DIFFUSION

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

∴ The components/particles/molecules are distributed uniformly
e.g: its $x$ ($\mu$, concentration, temperature etc.)

If there is change in any of the $x$

Thus $\rightarrow$ 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 \( \Delta S \) to obtain its equilibrium.

\[ f_d = -\frac{d}{dx}(\mu_i + kT \ln c_i) \] - single particle

BUT,

\[ f_v = \text{viscous ‘drag’ force} \]

created by the surrounding fluid

\[ f_d = Bv \]

where

\[ \nu = \text{velocity of the particle} \]

\[ B = \text{friction coefficient} \]

As the particle increase \( \nu \) to balance \( f_d \). To overcome this friction,

\[ f_d = B\nu_d \]

Where \( \nu_d \) - terminal diffusing velocity
FICK’S FIRST LAW OF DIFFUSION

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$^{-1}$
- $\left( \frac{dc}{dx} \right)$ - number of particle cm$^{-3}$ cm$^{-1}$
Cross–multiply and substitute

\[
D = -\left( \frac{J_i}{dc/dx} \right) = \frac{v_{dc}}{dc/dx}
\]

\[\therefore D = \frac{f_{dc}}{B(dc/\,dx)}\]

We can write \(D\) as,

\[D = \frac{kT}{B}\]

\[B = 6\pi \eta r\]

Where,

\[\eta = \text{viscosity}\]
\[r = \text{hydrodynamic radius}\]

\(B \propto \text{size and shape of the particle}\)

\[\therefore D = \frac{kT}{6\pi \eta r} \quad \text{STOKES – EINSTEIN EQUATION}\]

For Brownian motion

\[\text{Displacement } d - x\]

\[\text{EINSTEIN EQUATION :}\]
\[ x = \sqrt{2D_t} \] compare \( <x^2>^{1/2} = [(2D_t)^2]^{1/2} \)

For macromolecule radius 1nm

\[ D \approx 2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1} \]

Assume - uncharged

Example of \( D \) and Brownian displacement for uncharged spheres in H\(_2\)O at 20°C.

<table>
<thead>
<tr>
<th>Radius (m)</th>
<th>( D_{20} \text{ m}^2 \text{ s}^{-1} )</th>
<th>( x ) after 1 n, m</th>
</tr>
</thead>
<tbody>
<tr>
<td>( 10^{-9} )</td>
<td>( 2.1 \times 10^{-10} )</td>
<td>( 1.23 \times 10^{-3} )</td>
</tr>
<tr>
<td>( 10^{-8} )</td>
<td>( 2.1 \times 10^{-11} )</td>
<td>( 3.90 \times 10^{-4} )</td>
</tr>
<tr>
<td>( 10^{-7} )</td>
<td>( 2.1 \times 10^{-12} )</td>
<td>( 1.23 \times 10^{-4} )</td>
</tr>
<tr>
<td>( 10^{-7} )</td>
<td>( 2.1 \times 10^{-13} )</td>
<td>( 3.90 \times 10^{-5} )</td>
</tr>
</tbody>
</table>

**FICK’S SECOND LAW**

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

If \( dc/dx = \text{constant} \rightarrow J_i \) - same everywhere

What happened when in one area position has different concentration?
\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

using notation of partial derivative because this time \( c, \alpha, t, x \)

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 \textit{constant} at all point on the surface.

\( \therefore \) \( c \propto t \) 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,
\[
\text{Strain/deformation}, \quad \gamma = \tan \alpha
\]

What happens when force is removed?

1. return to its original shape \( \quad \) (solids)
2. remain in new position \( \rightarrow \) Flow \( \quad \) (liquids)
3. partial recovery \( \quad \) (plastic)
SHEARING STRESS OF A LIQUID

Say a simple liquid confined between two plates

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

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

\[
\frac{v}{h} \rightarrow v = \text{shear rate}
\]

\( h = \text{velocity gradient} \), \( s^{-1} \)

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

At \( z = 0, \quad v = 0 \)

\( z = h \quad v = v \)

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
- \( \eta \) – 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, $\eta$ depends on how the fluid flow through the capillary. Normally we arrange of $(r + \Delta r')$

Driving force for the flow

$$\Delta P \times \text{area} = (P_1 - P_2)2\pi r\Delta r$$

**OPPOSING FORCE TO THE FLOW**

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

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

AND pressure inside the capillary
IF we take $F$ upwards +ve
$F$ downward -ve

Thus,

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

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

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

$$
= G
$$

= constant

After integration,

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

$G \to -ve$ 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
\[
Q = \int_0^a 2\pi r vd r = -\frac{\pi Ga^4}{8\eta}
\]

By integrating 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,

\[
\frac{\eta_u}{\eta_o} = \frac{t u \rho_u}{t_o \rho_o}
\]

Where:

- \( \eta_o \) is the viscosity of the known solvent.
- \( \rho_o \) density of the known solvent.
- \( \eta_u \) viscosity of the unknown.
- \( \rho_u \) density of the unknown solute.

Viscosity of some common liquid at 15°C

<table>
<thead>
<tr>
<th>Substance</th>
<th>( \eta ), Nm(^{-2})s</th>
</tr>
</thead>
<tbody>
<tr>
<td>water</td>
<td>1.14</td>
</tr>
<tr>
<td>Hg</td>
<td>1.58</td>
</tr>
<tr>
<td>EtOH</td>
<td>1.34</td>
</tr>
</tbody>
</table>
Water will flow 2000 times more readily than glycerol.

**Importance!**

Icecream: has the right consistency or “feel” on tongue/lips

Paint: if viscosity $\eta$ 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**

<table>
<thead>
<tr>
<th>Shape factor</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>Sphere</td>
</tr>
<tr>
<td>8.0</td>
<td>Oblate</td>
</tr>
<tr>
<td>15</td>
<td>Prolate</td>
</tr>
</tbody>
</table>

\[
[\eta] = \nu(v_2 + \delta_1 V_1^\circ)
\]

$[\eta]$ - partial specific volume of particle, $v_2$ - hydration, $\delta_1$ - specific volume of solvent, $V_1^\circ$

$\delta_1$ - 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 | $\eta$ |
### Units

<table>
<thead>
<tr>
<th>units</th>
<th>kgm$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pa s (SI)</td>
</tr>
</tbody>
</table>

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,

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

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

$$K = \text{shape parameter} = 2.5 \text{ for sphere}$$

Thus, if we have $\phi =$ volume fraction of the solid, can also find $\eta_{solvent} \rightarrow \eta_{solution}$
Equation is part of series expansion
\[ \eta = \eta_{solvent} (1 + 2.5\phi + b\phi^2 + c\phi^3 + \ldots) \]
Velocity of the particle = velocity of the medium
\[ = v \]
\[ R = \text{radius of particle} \]

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

Assume NO particle – upper boundary of the particle
\[ \nu + R \frac{dv}{dz} \]
\[ \eta_i = 2.5\phi + 6.2\phi^2 + K_3\phi^3 + \ldots \]

Second term is when two particles at <2R

Third term is sticky business

Other equation,

Relative viscosity, \( \eta_{rel} = \frac{\eta_{solution}}{\eta_{solvent}} \)

Specific viscosity, \( \eta_{sp} = \eta_{rel}^{-1} \)

Reduced viscosity, \( \eta_{red} = \frac{\eta_{sp}}{c} \)
\[ c = \text{solute concentration} \]
\[ = gcm^{-3} \]

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

Thus,

\[ \eta_{rel} = 1 + K\phi \]

\[ \eta_{sp} = K\phi \]

\[ \phi = c\nu \]

Where \( \nu = \text{m/s g}^{-1} \)

= 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

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

Integrating this equation once gives

\[ \frac{1}{2} \text{Pr}^2 + c_1 = -\eta \text{Lr} (dv/dr) \]

and again

\[ \frac{1}{4} \text{Pr}^2 + c_1 \ln r + c_2 = -\eta \text{Lv} \]

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

At \( x=0 \)

\[ \frac{1}{4} \text{Pr}^2 + c_1 \ln r + c_2 = -\eta \text{L} v \]

cannot be infinite!!!

Therefore, \( c_1 = 0 \)

At \( r=r' \)

\[ \frac{1}{4} \text{Pr}^2 + c_2 = -\eta \text{L} v (= 0) \]

Therefore, \( c_2 = -\frac{1}{4} \text{Pr}^2 \)

Thus, we can write,

\[ v = \frac{P}{4\eta L} (r'^2 - r^2) \]

(flow velocity)

Unfortunately, flow velocity is not easily measured – better to use the volume rate of flow, which is defined as
\[
\frac{dV}{dt} = \int_{0}^{r'} 2\pi rvdr
\]

\[
= \frac{\pi P}{2\eta L} \int_{0}^{r'} (r'^2 - r^2) rdr
\]

\[
\frac{dV}{dt} = \frac{\pi Pr'^4}{8\eta L} \quad \text{Poiseuille’s Law}
\]

A fluid of density $\rho$ is allowed to fall from height $h_1$ to $h_2$, in a determined time $t$. The hydrostatic pressure felt by the solution is given by $\rho gh$.

Using the equation for the volume rate of flow,

\[
\frac{dV}{dt} = \frac{\pi P}{2\eta L} \int_{0}^{r'} (r'^2 - r^2) rdr
\]

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

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

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

\[ S = \frac{F}{A} = \eta \left( \frac{dv}{dr} \right) \]

-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:

\[ \frac{1}{2} \Pr^2 + c_1 = -\eta L \left( \frac{dv}{dr} \right) \]

where we know that \( c_1 = 0 \)

This allows us to write

\[ S_r = \eta \left( \frac{dv}{dr} \right) = -\frac{\Pr}{2L} \]

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

\[ \langle S \rangle = \frac{\int_{r_1}^{r_2} 2\pi r L dr S_r}{\int_{r_1}^{r_2} 2\pi r L dr} \]
\[
\frac{2\pi L (-P) \int r^2 dr}{2L} = \frac{-Pr^3}{(2L)(3)} \frac{r^2}{2}
\]

\[
\langle S \rangle = -\frac{Pr^2}{3L}
\]

shear stress depends on height of the capillary

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