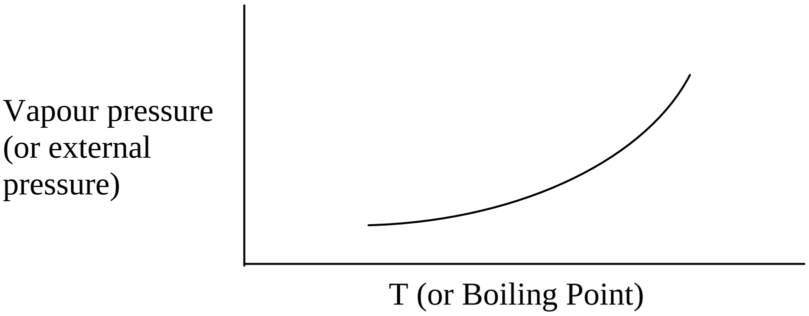
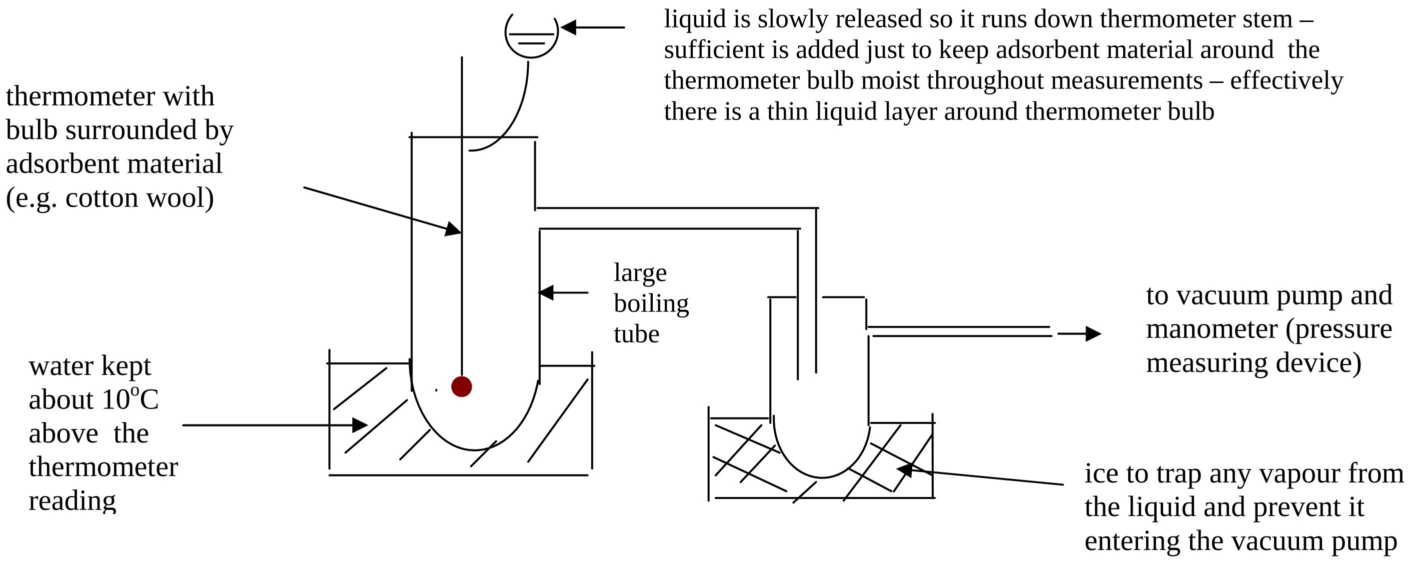
PHASE EQUILIBRIA

(A) Descriptive Questions

1. One method is to determine the boiling point of the liquid at a number of external pressures. Since a liquid boils when its vapour pressure equals the external pressure, a plot of external pressure versus the boiling point of the liquid is identical with that of vapour pressure of the liquid versus temperature:

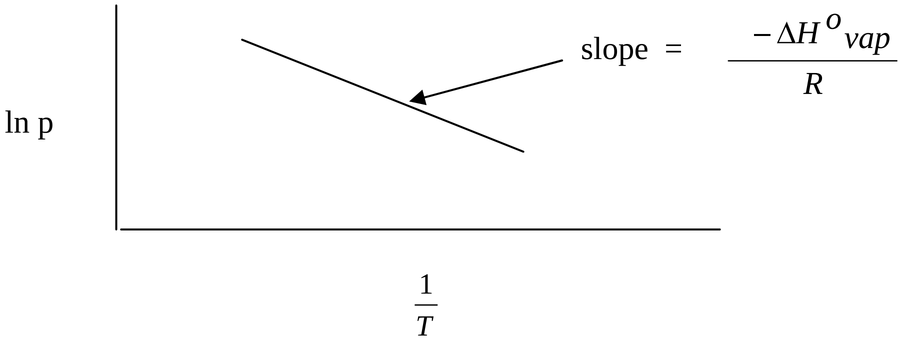


A simple laboratory experiment can be used to measure the boiling point of a suitable liquid at different external pressures. Only a small amount of the liquid is needed. The main features of the equipment used are illustrated below:-



The vacuum pump is used to produce a low pressure whose value is recorded from the manometer. It is then isolated from the apparatus, which should remain at this pressure provided there are no leaks. The thin layer of liquid around the thermometer bulk is warmed by heat transfer from the water in the beaker. Note that the liquid is not in direct contact with the heat source and is essentially heated by radiation (under these conditions no super-heating of the liquid occurs). The temperature of the liquid film will rise as it is warmed (as indicated by the thermometer reading) but will become constant at the boiling point. The pressure in the system is then increased and the new (higher) boiling point measured. These procedures are repeated a number of times.

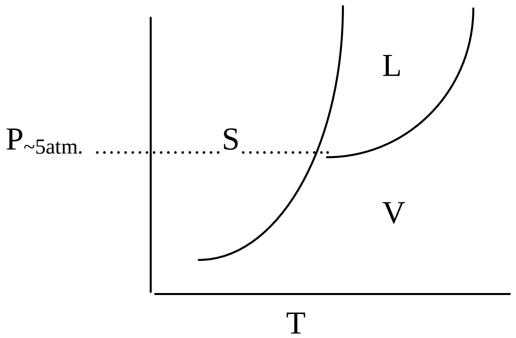
Plot *ln* (external pressure) vs $\frac{1}{B.pt/K}$ - should obtain a straight line



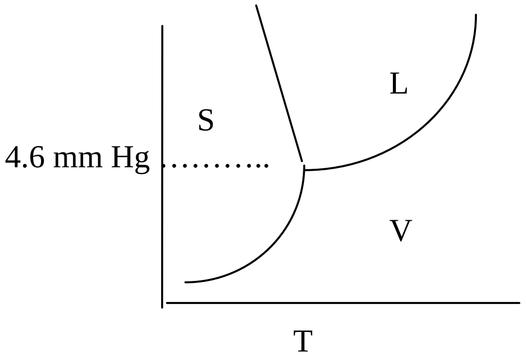
Hence $\frac{\Delta H^{o}vap}{R}$ (Heat of Vapourisation) of the liquid is evaluated from slope.

2. (a) At the triple point of a substance (a certain pressure and temperature) its solid, liquid and vapour forms exist together in equilibrium.

(b) The triple point pressure of carbon dioxide is above one atmosphere, whereas that of water is below atmospheric pressure. When a sample of solid CO_2 is brought to room temperature at 1 atm the solid/vapour phase boundary must be crossed, sublimation occurs, whereas for water the solid/liquid phase boundary will be crossed and melting occurs.

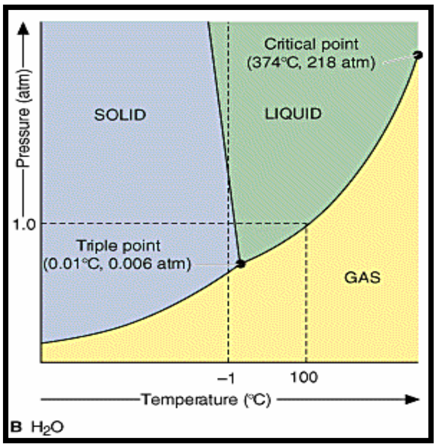


Phase Diagram for Carbon Dioxide



Phase Diagram for Water

(c) **Freeze-drying.** A substance (or solution) containing water is cooled (frozen) in a container below $0^{o}C$ and the container then attached to a vacuum pump so that the pressure of the system is reduced below the triple point pressure of water, i.e. < 4 mm Hg. The sample is then allowed to slowly warm, keeping a pressure of < 4 mm Hg. Under these conditions the frozen water within the sample will sublime (rather than melt) and the water vapour produced is removed by the pump. All the frozen water is removed this way, leaving a sample in a finely divided convenient form (in contrast to the case when water in the liquid state is pumped away).



3. An ideal solution is one that obeys Raoult's Law at all concentrations.

Vapour pressure of pure solvent

Vapour pressure above ideal solution

$$P_A = P_A^o x_A$$

Mole fraction of solvent

- R.L. expression (solute non-volatile)

$$\left.\begin{array}{l} P_A = P_A^o x_A \\ \\ P_B = P_B^o x_B \end{array}\right\}$$

R.L. expressions for ideal solution solute and solvent both volatile (liquid / liquid)

Vapour pressure of solute

Mole fraction of solute

Vapour pressure of pure solute

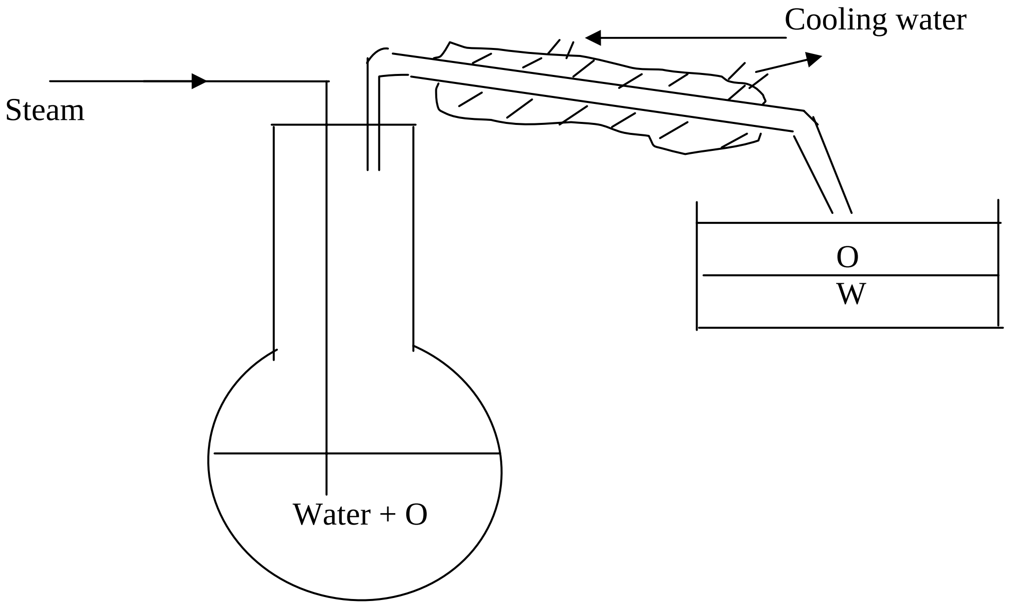
4. **Steam Distillation.** In this process a mixture of water(W) and an organic liquid (O) immiscible with water, is boiled. Because the total vapour pressure at any temperature is $P_{total} = P_w^o + P_o^o$, where P_w^o and P_o^o are the vapour pressures of pure water, and the organic, respectively, the mixture will boil at a temperature less than either the boiling point of pure organic or that of water (100°C at 1 atmosphere). The boiling point of the mixture will remain constant until one of the components (O or W) has been completely removed from the mixture. The composition of the distillate will also be constant with time until one component has been completely removed from the boiling mixture. The weight composition of the distillate is given by:

Values at boiling point of mixture

$$\frac{m_o}{m_w} = \frac{P_o^o M_o}{P_w^o M_w}$$

Molecular weights of Organic and Water

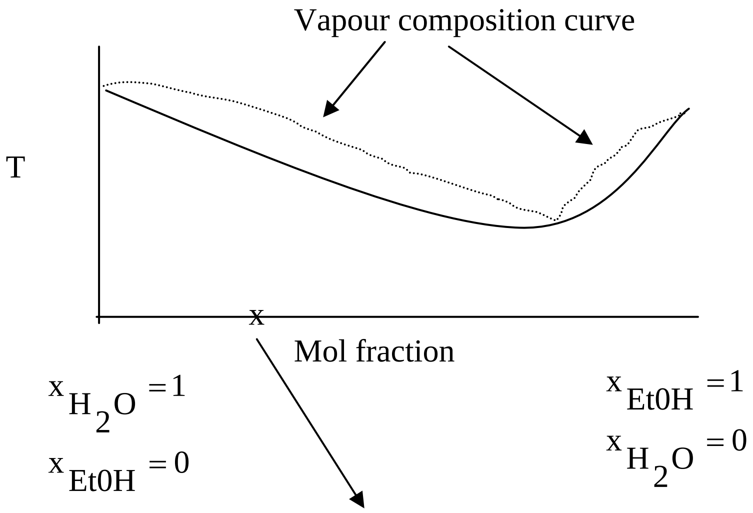
In steam distillation steam is passed through a mixture of heated water and the organic material.



Distillation Flask
(usually heated gently)

The steam keeps the liquid mixture in the flask agitated and boiling. The vapour above the boiling mixture moves into the condenser to give the distillate (two liquid layers). This technique is used to extract oils from substrates (e.g. gum leaves) and to purify organic liquids (distil below 100°C, leaving non-volatile impurities in the distillation flask).

5. Minimium boiling point mixture.



Mixture being fractionally distilled

From the above diagram:

<u>First Fraction</u> – Azeotropic Mixture, we move down the boiling point curve until the constant boiling azeotrope is obtained. The vapour composition does not change until all the more volatile component (EtOH) has been removed at this constant boiling point.

<u>Second Fraction</u> - Water At this stage all the EtOH has been removed.

(B) Calculations

1.

$$\ell n\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\left[\frac{-R}{\Delta H_{vap}}\ell n\left(\frac{P_2}{P_1}\right)\right]+\frac{1}{T_1}=\frac{1}{T_2}$$

$$\left[\frac{-8.314}{44.5\,\mathrm{x}\,10^3}\ell n\left(\frac{2666.4}{1.013\,\mathrm{x}\,10^5}\right)\right]+\frac{1}{391} = \frac{1}{T_2}$$

$6.7957\mathrm{x}10^{-4} + 0.002557 = 1/T_2$

T_2 = 308.9 K

= 35.8°C (to 3 significant figures)

2.

$$\ell n\left(\frac{P_2}{P_1}\right) = \frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\left[-R\,\mathrm{x}\,\ell n\left(\frac{P_2}{P_1}\right)\right]\ \mathrm{x}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)^{-1} = \Delta H_{vap}$$

$$\left[-8.314\,\mathrm{x}\,\ell n\left(\frac{8.95}{3.41}\right)\right]\ \mathrm{x}\left(\frac{1}{343}-\frac{1}{303}\right)^{-1} = \Delta H_{vap}$$

$-8.0225 \mathrm{x} -2598.225 = \Delta H_{vap}$

20844.316 J = ΔH_{vap}

ΔH_{vap} = **20.8 kJ / mol**

3. Equal wts, say *y* g of benzene and *y* g of toluene
(C_6H_6) ($C_6H_5CH_3$)

For an ideal solution
V.P. above solution → $p_B = p_B^o\ x_B$ ← mole-fraction benzene in solution
due to benzene
i.e. partial pressure $p_T = p_T^o\ x_T$ ← mole-fraction toluene in solution

molar mass benzene in g mol^{-1}
Number of moles in benzene solution $= y / M_B$
$= y / 78$

Number of moles of toluene = $y / 92$

$p_B = p_B^o x_B = p_B^o n_{B/(} n_{T+} n_B)$

$$\therefore\ p_B = \frac{119.6 \text{ x } y/78}{(y/78 + y/92)} = \frac{119.6}{78\left(\frac{1}{78} + \frac{1}{92}\right)} = 64.7 \text{ torr}$$

Similarly $$p_T = \frac{36.7 \text{ x } y/92}{(y/78 + y/92)} = 16.8 \text{ torr}$$

$p_{benzene}$ = 64.7 torr
$p_{toluene}$ = 16.8 torr

Total gas pressure = 64.7 + 16.8 = **81.5 torr**

Apply relationship $Pi = P_T \text{ x } x_i$ ⟵ P_T = 81.5torr

$\therefore$ **x_B(in vapour phase) = 0.79** = $\frac{64.7}{81.5}$

$\therefore$ **x_T(vapour phase)** = 1 – 0.79 = **0.21**

4. (a) $$\text{Initial} \frac{\text{Benzene}(500^3)}{1g \text{ Aniline in } 1000 \text{ cm}^3 H_2O} \xrightarrow{\text{Mix}} \therefore \frac{xg/500cm^3 Benzene}{(1-x)/1000cm^3 H_2O}$$

Let x g of Aniline (A) go into benzene layer

$$\therefore \frac{2x}{1-x} = 10.0$$

$\therefore$ 2x = 10 – 10x

$\therefore$ x = $\frac{10}{12} = 0.833$

$\therefore$ Must have 1 - 0.833 = **0.167 g** remaining in water.

(b) **After first mixing** $$\frac{x/250cm^3 C_6H_6}{(1-x)/1000H_2O}$$

$$\therefore \frac{4x}{1-x} = 10$$

$\therefore 4x = 10 - 10x$ $\therefore x = \frac{10}{14} = 0.714$

$\therefore$ Must have 1 - 0.714 = 0.286 g remaining in aqueous phase.

After second extraction you have $\frac{x g / 250 cm^3 C_6H_6}{(0.286 - x)/1000 H_2O}$

$\therefore \frac{4x}{0.286 - x} = 10$

$\therefore 4x = 2.86 - 10x$

$x = 0.204$

$\therefore$ **Must have 0.286 - 0.204 = 0.082 g left in water**

5. Total vapour pressure = 760 torr (l atm) = p_{total}

CB = C_6H_5Cl M = 112.5 g mol^{-1}

Steam distillation $p_{total} = p^o_{H2O} + p^o_{organic}$

P^o_{CB} = 214 torr ⇒ P^o_{H2O} = (760 – 214) = 546 torr

For the mixture of vapours

$P_{CB} = P_{Total} \times x_{CB}$ ⟵ mole fractions in

$P_{H20} = P_{Total} \times xH_2O$ ⟵ the vapour phase

$$\therefore \left.\begin{array}{l} 214 = 760 \times x_{CB} \\ 546 = 760 \times xH_2O \end{array}\right\} \begin{array}{l} \Rightarrow x_{CB} = 0.28 \\ \Rightarrow xH_2O = 0.72 \end{array}$$

∴ Ratio on a mol / mol basis 0.28 moles CB / 0.72 moles H_2O

∴ Ratio on a g / g basis 0.28 x 112.5 g CB / 0.72 x 18 g H_2O

We need to know how many g of water are required to obtain 10g of CB.

0.28 x 112.5 g CB / 0.72 x 18 g H_2O = 10g CB / *z* g H_2O

$\therefore$ z g H_2O = 10 g CB x $\frac{0.72 \times 18}{0.28 \times 112.5}$

= 4.1 g i.e. 10g CB / 4.1g of water.

$\therefore$ Distillation of **4.1g** of water would bring over 10g of purified chlorobenzene.

COLLOIDS

1.

(a) A colloid is a disperse system in which the particles have approximate diameters in the range 1-1000 nm. (As a consequence, the particles are not retained by conventional filters and are only visible in the electron microscope.)

(b) An emulsion is a dispersion of a liquid in a liquid.

(c) A gel is a dispersion of a liquid throughout a solid.

(d) A foam is a dispersion of a gas throughout a liquid or solid (solid foam).

(e) A lyophobic colloid is a dispersion of solid particles (with approximate diameters in the range 1-1000 nm) in a liquid. The particles are made up of aggregates of large numbers of molecules or ions that are insoluble in the liquid. Lyophobic colloids are thermodynamically unstable. Lyophobic means "solvent hating" which indicates that the polarity of the colloid particles is considerably different to the liquid medium.

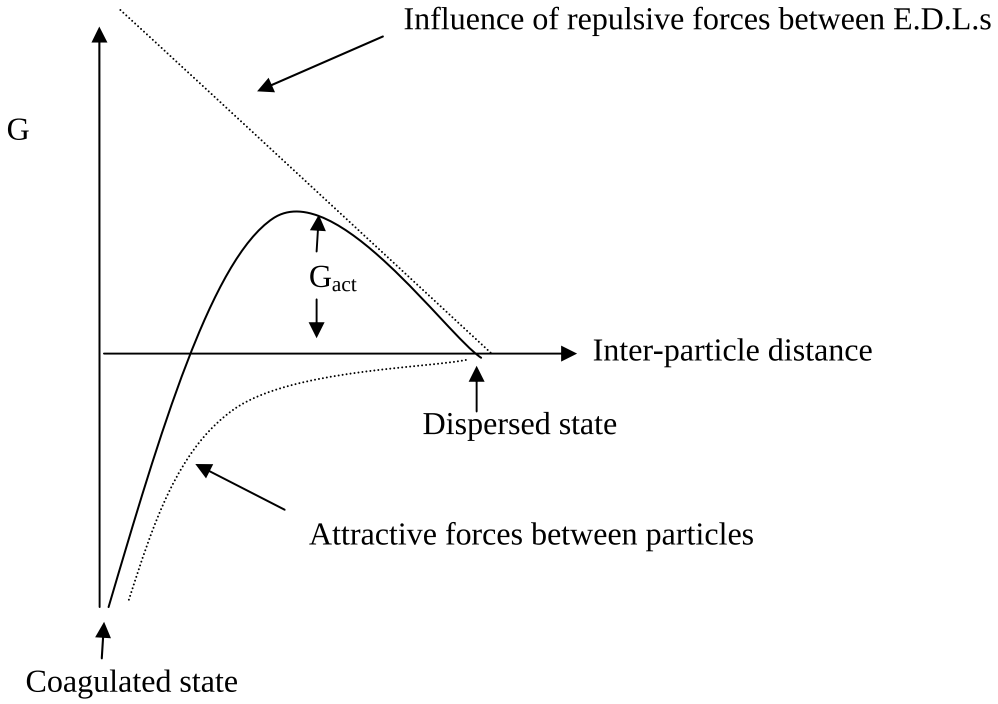
(f) Electrical Double Layer. The distribution of ions which occurs in a medium in the proximity of a charged surface (e.g. lyophobic colloid particles, electrode surface.)

negatively
charged
surface

	Medium			
–	+	+	+	–
–	+	+	–	+
–	+	–	+	–
–	–	+	+	+
–	+	+	+	–
–	+	+	–	+
–	+	–	+	–
–	+	+	+	+

Electrical Double Layer – may be several ions thick, i.e. > 3 as shown

2. Lyophobic colloids are thermodynamically unstable because their free energy is much greater than if they coagulated and thereby settled out. (This is because the surface area/volume ratio of very small particles is >> that of large ones, and molecules or ions at the surface of the particles (or at any phase boundary) have higher energy than those in the bulk phase.) Coagulation is therefore a spontaneous process in the thermodynamic sense. It does not occur in some circumstances because the particles are kinetically stable. The basis of this is the repulsive forces which exist between the electrical double layers of each colloid particle. These increase in magnitude as the colloid particles become closer. Van der Waal's attractive forces also exist between the particles; however, in the absence of moderate to large concentrations of electrolytes, these are insufficient to overcome the repulsive forces. The situation is represented by the following free energy diagram:

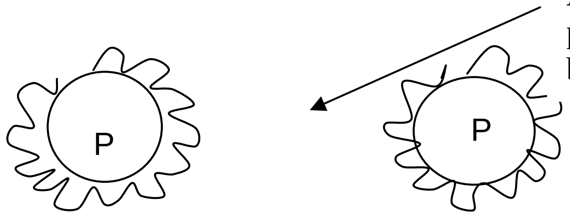


Only the particles with kinetic energy ≥ G_{act} can coagulate. If the energy barrier, G_{act}, is large enough, no coagulation will occur even over long periods of time.

3.

(a) The answer to this question requires a description of the state of the lyophobic colloid before adding electrolyte. This is summarised in the diagram and description given above on this page as part of the answer to Q.2.
Continuing: the effect of the addition of electrolyte is to reduce the magnitude of the repulsive forces between the particles, particularly at larger inter-particle distances. If sufficient electrolyte is added the energy barrier, G_{act} can be eliminated (or at least significantly reduced) so that coagulation occurs. The higher the valency of the counter ion (the ion of the electrolyte whose charge is opposite to that of the colloid particles), the more effective is the electrolyte in causing coagulation. This is because the higher the valency of the counter ion, the greater its effect in compressing the E.D.L.

(b) The addition of certain polymers to some lyophobic colloids can increase their kinetic stability, i.e. more electrolyte is needed to induce coagulation than in the absence of the polymer. This is the so-called "Protective Effect" - steric stabilisation. The polymer molecules are adsorbed at the particle surface to a degree which allows "loops" or segments of the polymer molecules to extend into the medium.

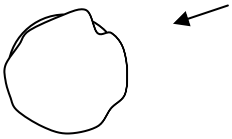


As particles move closer, steric crowding of polymer loops results in extra repulsive force between particles.

There may be many polymer molecules adsorbed at surface of one particle. Usually the polymer molecule has a high molecular weight in range 20-100,000.

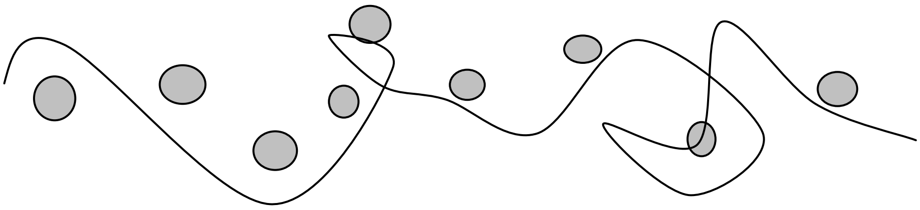
As the particles become closer, the polymer "loops" penetrate one another at the expense of their interactions with the medium molecules. This leads to an increase in free energy, which results in the existence of an extra repulsive force between the particles.

(Note: if the polymer molecules are adsorbed too strongly, this repulsive force will not exist)

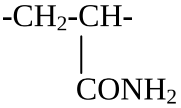


Polymer molecules flat on surface and no loops extended

Polymer molecules can also sometimes induce coagulation of lyophobic colloid particles. (This was called flocculation to distinguish the process from coagulation induced by the addition of electrolytes. However, the terms coagulation and flocculation (and even precipitation) are often used as alternatives for either process. In this case, the polymer molecules are very weakly adsorbed so that only an occasional segment becomes associated with one particle. Each polymer molecule is, however, associated with many particles so that it bridges between them.

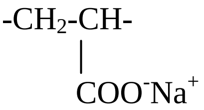


The effect is to pull the particles together so that their density effectively increases and sedimentation occurs. [Polymers that are active flocculants are polyelectrolytes, e.g. polymers made up of units such as:



$$-CH_2-\underset{\displaystyle CONH_2}{\underset{|}{CH}}-$$

and



$$-CH_2-\underset{\displaystyle COO^-Na^+}{\underset{|}{CH}}-$$

randomly arranged along the chain.

They also have very high mol wts, e.g. 20×10^6 and are used at the ppm level.

Surprisingly, perhaps, anionic polyelectrolytes are more effective in flocculating negatively charged particles than cationic polyelectrolytes. This is because repulsion between the negative particles and the negative groups along the polymer chain ensures only weak adsorption occurs and that the polymer molecules become associated with a number of particles.

MOLECULAR ORBITAL THEORY

1. What do you understand by the following?

(a) *Hund's rule* as applied to Molecular Orbitals

When molecular orbitals of *equal energy* are available, the electronic sconfiguration of lowest energy for the molecule has the *maximum number of unpaired electrons with parallel spins*.
eg. if 2 electrons are placed in the $\pi 2p_y$, $\pi 2p_z$ MOs then these electrons will be unpaired and will have parallel spin.

(b) The Linear Combination of Atomic Orbitals (LCAO) approximation.

The LCAO approximation is the mathematically based model that is used to construct molecular orbitals (MOs) from atomic orbitals (AOs). Only AOs with similar energies and orientation may combine to form MOs, in practice this means that the quantum numbers of the AOs involved must be the nearly the same. The combination of *n* AOs will generate *n* MOs of which n/2 will be bonding orbitals and n/2 will be antibonding orbitals. The bonding MOs are formed by additive combination of the AOS while the antibonding orbitals are formed by subtractive combination of the AOs.

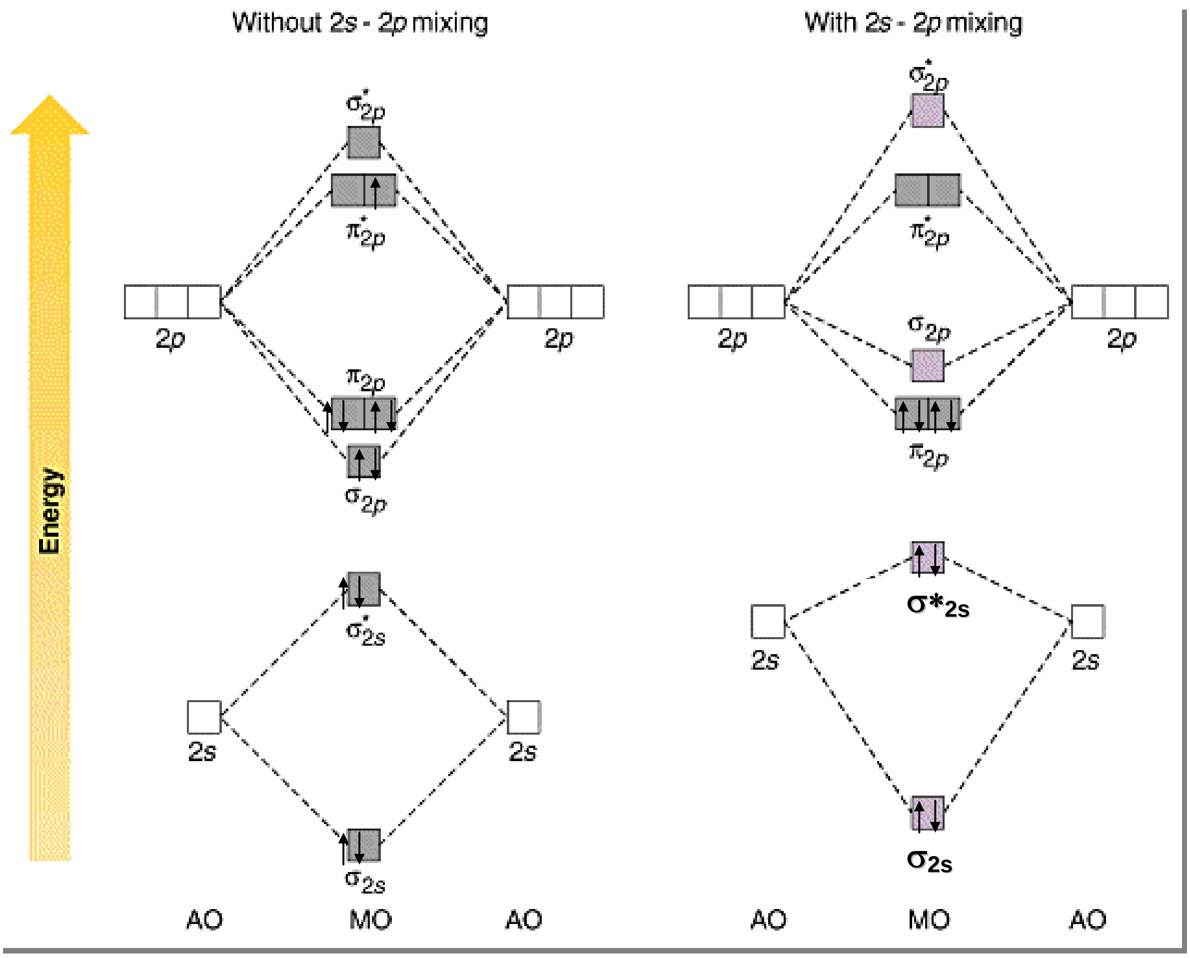
Eg.	1s + 1s $\rightarrow \sigma_{1s}$ (bonding)	1s - 1s $\rightarrow \sigma_{1s}^*$ (antibonding)
Amplitude	**+** + **+** **++**	**+** - **+** **+ -**

(c) The *bond order* of a diatomic molecule.

The bond order is a measure of the net bonding in a diatomic molecule and is defined by the following expression:
Bond order = 1/2 [no. of bonding e^- - no. of antibonding e^-]
The bond order correlates with the bond strength and inversely correlates with the length of the bond. Ie. a high bond order indicates a high bond strength and a short bond.

1. Calculate the bond orders and predict the stability of C_2, C_2^-, O_2, O_2^+ using the above MO scheme.
Which of these molecules would be expected to display paramagnetic behaviour?

C_2 bond order = 1/2(6 - 2) = 2	
C_2^- bond order = 1/2(7 - 2) = 2.5	paramagnetic
O_2 bond order = 1/2(8 - 4) = 2	paramagnetic
O_2^+ bond order = 1/2(8 - 3) = 2.5	paramagnetic



O_2^+ MO structure

C_2 MO structure