# UNIT III
# LIQUIDS AND SOLUTIONS

## LIQUIDS

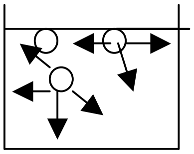
### 1) FORCES OF ATTRACTION AND THE THREE PHYSICAL STATES OF MATTER.

### 2) TEMPERATURE AND THE THREE PHYSICAL STATES OF MATTER.

### 3) EVAPORATION OF LIQUIDS:

Definition:

Which molecules will evaporate first?



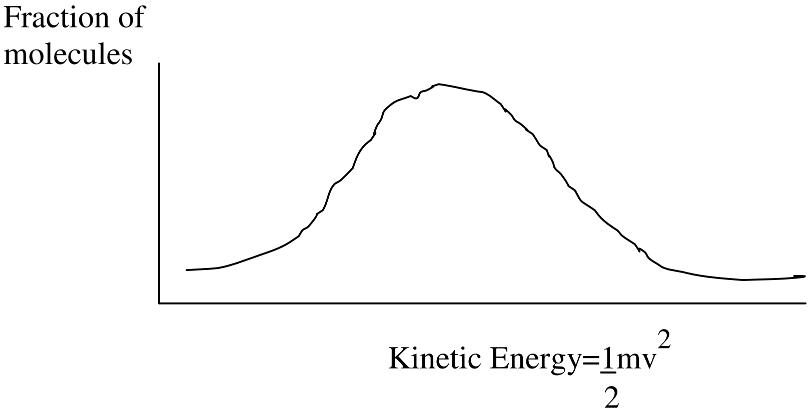


Figure: Molecular distribution

### 4) COOLING DUE TO EVAPORATION.

$$\boxed{\overline{K.E.} \propto T}$$

Particles of high kinetic energy will escape first, leaving behind the particles of lower kinetic energy. After evaporation, the average kinetic energy of the molecules remaining in the liquid drops, hence the temperature of the remaining liquid drops too. It takes energy for the particles to get detached and escape (heat energy is lost).

Applications:

a) Perspiration.

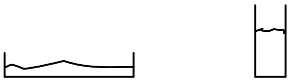
Heat from the body flows into the liquid to compensate for heat lost due to evaporation.

b) The wet sponge.

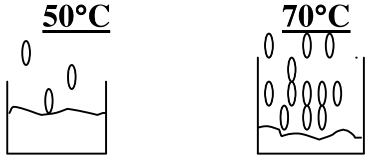
It is the principle that makes it possible to cool fever stricken patients .

### 5) FFACTORS AFFECTING THE RATE OF EVAPORATION

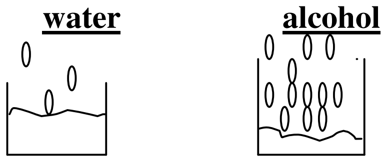
a) Surface area.



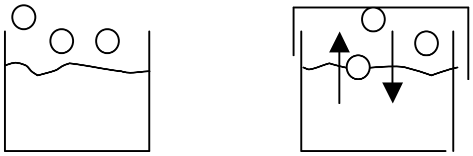
b) Temperature.



c) Strength of attractive forces.



## 6) DYNAMIC EQUILIBRIUM AND EVAPORATION



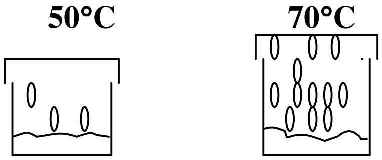
At equilibrium: The rate of evaporation= The rate of condensation
(at constant temperature)

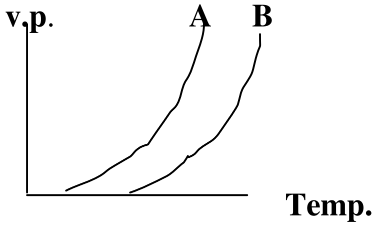
## 7) VAPOR PRESSURE

Definition: Pressure of gas above the liquid at a fixed temperature in a closed container.

## 8) THE EFFECT OF TEMPERATURE ON THE VAPOR PRESSURE

Since the number of molecules above the liquid remains the same, the number of collisions of molecules with the wall of the container is constant. Hence, the vapor pressure is constant at constant temperature. $\boxed{\text{V.p. } \alpha \text{ Temp}}$.



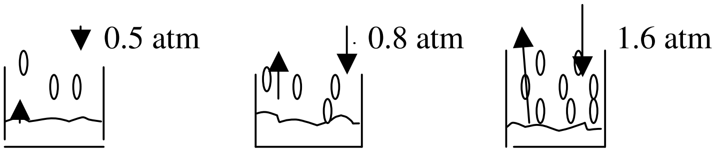


## 9) THE VAPOR PRESSURE IS A MEASURE OF THE ATTRACTIVE FORCES BETWEEN THE MOLECULES.

Refer to the diagram in part 5-c above.
Which liquid has a stronger attractive forces ? Water or alcohol? __________

**Note**: The vapor pressure of a liquid is independent of the volume of the container, provided that there is some liquid present so that an equilibrium may be established.

10) ***Normal*** Boiling Point: It is the temperature at which the vapor pressure equals the atmospheric pressure/external pressure ***= 1 atm***
Here the evaporation (liquid is changing into gas) is taking place within the liquid-not at the surface!



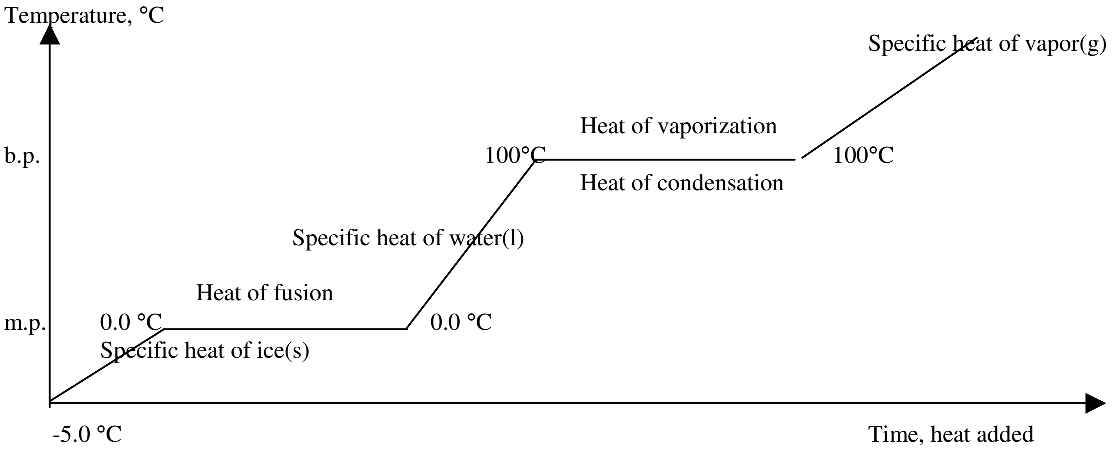
The higher the external pressure, the higher the required temperature necessary to detach enough particles into the vapor state to overcome the external pressure. The liquid will start to boil when the pressure of the vapor reaches that of the atmosphere.
Because of the variation of boiling point with the pressure, it is necessary to define *normal* boiling point. *Normal boiling point* is the temperature at which the vapor pressure of the liquid is 1atm,i.e.760 torr.

What is the effect of pressure on the boiling point? Answer: The higher the external pressure, the ______________ the boiling point.
(higher, or lower)

Applications:
a) Water boils at a lower temperature on the mountain where the atmospheric pressure is low.
b) The pressure cooker. Increasing the pressure in a closed pressure cooker allows to cook the food at a temperature greater than 100°C .
c) The autoclave used to sterilize hospital equipments.
d) Concentrating fruit juice.

## 11) **Changes of State: Heating-Cooling Curve**

Why is it a waste of energy to turn up the stove burner on the food or water that is already boiling?



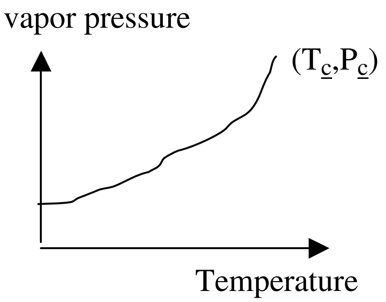
Ans: Heat energy being added to the liquid is used to break the forces holding the molecules in the liquid state rather than to raise the temperature which increases the average kinetic energy of the molecules

## The Critical Temperature, $T_c$, and The Critical Pressure, $P_c$

To liquefy a gas:

a) lower the temperature to slow down the motion of the molecules.

b) increase the pressure.



Critical Temperature: It is the highest temperature at which the substance can exist as a liquid. It is the temperature above which no pressure is high enough to liquefy a gas.

Critical Pressure: The vapor pressure at the critical temperature.

Critical Point: The vapor pressure-temperature curve terminates at $T_c$ and $P_c$ and the point at the end of the curve is called the critical point.

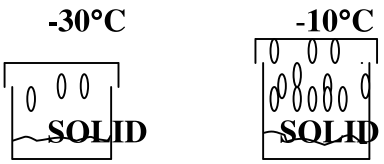
When the temperature of a substance is below its critical temperature, its vapor can be liquefied by increasing the pressure. For example, helium cannot be liquefied until it is first cooled to at least –267.8 °C.

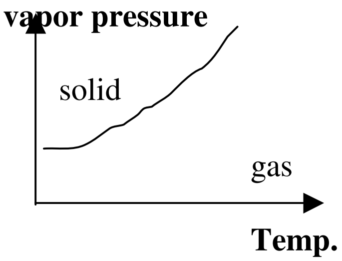
The weaker the attractive forces, the lower the $T_c$ and . Each substance has its own $T_c$ and $P_c$ that are controlled by the strength of the intermolecular attractions. When the attraction is very weak, as in He(g), the molecules must be slowed down a great deal before they stick together by cooling to a low temperature.

Table: Some critical temperatures and pressures

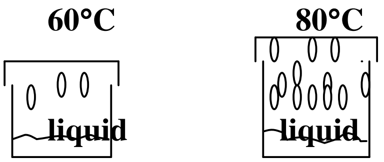
| | $T_c$ | $P_c$ | Forces of attraction |
|---|---|---|---|
| water | 374 | 219 | |
| $CO_2$ | 31 | 73 | |
| $NH_3$ | 132 | 111 | |

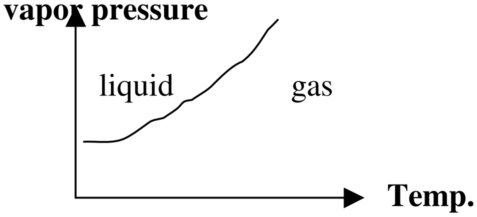
Equilibrium vapor pressure of solids





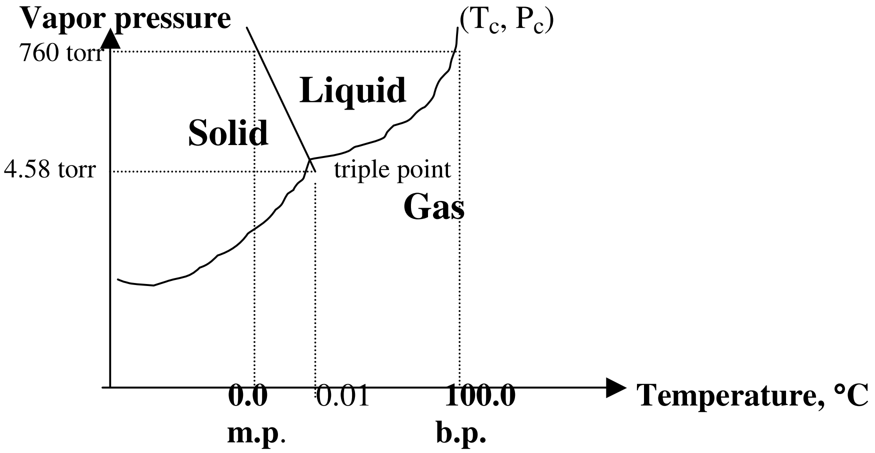
Equilibrium vapor pressure of liquids



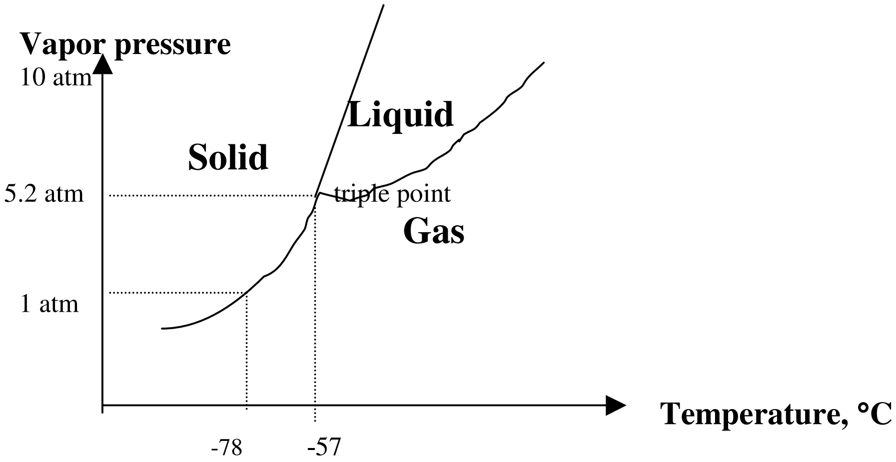


## Phase Diagram for water:

The phase diagram shows the temperature and vapor pressures at which the substance can exist in different phases. Each point on the line represents equilibrium between two phases.



## Phase Diagram for $CO_2$:



a)Why is it impossible to form $CO_2$ liquid at 1 atm?

b)Compare the solid-liquid equilibrium line in the above two diagrams.

- i) Explain the difference in terms of the presence of Hydrogen bonding.
- ii) How does the increase in pressure effect the melting point of ice?

Compare the above two phase diagrams.

## Types of mixtures depending on the particle size:

1) True solution: Particle size is less than 1nm.
2) Colloid: .Particle size is between 1-100nm.
3) Suspension: Particle size is larger than 100 nm.

# Colloids

A colloid is a dispersion of particles of one substance (the dispersed phase) throughout another substance or solution (the continuous phase or dispersed phase). The colloid is different from a solution in that the dispersed particles are larger than normal solute particles.

## Types of colloids:

Colloids are classified according to the state(solid, liquid, or gas) of the dispersed phase and the continuous phase.

| Name of colloid | Dispersed phase | Continuous phase | Examples |
|---|---|---|---|
| liquid aerosol | liquid | gas | fog, mist, cloud |
| solid aerosol | solid | gas | smoke, dust |
| foam | gas | liquid | beer froth, soap suds, whipped cream |
| emulsion | liquid | liquid | milk(cream in milk), mayonnaise(oil dispersed in water. |
| sol | solid | liquid | AgCl ppt in $H_2O$, paint, milk of magnesia. |
| solid foam | gas | solid | marshmallow. |
| gel | liquid | solid | cheese, butter, jelly. |
| solid sol | solid | solid | Ruby (glass with dispersed metal alloy) |

**Methods of preparing colloidal systems**:

1) **Dispersion method**:

Large pieces of substances are broken into smaller pieces of colloidal size and then dispersed in another substance. This could be done by grinding, stirring, whipping or adding chemical reagent (peptizing agent) that will make the large particles disintegrate. For example, starch is peptized into colloidal particles when placed in water. The process of preparing a colloidal dispersion by the addition of a substance which acts upon the suspended particles reducing them to colloidal dimensions is called peptization.

2) **Condensation method**:

Small molecules, ions, or atoms are made to cluster together to form particles of colloidal size. For example, the formation of fog and clouds by the clustering together of $H_2O$ molecules. Also, any insoluble precipitates passes through the colloidal state before it is formed.

## Liquid colloidal systems (colloidal matter dispersed in a liquid):

1) **Lyophilic system**: (If the continuous phase is water, it is called **hydrophilic system**)

This is a system where colloidal particles are more attracted to the dispersing medium than to each other. This type of attraction prevents the colloidal particles from clumping together to form larger particles that would settle out.

a) **Colloidal dispersion of macromolecules**: Examples: starch, hemoglobin, glue, gelatin, and simple protein. These are large molecules that tend to form stable dispersions in water. The macromolecules are attracted to the dispersing liquid to a small extent due to the presence of polar groups attracted at frequent intervals to carbon atoms. There is a strong attraction between the polar groups and the polar water. We call the particles colloidal particles because their size is in the colloidal range.

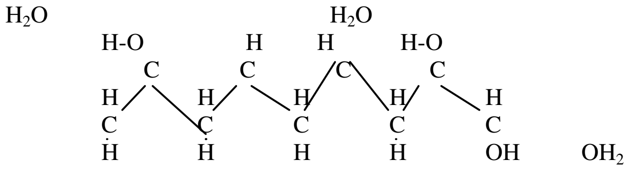
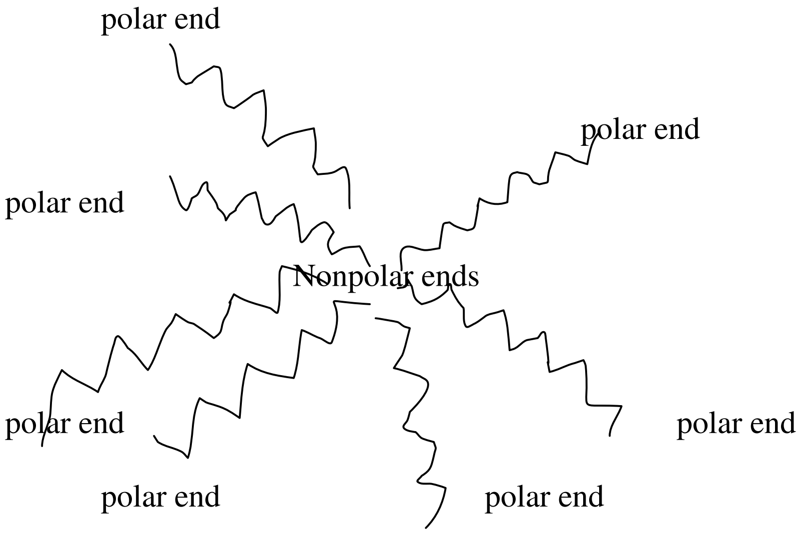


Figure: Attraction between the polar groups and the continuous phase, $H_2O$

b) **Colloidal dispersion of associated colloids, micelles:** These are clusters of large molecules. Each molecule has one end which is nonpolar (lyophobic) and the other is polar (lyophylic). The molecules cluster together to form a particle that has hydrophilic parts at the surface in contact with the water and the hydrophobic parts in the interior of the particle where they attract each other.



The clusters are colloidal because of their large size that has been formed in the process. These large particles are called micelles or associated colloids.

2) **Lyophobic system**: (If the continuous phase is water, it is called **hydrophobic system**.) This is a system where the attraction of the colloidal particles to the dispersing medium is not strong enough to prevent clumping. It requires a third component to stabilize. Some hydrophobic systems have a transitory existence like:

a) colloidal AgCl that will eventually clump together to form a precipitate.
b) shaking oil in water vigorously .

Lyophobic colloidal dispersions are intrinsically unstable, but can be made to persist for indefinite periods of time.

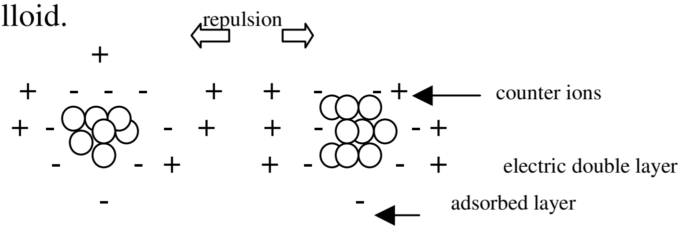
Examples of hydrophobic systems:

a) Oil-water emulsion
b) Water dispersions of metallic oxides.

## Stabilization of hydrophobic dispersions:

### 1) Stabilization by adsorbed ions

The attachment of molecules, atoms, or ions to the surface of solids or liquids by weak forces is called adsorption. For example, gold metal particles can become negatively charged due to the adsorption of negative ions. They repel one another. The repulsion prevents them from colliding and prevents further coagulation which would precipitate the colloid.



The ions adsorbed on the surface of a colloidal particle will have near them an equivalent number of oppositely charged ions, called counter ions, so the region as a whole is electrically neutral. This gives rise to an electric double layer surrounding the colloidal particle. The counter ions can move somewhat independently. The adsorbed particles determine the charge on the colloidal particle.

In lab, you will prepare a dispersion of $Fe_2O_3$ in water solution by reacting $FeCl_3$ with hot water.

$2\ FeCl_3(aq) + 3\ H_2O\ (l) \rightarrow Fe_2O_3\ (s) + 6\ HCl\ (aq)$ Molecular equation

$2\ Fe^{3+}\ (aq) + 6\ Cl^-\ (aq) + 3\ H_2O\ (l) \rightarrow Fe_2O_3\ (s) + 6\ H^+\ (aq) + 6\ Cl^-\ (aq)$ Total- ionic equation

The $Fe_2O_3$ colloidal particles are prevented from precipitating out due to their adsorption to the positively charged $H^+$ ions.

### 2) Stabilization by a protective colloid

An emulsifying agent is a protective colloid that stabilizes an emulsion (a colloidal dispersion of two immiscible liquids). The emulsifying agent protects the second colloid from coagulating. The molecules of the emulsifying agent have an attraction for both, the dispersed and the dispersing, substances of the colloid it stabilizes.

or example, soap in water acts as a protective colloid when it is used to wash dirt and grease off objects. The tiny particles of dirt and grease are coated with the soap and are attracted by the water and carried away.

# Coagulation of hydrophobic colloids

Coagulation is the process of destroying a colloid by making fine particles clump together to create bigger particles that would settle out.

## Methods of coagulation

1) **Heating**: Increasing the temperature increases the kinetic energy of the particles and makes the colloidal particles collide with enough energy to overcome the repulsion between the charged particles. The particles increase in size as they stick together after colliding.

2) **Adding an electrolyte**: This introduces ions that remove the adsorbed ions, so that the colloidal particles no longer repel one another, but coalesce rapidly into larger particles. The choice of electrolyte is dependent on the type of adsorbed ions to be removed.

For negative adsorbed layers, the most effective coagulating electrolytes are those which have positive ions with high charge. For example, $AlCl_3$ is more effective than NaCl in coagulating gold sols. The substance that is added to cause particles to coagulate is called a flocculating agent.

## Properties of colloidal systems:

1) **Tyndall effect**: Although a colloid appears to be homogeneous because the dispersed particles are quite small, yet it can be distinguished from a true solution by its ability to scatter light. The scattering of light by colloidal sized particles is known as Tyndall effect.

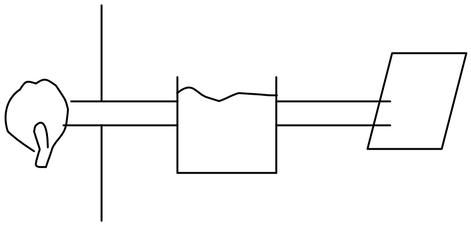


Figure: The ray passes through the solution

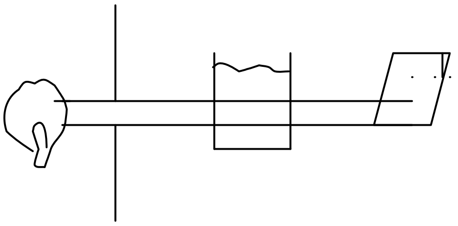
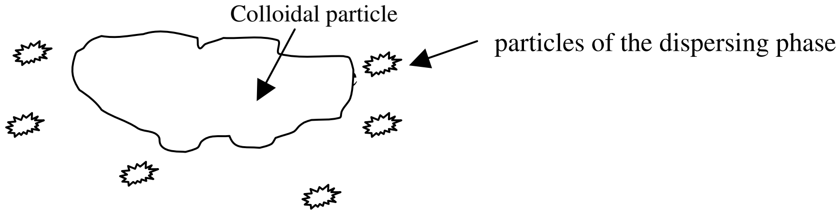


Figure: The ray is scattered by the colloid

2) **Brownian movement**: It is a unique property of colloids. The dispersed particles in a colloid can be seen in constant irregular motion as they reflect the light. The dispersed colloidal particles move randomly because at any one time, more molecules of the dispersing phase hit on one side of the particles than on another. An increase in temperature increases the rate of the Brownian motion.



3) **Filtration** : Most suspensions of solids in liquids can be separated by filtration. A true solution and most colloids cannot be separated by filtration. Some colloidal particles cannot pass through filter paper.

4) **Gel penetration**: True solutions penetrate through the gel. Colloids do not penetrate through a gel.

5) **Dialysis**: True solutions undergo dialysis, that is, the passage of small particles through a semi-permeable membrane, while colloids do not.

6) **Rate of settling**: One of the striking characteristics of colloidal systems is the fact that very dense dispersed particles do not sink, but mat remain dispersed indefinitely.

7) **Adsorption**: Matter in a colloidal state has a tremendous amount of surface. This huge area of colloidal matter makes it particularly efficient in adsorption, i.e. attracting and holding molecules, atoms, and ions of other substances.

# UNITS OF CONCENTRATION

**Molarity=** $\frac{\textbf{\# moles solute}}{\textbf{Liters of solution}}$ **Molality =** $\frac{\textbf{moles solute}}{\textbf{kg of solvent}}$ **percent=** $\frac{\textbf{part(solute)}}{\textbf{total(solution)}}$**x100**

1) Calculate the molality of $H_2SO_4$ solution containing 24.4 g $H_2SO_4$ in 198 g $H_2O$. The molar mass of $H_2SO_4$ is 98.1 g/mole. Answer: 1.26 m

2) Calculate the molarity of 0.396 molal glucose solution. The molar mass of glucose is 180.2 g/mole and the density of the solution is 1.16 g/ml. Answer: 0.429 M

3) The density of 2.45 M aqueous methanol, $CH_3OH$, solution is 0.976 g/ml. What is the molality of the solution? (The molar mass of methanol is 32.04 g/mole) Ans: 2.73 m

4) Calculate the molality of a 35.4% (by mass) aqueous solution of phosphoric acid.
Ans: 5.59 m

## Solution stoichiometry:

1) How many grams of $PbI_2$ will precipitate by the addition of excess KI solution to 50.0 ml of 1.22 M $Pb(NO_3)_2$ ? Ans: 28.1 g

$$Pb(NO_3)_2\ (aq) + 2\ KI(aq) \longrightarrow PbI_2(s) + 2\ KNO_3\ (aq)$$

2) Calculate the volume of 0.842 M NaOH (aq) that will be required to precipitate, as $Cu(OH)_2$ (s), all the copper ions in 30.0 ml of a 0.635 M $CuSO_4$(aq). Ans: 0.0452 L

$$2\ NaOH(aq) + CuSO_4(aq) \longrightarrow Cu(OH)_2\ (s) + Na_2SO_4(aq)$$

**Solution Inventory:**

1) 50.0 ml of 0.240 M $BaCl_2$ were added to 45.0 ml of 0.180 M $Fe_2(SO_4)_3$.

a) What weight of $BaSO_4$(s) is formed?

b) What are the concentrations of the remaining ions in the solution?

$$3\ BaCl_2\ (aq) + Fe_2(SO_4)_3\ (aq) \rightarrow 3\ BaSO_4\ (s) + 2\ FeCl_3\ (aq)$$

i) Moles $BaCl_2$(aq) initially available= $M_{BaCl_2} . V_{BaCl_2}$

__________initial moles $BaCl_2$

ii) Moles $Fe_2(SO_4)_3$(aq) initially available= $M_{Fe_2(SO_4)_3} . V_{Fe_2(SO_4)_3}$

__________initial mole $Fe_2(SO_4)_3$

iii) Find the limiting reagent and decide on the mass of $BaSO_4$ produced.

The limiting reagent is ______ . The limiting reagent will be consumed completely. The excess reagent is_________.

Find mass of $BaSO_4$ formed.

Setup:

_______g $BaSO_4$

iv) Some of the excess reagent will react and some will be left over.

a) Find the number of moles excess reagent reacting.

__________moles $Fe_2(SO_4)_3$ reacting

b) Find the number of moles excess left over.

__________ moles $Fe_2(SO_4)_3$ left over

iv) Find moles $FeCl_3$ formed

__________ moles $FeCl_3$ formed

**Continue next page**

Continue problem #1: Solution Inventory

Answer:

$[Fe^{3+}]$=______M, $[Cl^{-}]$=________M, $[SO_4^{2-}]$=_______M, $[Ba^{2+}]$=________M

2) 40.0 ml of a 0.450 M barium nitrate solution is mixed with 20.0 ml of 0.75 M sodium phosphate and allowed to react according to the equation:

$$3\ Ba(NO_3)_2(aq) + 2\ Na_3PO_4(aq) \longrightarrow Ba_3PO_4(s) + 6\ NaNO_3\ (aq)$$

a) Calculate the mass of any precipitate formed.

b) Calculate the molar concentrations of all species remaining in solution after reaction.

i) Moles Ba $(NO_3)_2$ (aq) initially available

__________initial moles Ba $(NO_3)_2$

ii) Moles $Na_3PO_4$ (aq) initially available

___________initial mole $Na_3PO_4$

iii) Find the <u>limiting reagent</u> and decide on the mass of $Ba_3PO_4$ produced.

The limiting reagent is ______ . The limiting reagent will be consumed completely. The excess reagent is_________.

Find mass of $Ba_3PO_4$ formed.

<u>Setup:</u>

______g $Ba_3PO_{44}$

iv) Some of the excess reagent will react and some will be left over.

a) Find the number of moles excess reagent <u>reacting</u>.

__________moles $Na_3PO_4$ <u>reacting</u>

b) Find the number of moles excess <u>left over</u>.

__________ moles $Na_3PO_4$ <u>left over</u>

v) Find moles $NaNO_3$ <u>formed</u>

__________ moles $NaNO_3$ <u>formed</u>

**Continue next page**

**Continue problem #2:**

Answer:

$[Ba^{2+}]$=________M, $[Na^{+}]$=______M, $[NO_3^{-}]$=________M, $[PO_4^{3-}]$=_______M

# Electrolytes and Nonelectrolytes

All solutes in aqueous solutions can be divided into two categories: electrolytes and nonelectrolytes.

a) An **electrolyte** is a **substance** that, when dissolved in water, results in a solution that can conduct electricity. An electrolyte produces ions in solution.

$$HCl\ (g) \xrightarrow{\text{(in water)}} H^+\ (aq) + Cl^-\ (aq)$$

b) A **nonelectrolyte** is a **substance** that does not conduct electricity when dissolved in water. A nonelectrolyte does not produce ions in aqueous solution.

$$C_6H_{12}O_6\ (s) \xrightarrow{\text{( in water)}} C_6H_{12}O_6\ (aq)$$

A **weak electrolyte** is a substance that ionizes partially when dissolved in water. The solution conducts electricity partially.

$$HC_2H_3O_2\ (l) \xrightarrow{\text{(in water )}} HC_2H_3O_2\ (aq)$$

## Total-ionic and net-ionic equations for double-displacement reactions (Metathesis reactions):

<u>A double displacement reaction will actually take place if at least one of the following is produced:</u>

**a) an insoluble compound ( a precipitate).**
**b) a gas.**
**c) a weakly ionized compound ( examples: a weak acid, a weak base, or $H_2O$).**

## Exercise:

( Any soluble substance given below is in aqueous solution.)
Write the molecular, total-ionic and net-ionic equations for each of the following:

1) Lead (II) nitrate and potassium iodide solutions .

Molecular equation:

Total-ionic:

Net-ionic:

2) Aluminum acetate and sodium hydroxide.

Molecular equation:

Total-ionic:

Net-ionic:

3) Sodium hydroxide and sulfuric acid.

Molecular equation:

Total-ionic:

Net-ionic:

**(next page)**

4) Ammonium chloride and potassium hydroxide.

Molecular equation:

Total-ionic:

Net-ionic:

5) Strontium nitrate and ammonium chloride.

Molecular equation:

Total-ionic:

Net-ionic:

6) Barium hydroxide and sulfuric acid.

Molecular equation:

Total-ionic:

Net-ionic:

7) Hydrochloric acid and calcium carbonate.

Molecular equation:

Total-ionic:

Net-ionic:

*Note: Learn well the solubility rules and the list of strong acids and strong bases*

# COLLIGATIVE PROPERTIES:

Colligative properties are physical properties of solutions that depend on the number of solute particles present, but not on the identity of the solute.

Consider solutions containing nonvolatile solute:

## 1) Vapor pressure lowering:

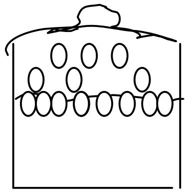


Figure:Pure solvent

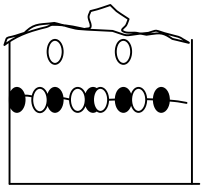


Figure: solution

If a nonvolatile solute is added to a solvent, the vapor pressure of the solvent is decreased. Experiments showed that the vapor pressure lowering depends on the concentration of the solute particles.

**Raoult's law:**

$$\text{v.p.}_{\text{solution}} = \chi_{\text{solvent}} P^\circ_{\text{solvent}}$$

$$\Delta\text{v.p.} = \chi_{\text{solute}} P^\circ_{\text{solvent}}$$

1.0 mole of sugar,$C_6H_{12}O_6$ (a nonvolatile non-dissociating solute) will produce essentially the same vapor pressure lowering as 0.5 mole of NaCl in a given quantity of water. There will be 1.0 mole particles in both solutions.

**Exercise:**

Calculate the vapor pressure lowering caused by the addition of 100. g sucrose, $C_{12}H_{22}O_{11}$ , to 1000. g of $H_2O$. The vapor pressure of pure water is 23.8 torr.

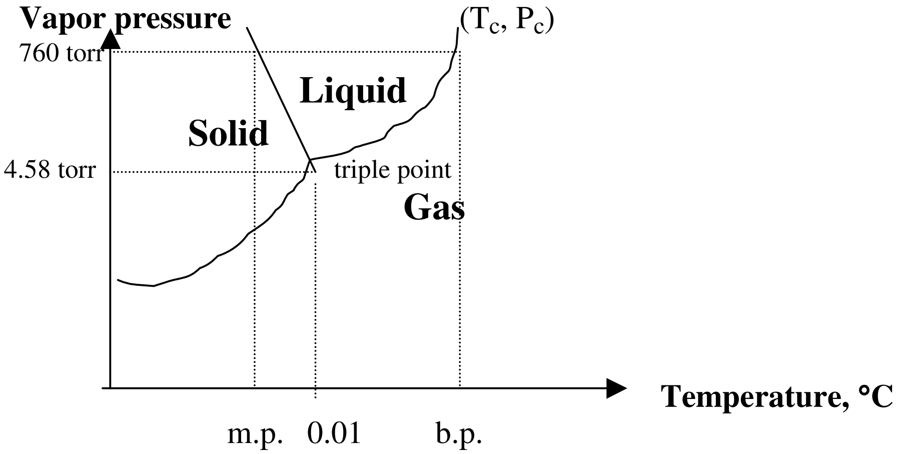
Ans: 0.125 torr

**2) Boiling point elevation**:

A liquid starts to boil when the vapor pressure is equal to the external pressure. Because nonvolatile solutes lower the vapor pressure of the solution, a higher temperature is required to cause the solution to boil.

$$\boxed{\Delta T_{b.p.} = K_b \text{ molality}}$$

$K_b$ is the molal boiling point elevation constant. It is defined as the elevation of the boiling point of a solvent brought about by dissolving one mole of a nonvolatile, non-dissociating solute in 1000 g of the solvent; the value of $K_b$ is specific to the solvent considered. $K_b$ for water is 0.52 °C/mole.kg. A 1.0 m aqueous solution of sucrose( or any aqueous solution that is 1.0 m in nonvolatile solute particles) will boil at a temperature 0.52°C higher than pure water.



**Freezing point depression**:

$$\boxed{\Delta T_{f.p.} = K_f \text{ molality}}$$

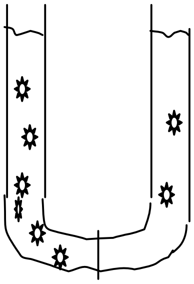
The solute is not normally soluble in the solid phase of the solvent. For example, pure ice almost always separates when aqueous solutions freeze. ( Heat energy is used to orient and gather the $H_2O$ molecules away from the solute particles. As a result, temperature drops.) $K_f$ is the molal freezing point depression constant. It is defined as the depression of the freezing point of a solvent brought about by dissolving one mole of a nonvolatile, non-dissociating solute in 1000 g of the solvent; the value of $K_f$ is specific to the solvent considered. $K_f$ for water is 1.86 °C/mole.kg. 1.0 m solution of a nonelectrolyte or 0.5 m solution of NaCl will freeze 1.86 °C lower than pure water.

Exercise: List the following solutions in order of their expected freezing point:

0.05 m $CaCl_2$, 0.15 m NaCl, 0.10 m HCl, 0.05 m $HC_2H_3O_2$, 0.10 m $C_{12}H_{22}O_{11}$.

4) **Osmosis:**

Osmosis is the net movement of solvent molecules, but not solute particles through a semi permeable membrane from amore dilute solution into a more concentrated one. The net migration of solvent occurs from the right arm to the left arm, as if the solutions were trying to equalize their concentrations.



Semi-permeable membrane

Pressure could be applied to the left arm to prevent osmosis. The pressure required to stop osmosis from pure solvent into a solution is known as osmotic pressure.

$$\boxed{\Pi = MRT}$$

Determination of molar mass by measuring a colligative property:

The colligative properties of solutions provide an important means of experimentally determining molar mass.

**Exercise 1**: A solution of an unknown nonvolatile non electrolyte was prepared by dissolving 0.250 g in 40.0 g of $CCl_4$. The normal boiling point of the resulting solution was increased by 0.357. Calculate the molar mass of the solute. $K_b$ is 5.02 °C/mole.kg.

**Exercise 2**:The osmotic pressure of 0.200 g Hemoglobin in 20.0 ml solution is 2.88 torr at 25 °C. Find the molar mass of hemoglobin. R= 0.0821 L.atm/mole.K.

**Colligative Properties of Electrolyte Solutions and the Vant'Hoff Factor**:
A fully hydrated ion is called a free ion.

$H_2O$ $H_2O$ $H_2O$ $H_2O$
$H_2O$ $\mathbf{Na^+}$ $H_2O$ $H_2O$ $\mathbf{Cl^-}$ 2 particles

At higher concentrations, cations and anions tend to pair up to form "***ion pairs".*** The ion pairs are held closely together by attractive forces with few or no water molecules between them. There is a residual attraction between ions, even when separated by solvent molecules. Ions cannot move freely as individual units. Vant' Hoff factor, i, is the actual number of particles after dissociation in solution per formula units initially dissolved.

| **Electrolyte** | **i, measured** | **i, calculated** |
|---|---|---|
| sucrose | 1 | 1.0 |
| HCl | 1.9 | 2.0 |
| MgSO4 | 1.3 | 2.0 |
| MgCl2 | 2.7 | 3.0 |

$\Delta T_{b.p.=}$ **i** $K_b$ molality

$\Delta T_{f.p.}=$ **i** $K_f$ molality

$\Pi=$ **i** MRT

**Exercise 3**: The osmotic pressure of 0.010 M solution of KI (aq) at 25 ºC is 0.465 atm. Calculate the Vant' Hoff factor, i.

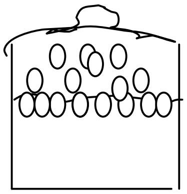
## Solutions containing more than one volatile component (Solutions containing a volatile solute) Example, alcohol and water

Here both, the solute and the solvent are volatile.

$$\mathbf{V.P._{total\ solution} = P_A + P_B}$$

Where $P_A$ is the partial vapor pressure of component **A** above the solution, and $P_B$ is the partial vapor pressure of component **B** above the solution.

$$\mathbf{V.P._{total\ solution} = X_A P°_A + X_B P°_B}$$



Figur : Component A

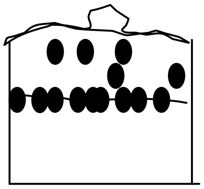


Figure: Component B

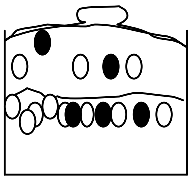
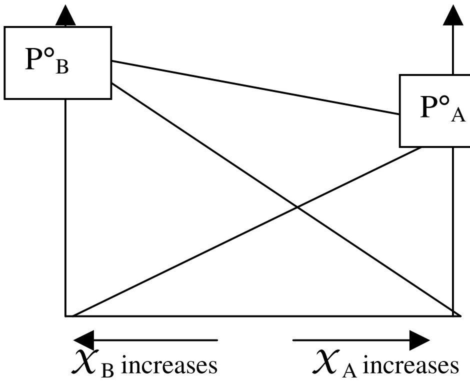


Figure: Components A and B

Ideal solution: A solution whose vapor pressure obeys Raoult's law.

| %B | 100 | 80 | 60 | 40 | 20 | 0 |
|---|---|---|---|---|---|---|
| **$X_B$** | 1.0 | 0.80 | 0.60 | 0.40 | 0.20 | 0 |
| %A | 0 | 20 | 40 | 60 | 80 | 100 |
| **$X_A$** | 0 | 0.20 | 0.40 | 0.60 | 0.80 | 1.00 |

Start with 100% component **B**. Then decrease **B** and increase component **A**.

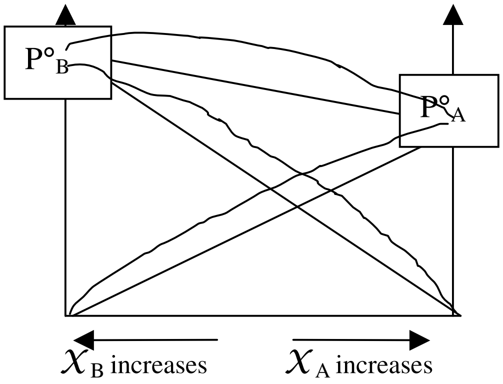


## Positive Deviation from ideal solution:

Neither solute nor solvent particles are held as tightly in the solution as they are in the pure substances. The escaping tendency of each is therefore greater in the solution than in the solute or solvent alone. The partial pressures of both of them over the solution are greater than predicted by Raoult's law.

$P_{\textbf{total}(\text{experimental})} > P_{\textbf{A}(\text{theoretical})} + P_{\textbf{B}(\text{theoretical})}$

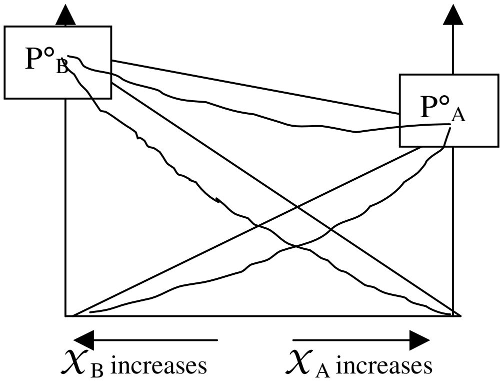
The solution exhibits larger vapor pressure than expected. Attraction between solute and solvent is less than solute-solute attraction or solvent-solvent attraction The formation of the solution occurs with absorption of heat (endothermic).



## Negative Deviation from ideal solution:

Each substance, in the presence of the other, is held more tightly than in the pure material. The vapor pressure of the solution is less than Raoult's law would predict. Heat is given off (exothermic).

$P_{\textbf{total}(\text{experimental})} < P_{\textbf{A}(\text{theoretical})} + P_{\textbf{B}(\text{theoretical})}$



**Exercise**: A solution is prepared by mixing 5.81 g acetone ($C_3H_6O$, molar mass is 58.1 g/mole) and 11.9 g chloroform ($CHCl_3$, molar mass is 119.4 g/mole). At 35°C the solution has a total pressure of 260 torr. Is this an ideal solution? ( The vapor pressure of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.)