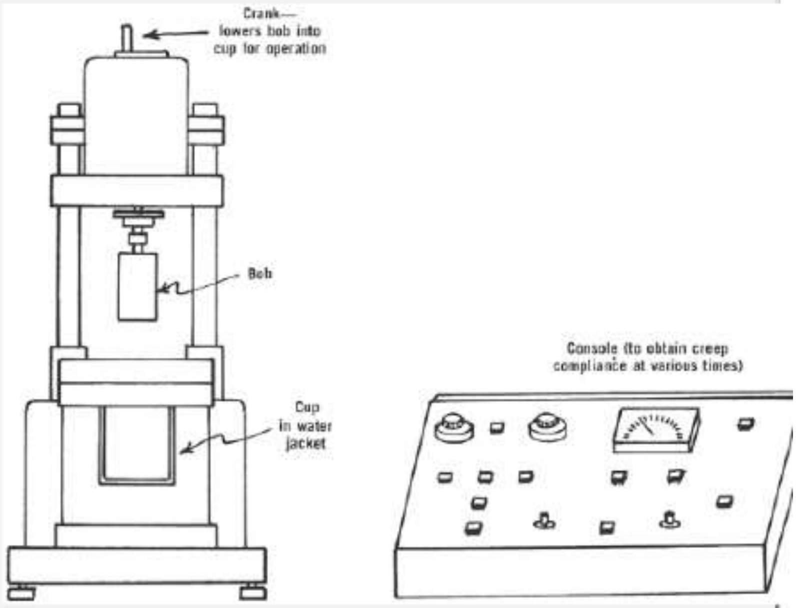
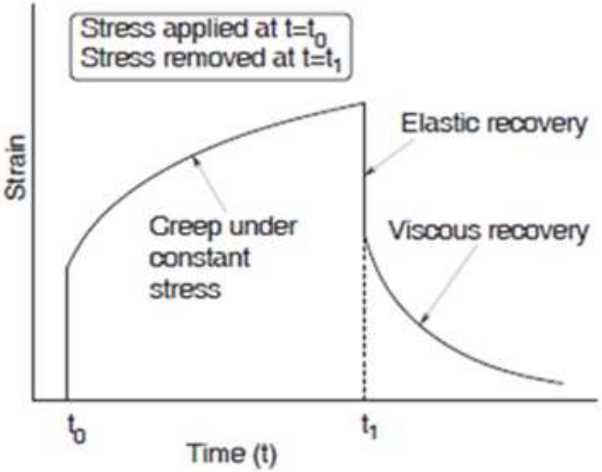


Fig. 19-23. Main components of a creep viscometer used to obtain creep compliance curves such as those found in Figures 19-22 and 19-24.

- Controlled stress rheometers are the instrument type used to characterize this behavior.
- The first order of business is to determine the amount of force that will cause the material to flow. This is called the yield stress.
- Increasing torque is gradually applied to the cone spindle until the slightest amount of rotational movement is detected. An optical encoder inside the instrument makes it possible to know with great precision when the spindle changes from its stationary position and first starts to rotate

- Initially the movement will be due to elastic, and therefore fully recoverable, stretch of the sample structure.
- After yield has occurred, the question is whether the flow movement will continue, especially if the force applied to the material reduces or is removed altogether
- Creep is the term used to characterize continuing deformation at a slow rate of movement after yield



- The controlled stress rheometer is uniquely qualified to make this measurement because it can continue to apply the low level force to the material that simulates the real-life situation, such as gravity causing a medicinal lotion to sag after application.
- The final piece of this analytical picture is what happens to the material when the stress is removed. This is called “recovery”
- Recovery: is an assessment of the material’s elastic property which gives it the ability to return to its original position after being sheared

Creep Curve

- Compliance also can be represented by the angle of deflection
- Compliance J=strain/(F/area)

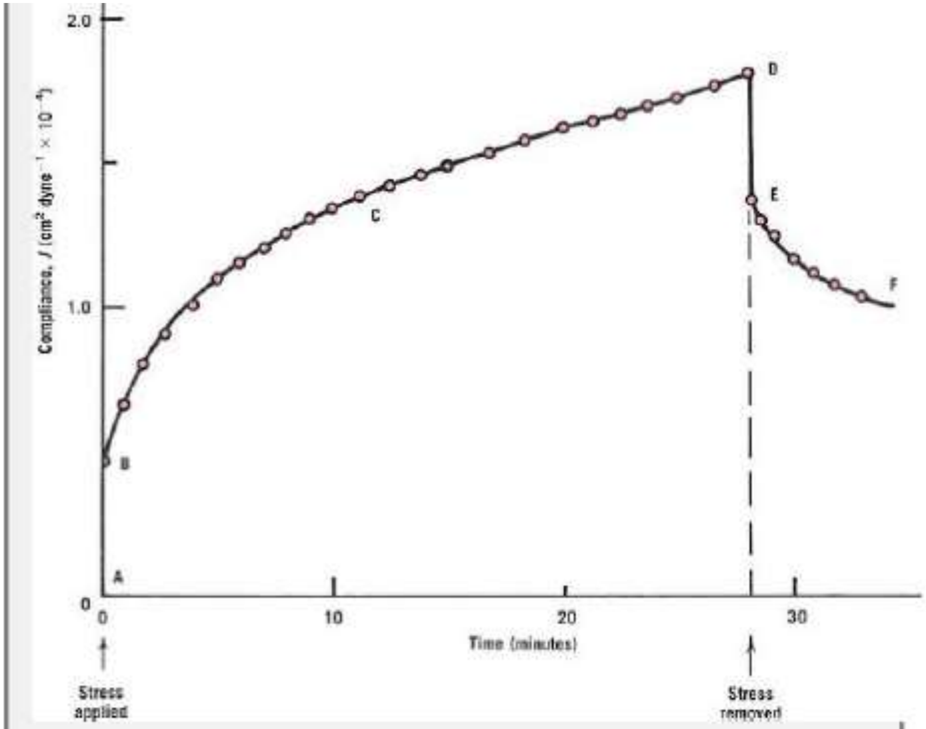
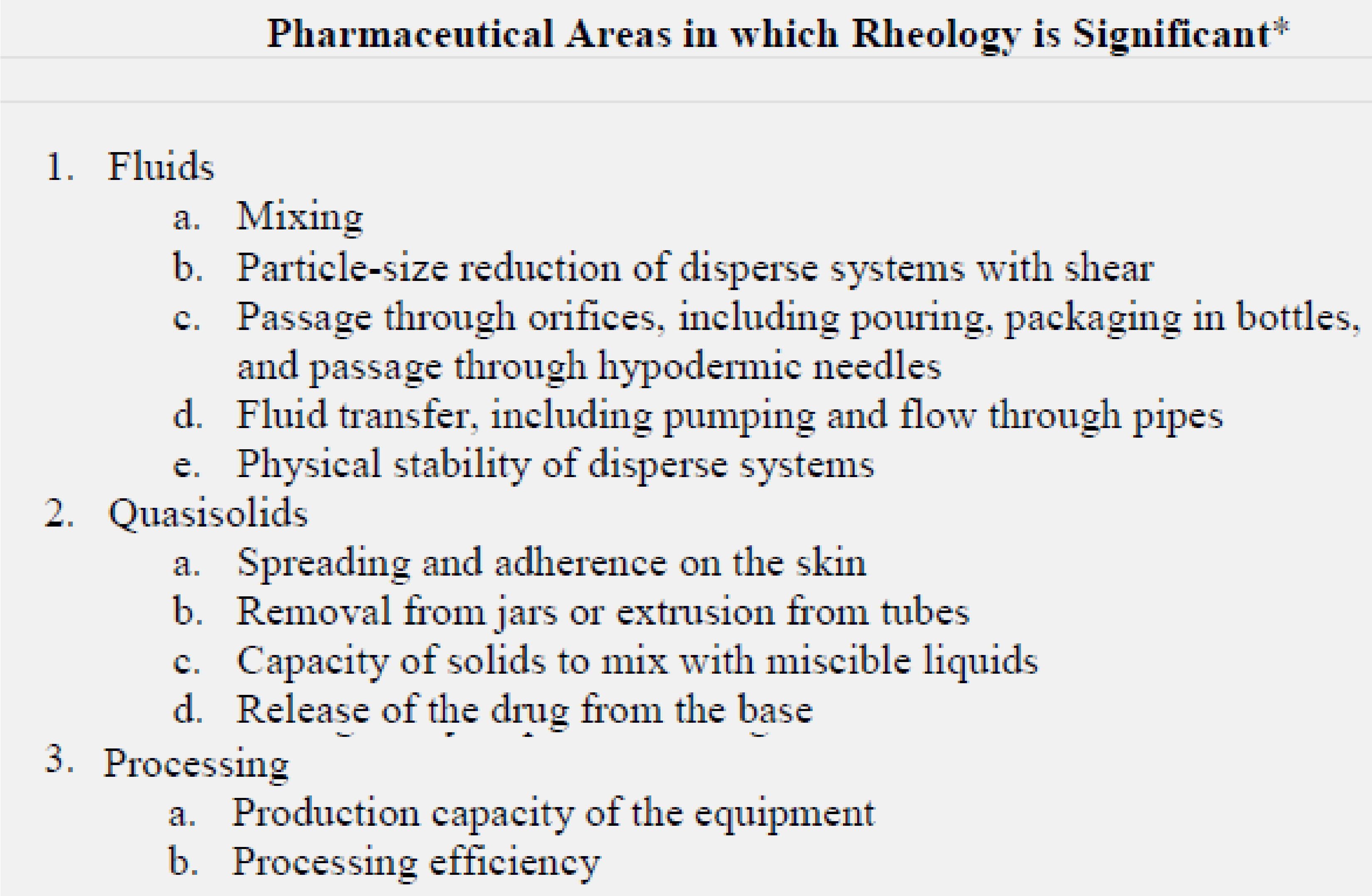


Fig. 19-22. A creep curve obtained by analyzing a sample of wool fat in a creep viscometer (Fig. 19-23) at 30°C. The creep curve results from a plot of compliance, *J*, equation (19-31), against the time in minutes during which a stress is applied to the sample.

Viscosity Modifier

Cellulose Derivatives	Methylcellulose Sodium Carboxymethylcellulose Hydroxyethyl Cellulose Hydroxypropyl Cellulose **Hydroxypropyl Methylcellulose**
Natural Gums	Acacia Tragacanth Xanthan Carrageenan
Sodium Alginate	
Poly(Acrylic Acid) Resin	Homopolymer Resins Copolymer Resins Sodium Salt Resins Poly(N-vinylpyrrolidone)
Pluronic Copolymers	
Clays	Bentonite



Pharmaceutical Areas in which Rheology is Significant*

1. Fluids
    a. Mixing
    b. Particle-size reduction of disperse systems with shear
    c. Passage through orifices, including pouring, packaging in bottles, and passage through hypodermic needles
    d. Fluid transfer, including pumping and flow through pipes
    e. Physical stability of disperse systems
2. Quasisolids
    a. Spreading and adherence on the skin
    b. Removal from jars or extrusion from tubes
    c. Capacity of solids to mix with miscible liquids
    d. Release of the drug from the base
3. Processing
    a. Production capacity of the equipment
    b. Processing efficiency

Factors affecting rheological properties

1. Chemical factors

A- Degree of polymerization

-The longer polymer molecules will be accompanied by increase in viscosity

- Sodium alginate (the flow viscosity at a given temperature rises rapidly with increasing DP for all polymers).

C- Impurities, Trace Ions and Electrolytes

Chemical impurities are the major factors in changing the viscosity of natural polymers e.g. in Na alginate solution, the viscosity increase if traces of Ca are present, due to the formation of calcium alginate.

D- Effect of pH

Changes in pH greatly affect the viscosity and stability of the hydrophilic natural and synthetic gums.The natural gums usually have a relatively stable viscosity over 5 or 4 pH . Above and below this pH range viscosity decreases sharply.

2- Physical Factors

A- Temperature

A temperature increase usually produces a rapid viscosity decrease, with the exception of certain synthetic polymers such as methyl cellulose,

(c) Light

Various hydrocolloids in aqueous solutions are reported to be sensitive to light. These colloids include carbopol, Na alginate, and Na CMC. To protect photosensitive hydrocolloids from decomposition and resultant viscosity change use light-resistant containers

- Thank You