DIFFUSION

A phase will be at equilibrium in the absence of external fields.

$\therefore$The components/particles/molecules are distributed uniformly

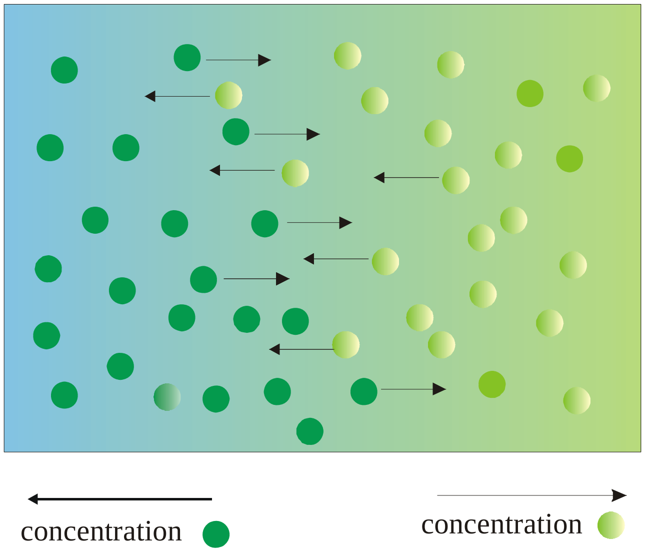
e.g : its x (μ , concentration , temperature etc.)

If there is change in any of the x

Thus → the substance will diffuse

e.g : from low concentration region to high concentration and from high concentration to low concentration.

A solution with two components ,



What is the driving force, F_d for this diffusion?

Chemical potential ;

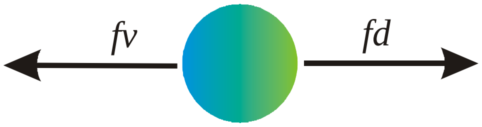
$$\mu_i = \mu_i + Rt \ln c_i$$

$$f_d = -\frac{d\mu}{dx}$$

Overall direction is towards low concentration gradient. i.e : optimise ΔS to obtain its equilibrium.

$$f_d = -\frac{d}{dx}(\mu_i^{\circ} + kT \ln c_i) \text{ - single particle}$$

BUT,



fv = viscous ‘drag’ force

created by the surrounding fluid

$f_d = \beta v$

where

v = *velocity of the particle*

β = *friction coefficient*

As the velocity of the particle increases, v increases $\longrightarrow$ f_v will also increase to balance f_d . In order to overcome this friction,

$$f_d = \beta v_d$$

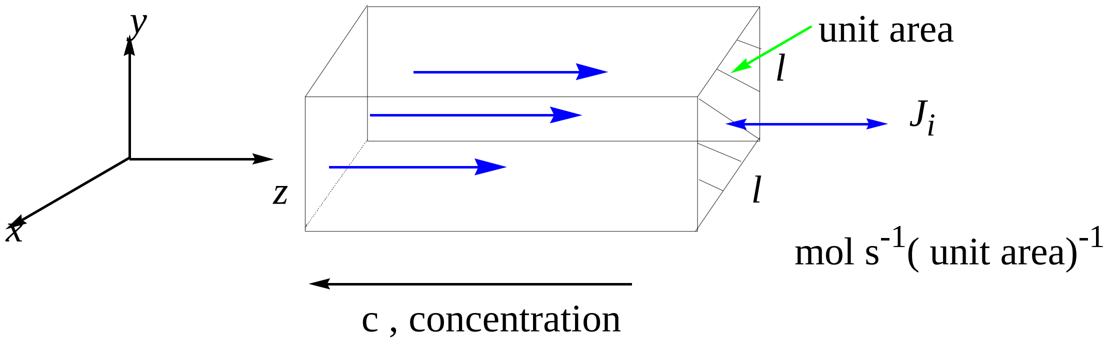
Where v_d – terminal diffusing velocity

FICK’S FIRST LAW OF DIFFUSSION

Fick’s first law describe the migration of substance from higher concentration to lower concentration

Mass Flux, $J_{i,}$

Defined as the amount of substance *i* which passes through a unit area placed at right angles to the direction of diffusion



Now we can have

$$J_i = -D\left(\frac{dc}{dx}\right)$$

where J – Mass Flux, number of particle per $cm^2\ s^{-1}$

D –diffusion coefficient, $cm^2\ s^{-1}$

$\left(dc/dx\right)$- number of particle $cm^{-3}\ cm^{-1}$

Cross –multiply and substitute

$$D = -\frac{J_i}{\left(dc/dx\right)} = \frac{v_d c}{\left(dc/dx\right)}$$

$$\therefore D = \frac{f_d c}{\beta(dc/dx)}$$

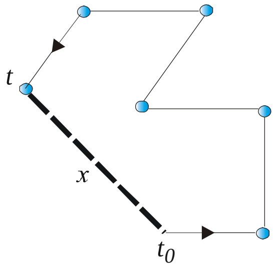
We can write D as, $$D = \frac{kT}{\beta}$$

$$\beta = 6\pi\eta r$$

Where, η = viscosity
r = hydrodynamic radius
$\beta \propto$ size and shape of the particle

$$\therefore D = \frac{kT}{6\pi\eta r} \qquad \text{STOKES – EINSTEIN EQUATION}$$

For Brownian motion



Displacement d - x

EINSTEIN EQUATION :

$$x = \sqrt{2D_t} \quad \text{compare} < x^2 >^{1/2} = [(2D_t)^2]^{1/2}$$

For macromolecule radius 1nm

$D \approx 2 \times 10^{-10}$ m^2 s^{-1}

Assuming that the particle is uncharged

Example of D and Brownian displacement for uncharged spheres in H_2O at 20°C.

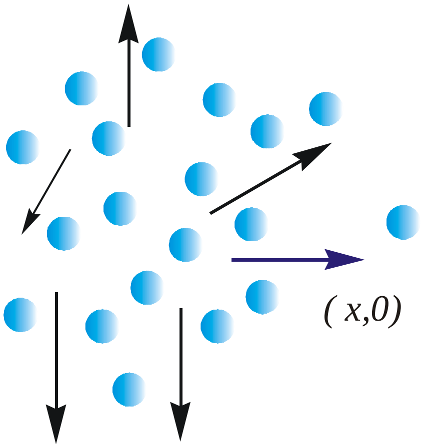
Radius (m)	D_{20} $m^2\ s^{-1}$	x after 1 min
10^{-9}	2.1×10^{-10}	1.23×10^{-3}
10^{-8}	2.1×10^{-11}	3.90×10^{-4}
10^{-7}	2.1×10^{-12}	1.23×10^{-4}
10^{-7}	2.1×10^{-13}	3.90×10^{-5}

FICK’S SECOND LAW

To describe the change in concentration gradient with time, $\frac{\Delta c}{\Delta t}$.

If dc/dx = constant $\longrightarrow$ J_i - same everywhere

What happened when in one are position has different concentration?



$\frac{\delta c}{dt} \propto \frac{\delta J}{\delta x}$ at position x

$\therefore$ more materials diffusing from left to right.

As $\dfrac{\delta J}{\delta x} < 0$; $\dfrac{\delta c}{\delta t > 0}$

$\therefore$ increase concentration with time.

Fick's Second Law

$$\left(\frac{\delta c}{\delta t}\right)_x = D\left(\frac{\delta^2 c}{\delta x^2}\right)_t$$

By using notation of partial derivative because this time $c \propto t, x$

solving the derivative,

$$c(x,t) = c_o\left(\frac{1}{4\pi Dt}\right)^{1/2} \exp\left(\frac{-x^2}{4dt}\right)$$

Justification $c \propto x$ and t *only*

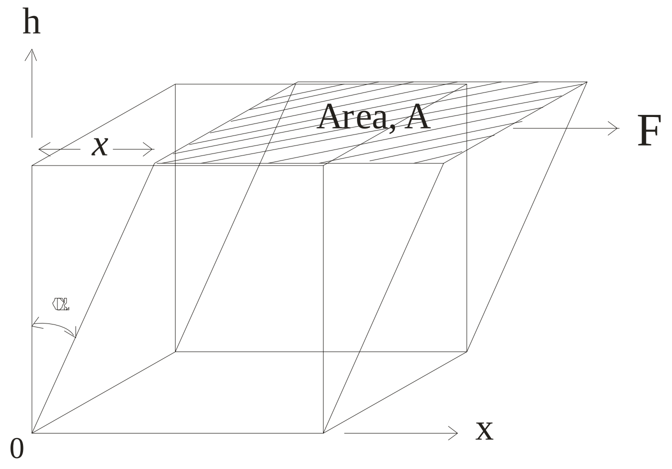
Consider 2D

Total amount of materials = same at all time at $t = 0$; $c = c_o$

At any time ; c is *constant* at all point on the surface.

$\therefore$ $c \; \alpha \; t$ and x.

VISCOSITY



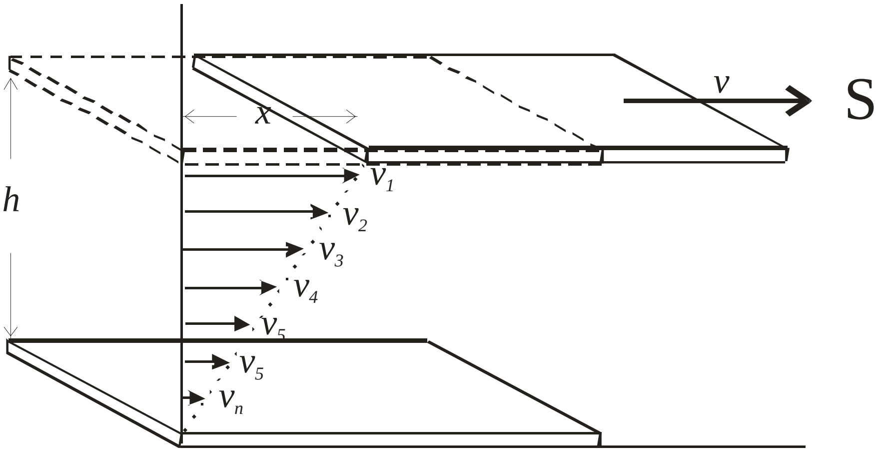
Apply stress on material – it will deform lower plane is held stationary upper plane is pulled with F in x direction.

The consequence,
Strain/deformation , $\gamma = \tan\alpha$

What happens when force is removed?

1. return to its original shape (solids)
2. remain in new position → Flow (liquids)
3. partial recovery (plastic)

SHEARING STRESS OF A LIQUID



Say a simple liquid confined between <u>two</u> plates

Upper plate is pulled with v by $S = \frac{F}{A}$

$$\therefore \frac{d\gamma}{dt} = \frac{d(\tan\alpha)}{dt} = \frac{v}{h}$$

$\frac{v}{h} \rightarrow$ *v = shear rate*
h = velocity gradient , s^{-1}

Assume no slip at solid (plate)/liquid interfaces. $\therefore v$ increases linearly

$$\text{At} \begin{array}{ll} z = 0, & v = 0 \\ z = h & v = v \end{array}$$

Most materials can behave in any of the 3 behaviours.
Strain?

Shorter time-scale -solid like
Longer time-scale – plastic like

e.g : solid like vs plastic like

-flow of rock

-person falling from a great height into water

Newtonian behaviour

$$S = \eta\left(\frac{d\gamma}{dt}\right)$$

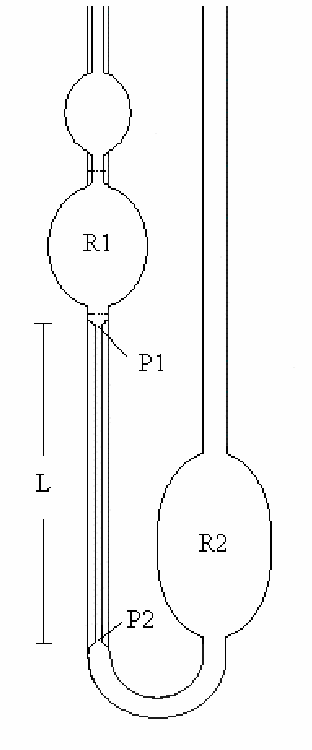
S – shearing stress

$\left(\frac{d\gamma}{dt}\right)$ - rate of shear

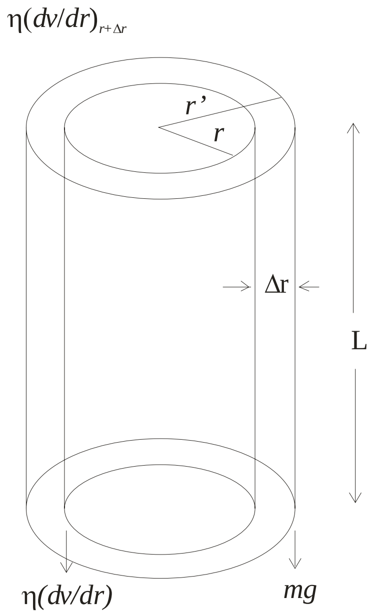
η – viscosity

to describe a liquid-like behaviour.

Ostwald viscometer



Viscosity of the liquid is determined by measuring time taken for the level to drop from upper to lower mark in R_1



Viscosity, η depends on how the fluid flow through the capillary. Normally we arrange of $(r+\Delta r)$

Driving force for the flow

$$\Delta P \times area = (P_1 \_ P_2) 2\pi r . \Delta r$$

OPPOSING FORCE TO THE FLOW

i.e : large force outside the surface due to slow moving fluid

$$F_{op} = (\eta 2\pi r L \frac{dv}{dr}) \text{ at } (r+\Delta r)$$

AND pressure inside the capillary

IF we take F upwards +ve
F downward -ve

Thus,

$$\Delta P 2\pi r \cdot \Delta r - 2\pi r \rho g L \Delta r = \eta 2\pi L[\left(r\frac{dv}{dr} \right)_{r+\Delta r} - (r\frac{dv}{dr})r]$$

$$= \eta 2\pi L[\frac{d}{dv}(v \cdot \frac{dv}{dr})]\Delta r$$

$$= \eta[\frac{1}{r} \cdot \frac{d}{dr} \cdot r(\frac{dv}{dr})] = [\frac{P_2 - P_1}{L} - \rho g]$$

$$= G$$

= constant

After integration,

$$v = -\frac{G}{4\eta}(a^2 - r^2)$$

$G \to -ve$ due to pressure gradient down the capillary.

Thus, drives the fluid downwards often refers as *V-volume*

a - tube cross-section

Flow profile is normally parabolic

Flow rate

$$Q = \int_0^a 2\pi r v dr = -\frac{\pi G a^4}{8\eta}$$

By intergrating the velocity over the tube cross-section.

Relationship with V,

$$V = \frac{\pi a^4 t \Delta P}{8\eta L},$$

fluid flowing through the capillary in time t

Comparison method,

$$\frac{\eta_u}{\eta_\circ} = \frac{t_u \rho_u}{t_\circ \rho_\circ}$$

Where ;

- η_o is the viscosity of the known solvent.
- ρ_o density of the known solvent.
- η_u viscosity of the unknown.
- ρ_u density of the unknown solute.

Viscosity of some common liquid at 15 $^\circ C$

Substance	η, Nm^{-2}s
water	1.14
Hg	1.58
EtOH	1.34

CCl4	1.04
Olive oil	99
Glycerol	2330

Water will flow 2000 times more readily then glycerol
Importance!
Icecream: has the right consistency or “feel” on tongue/lips

Paint: if viscosity η is higher in brush. There will be no dripping and has sufficient flow property after brushing against the wall. The result will be no brush marks, $\eta \propto$ time by shearing stress.

Viscosity

Shape factor

2.5	Sphere
8.0	Oblate
15	prolate

$$[\eta] = \nu(\overline{v_2} + \delta_1 V_1^\circ)$$

$[\eta]\alpha$ partial specific volume of particle, $\overline{v_2}$ hydration, δ_1 specific volume of solvent, v_1°

δ_1 – mass of solvent bound by a gram of solute

Viscosity is a measure of the resistance that a fluid offers to an applied shearing force

symbol	η

units	$kgm^{-1}s^{-1}$
	Pa s (SI)

i.e: 1N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} w.r.t a plane surface 1 m away and parallel to the moving plane. =1 Pa s

Can apply the equation to determine viscosity of a particular solution

$$\frac{\eta_{solution}}{\eta_{solvent}} = \frac{\rho_{solution} \cdot t_{solution}}{\rho_{solvent} \cdot t_{solvent}}$$

If we have macromolecule suspended particles in solution
-Non-Newtonian

Reasons:

hydrodynamic interactions between particles and liquid
attractive and repulsive
particle-particle collision

EINSTEIN EQUATION (1906)
For ideal system,

$$\eta_{solution} = \eta_{solvent}(1 + K\phi)$$

$\phi =$ volume fraction = $\frac{\text{volume solute}}{\text{total volume}}$

K = shape parameter = 2.5 for sphere

Thus, if we have ϕ = volume fraction of the solid, can also find $\eta_{solvent} \to \eta_{solution}$

Equation is part of series expansion

$$\eta = \eta_{solvent}(1 + 2.5\phi + b\phi^2 + c\phi^3 + \_\_\_)$$

Velocity of the particle = velocity of the medium

$= v$

R = radius of particle

Recall – velocity gradient as a result of a moving plate.

Assume NO particle – upper boundary of the particle

$$v + R\frac{dv}{dz}$$

$$\eta_i = 2.5\phi + 6.2\phi^2 + K_3\phi^3 + \_\_\_$$

Second term is when two particles at <2R

Third term is sticky business

Other equation,

Relative viscosity , $\eta_{el} = \frac{\eta_{solution}}{\eta_{solvent}}$

Specific viscocity, $\eta_{sp} = \eta_{rel}^{-1}$

Reduced viscosity, $\eta_{red} = \frac{\eta_{sp}}{c}$

$c =$ solute concentration

$= gcm^{-3}$

INTRINSIC VISCOSITY

$$[\eta] = \lim_{c \to 0} \left(\frac{\eta_{sp}}{c}\right)$$

Thus,

$$\eta_{rel} = 1 + K\phi$$

$$\eta_{sp} = K\phi$$

$$\phi = c\bar{v}$$

Where $\bar{v} =$ m/s g^{-1}

= partial specific volume

= volume taken up by lg of solute

Can get intrinsic viscosity

Slope of the graph reflects interactions between solute particles

The measure viscosity, the capillary effect is used. The force for the movement of solvent depends on the hydrostatic pressure, i.e

$$F_{up} = P\pi r'^2$$

For a small cylindrical sheet, at a radial distance r, the differential force will be

$$dF_{up} = 2P\pi r dr$$

If the fluid is flowing through the capillary at a steady state, this force must be balanced by a frictional force i.e.

$$F_{down} = -A\eta \frac{dv}{dr}$$

$$= -2\pi r L\eta \frac{dv}{dr}$$

where the negative sign indicates that it is in the direction opposite to the applied force.

The net force on the sheet due to fluid motion is the differential force felt by the two sides of the sheet i.e :

$$dF_{down} = -2\pi L\eta \frac{d[r(dv/dr)]dr}{dr}$$

These two differential forces (up and down) are equal, therefore

$$2P\pi r dr = -2\pi L\eta \frac{d[r(dv/dr)]dr}{dr}$$

$$\mathrm{Pr} = -L\eta \frac{d[r(dv/dr)]}{dr}$$

Integrating this equation once gives

$$1/2\,\mathrm{Pr}^2 + c_1 = -\eta L r(dv/dr)$$

and again $\frac{1}{4}\mathrm{Pr}^2 + c_1 \ln r + c_2 = -\eta L v$

where c_1 and c_2 are integration constants.
The integration constants can be obtained by looking at the boundary conditions.

At $x = 0$

$$1/4\,\mathrm{Pr}^2 + \underset{\underset{-\infty}{\downarrow}}{c_1 \ln r} + c_2 = -\eta L v \nwarrow$$

cannot be infinit!!!

Therefore, $c_1 = 0$

At $r = r'$

$$\frac{1}{4}\mathrm{Pr}'^2 + c_2 = -\eta L v (= 0)$$

Therefore, $c_2 = -\frac{1}{4}\mathrm{Pr}'^2$

Thus, we can write,

$$v = \frac{P}{4\eta L}(r'^2 - r^2) \qquad \text{(flow velocity)}$$

Unfortunately, flow velocity is not easily measured – better to use the volume rate of flow, which is defined as

$$\frac{dV}{dt} = \int_0^{r'} 2\pi rv dr$$

$$= \frac{\pi P}{2\eta L} \int_0^{r'} (r'^2 - r^2) r dr$$

$$\frac{dV}{dt} = \frac{\pi \Pr'^4}{8\eta L} \qquad \text{Poiseuille's Law}$$

A fluid of density ρ is allowed to fall from height h_1 to h_2, in a determined time t.Te hydrostatic pressure felt by the solution is given by ρgh.

Using the equation for the volume rate of flow,

$$\frac{dV}{dt} = \frac{\pi P}{2\eta L} \int_0^{r'} (r'^2 - r^2) r dr$$

we can determine the time required for the total volume V to flow by integrating. The results is

$$t = \frac{8\eta L}{\pi g \rho r'^4} \int_{h_1}^{h_2} dV / h$$

The integral is a constant for a given apparatus , which is determined by measuring the time it takes for a solution of known density to fall from $h_1$to h_2. Typically one uses the pure solvent in which the macromolecule will be studied subsequently.

Disadvantages

Large volume of solution is required.

Shearing forces generated by the flow gradient are large.

Shear stress $S = F / A = \eta(dv / dr)$

-can cause distortions in the coil distribution of flexible molecules, which in turns means that the viscosity can be altered.

The average shear stress in a capillary viscometer can be determined by using the equation:

$$\tfrac{1}{2}\Pr^2 + c_1 = -\eta L r (dv / dr)$$

where we know that $c_1 = 0$

This allows us to write

$$S_r = \eta(dv / dr) = -\frac{\Pr}{2L}$$

For a cylindrical sheet of fluid with radius r. To obtain the average shear stress, we need to integrate the expression over all sheets,

$$\langle S \rangle = \frac{\int_0^{r'^2} 2\pi r L dr S r}{\int_0^{r'^2} 2\pi r L dr}$$

$$= \frac{\dfrac{2\pi L(-P)\int r^2 dr}{2L}}{2\pi L\int r dr} = \frac{\dfrac{-\mathrm{Pr}'^{3}}{(2L)(3)}}{r'^{2}/2}$$

$$\langle S\rangle = -\frac{\mathrm{Pr}'^{2}}{3L}$$

shear stress depends on height of the capillary

Assumption : that the pressure remains constant during capillary viscosity measurement-not the case!