

General Chemistry

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Chapter 2: Properties of Solution

Phase equilibrium:

- **Phase:** Any **homogeneous part of a system** (i.e. **uniform part**). It is a region of material that is chemically uniform, physically distinct, and (often) mechanically separable.
- A system may be of **one phase** or **more than one phases**. A system only with **liquid water** is **1-phase system**; a system with **liquid water and water vapor** is **2-phase system**; and a system with **liquid water, water vapor and solid ice** is **3-phase system**.
- A system with *single phase –homogeneous system*. While system **with two or more phases – heterogeneous system**
- So, ordinarily **three states of matter-gas, liquid, and solid** are known as **phases**. However in phase rule, a **uniform part of a system in equilibrium** is termed a '**phase**'. Thus a **liquid** or a **solid mixture** could have **two or more phases**.

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- **Some examples;**

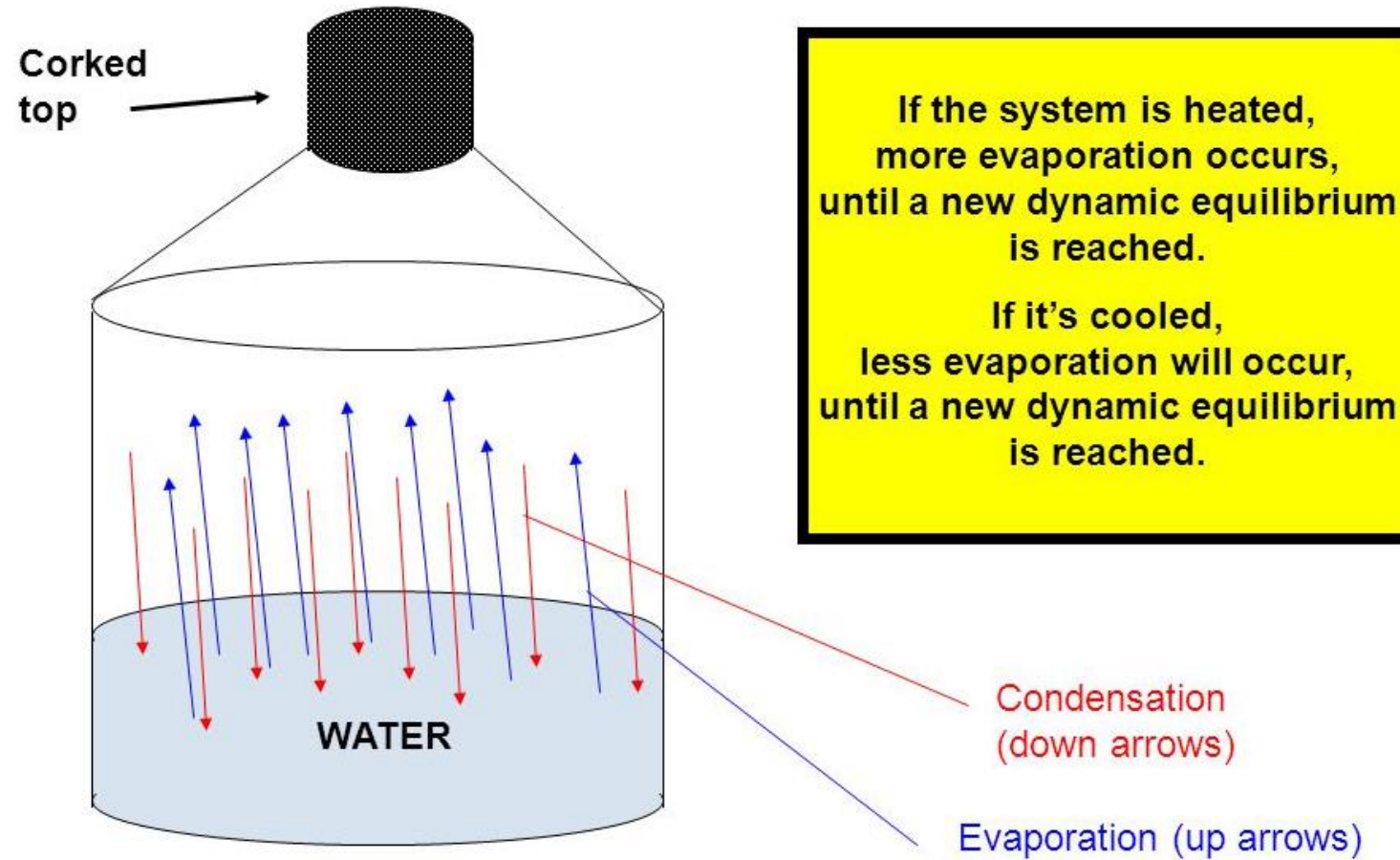
- ***All pure substances*** (oxygen, O_2 ; benzene, C_6H_6 ; Solid Ice, H_2O .) with *one chemical species* only are taken as ***one phase***.
- ***Mixture of gases*** (O_2 and N_2 ; **1-phase system**).
- ***Miscible liquids*** (soln. of ethanol and water; **1-phase system**).
- ***Non-miscible liquids*** (mixture of $CHCl_3$ and H_2O ; **2- phase system**).
- ***Aqueous solutions*** (Solution of salt or sugar; **1- phase system**).
- ***Mixture of two allotropes*** (same chemical species but different physical props.) is **2-phase system**. Like allotropes of sulphur (a mixture of **monoclinic** and **rhombic**)
- ***Mixture of two or more chemical substances*** –*as many phases*, mixture of $CaCO_3$ and CaO – **2 phases** (different physical and chemical props.)



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- **Phase equilibrium:**
- Suppose, **the evaporation of water in a closed system,**
 - [Liquid water (1-phase) = Water vapor(1-phase)] **2-phase system**
 - Here, water molecules gradually escape into water vapor. After collection of larger number of water vapor in contact with liquid water, water vapors again come back to liquid water. At one stage, **these two processes reach at equilibrium**, which is known as ***phase equilibrium***.
- *Phase equilibrium* is defined as state of equilibrium when **there is no net conversion of one phase to another phase**.
- Phase equilibrium provides **a number of simple illustrations of important general features of all equilibrium** (coexistence of different phase of a substance).

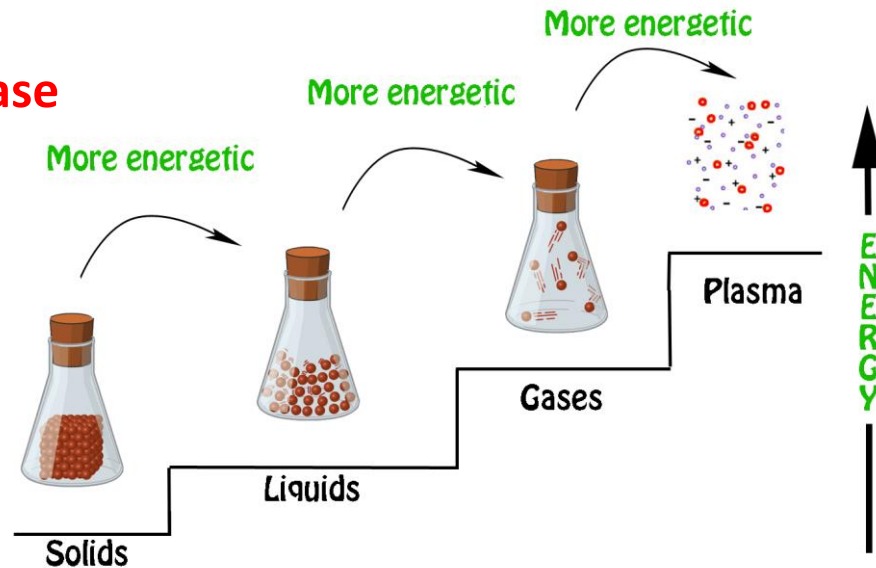
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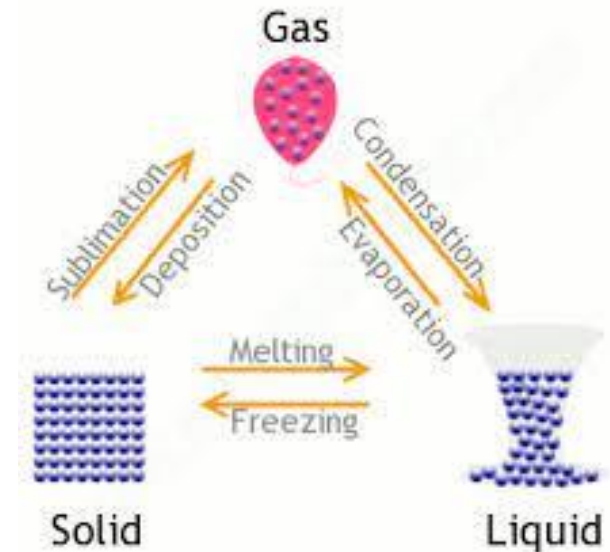
Energetics of Phase changes:

- **System** – any part of universe which is under the investigation.
- **Surrounding** – external entities which may influence the behavior of the system.
- **Boundary** – simple imaginary line that separates system from the surrounding.

- **Energetics of Phase changes:**



As you go from solids, to liquids, to gases, and finally to plasma, the energy levels of the particles are **increasing**

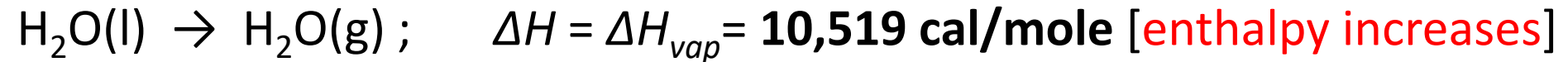


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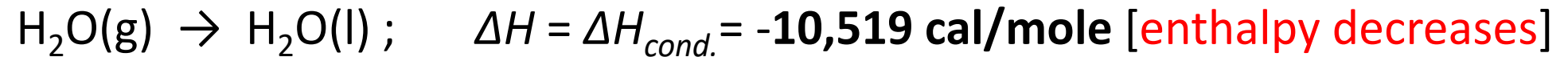
- Whenever a system changes from its **one phase to another**, there is **a change in energy** during the conversion, known as **Energetics of Phase changes**.
- When **water evaporates**, **it absorbs heat from surroundings**. Similarly, when a gas **condenses** to a liquid, **it releases heat to surroundings**.
- The **absorption of heat upon evaporation** and **its evolution of upon condensation** suggest that the **energy of a liquid is lower than that of a gas at the same temperature**.
- i.e ; system upon **condensation goes to a state of lower energy** and energy is transferred as **heat from system to its surroundings**. For a **liquid to evaporate**, **work must be done against the attractive forces between molecule** and **the energy required for this is supplied as heat from surroundings**.

Enthalpy change(ΔH): Amount of heat absorbed or evolved by a system in any change which takes place at constant pressure

- When one mole water is **completely vaporized**, it absorbs 10,519 cal from surroundings.



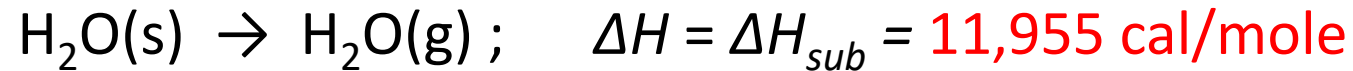
- For **condensation process**, we have



- Here, ΔH_{vap} is ***a measure of potential energy of attraction between molecules.*** Liquid with **high potential energy** (i.e. strong attractive force between molecules) would have **large values of ΔH_{vap} (enthalpy of vaporization)**.

Contd...

- The direct conversion of a solid to a vapor is called **sublimation**. For ice-water vapor conversion, we have



- The **enthalpy of fusion** (ΔH_{fus}) for ice-water transition is ;



- Now, **direct conversion of solid ice-water to vapor** is given by;

$$\Delta H_{\text{sub}} = \Delta H_{\text{fus}} + \Delta H_{\text{vap}}$$

- From the observation of data, it is found that
- $\Delta H_{\text{fus}} < \Delta H_{\text{vap}}$ [relatively small amount of energy is required to convert a solid to a liquid while Evaporation reduces essentially to zero attractive forces between molecules]

Liquid-vapor equilibrium

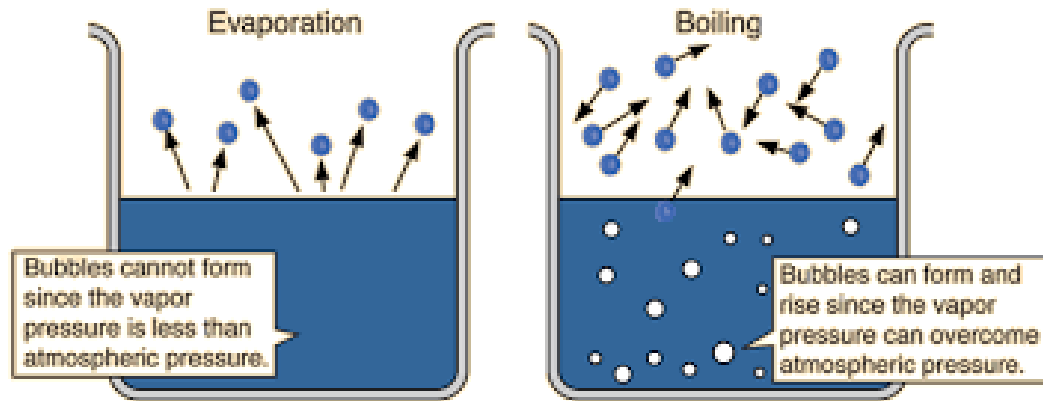


Fig. A liquid of low boiling temperature in an **open vessel**

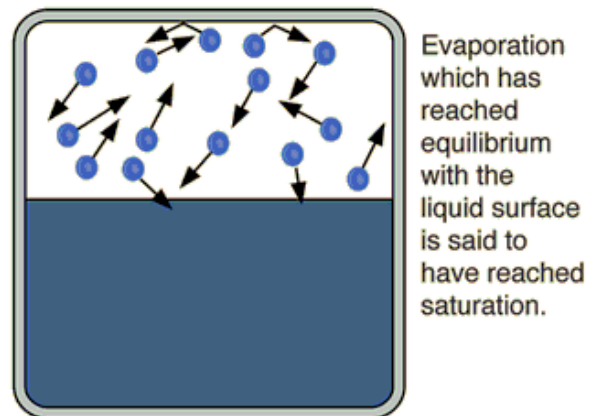


Fig. A liquid of low boiling temperature in a **closed vessel**

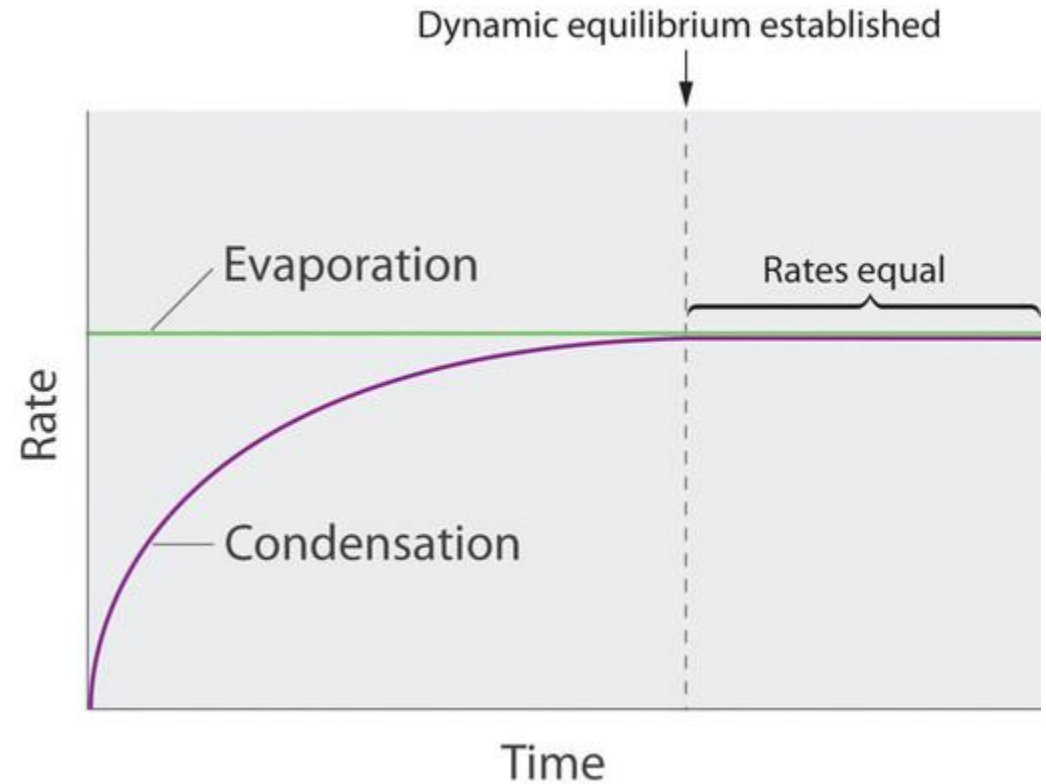


Fig. Time dependence of *evaporation* and *condensation* rates for a liquid evaporating in closed vessel

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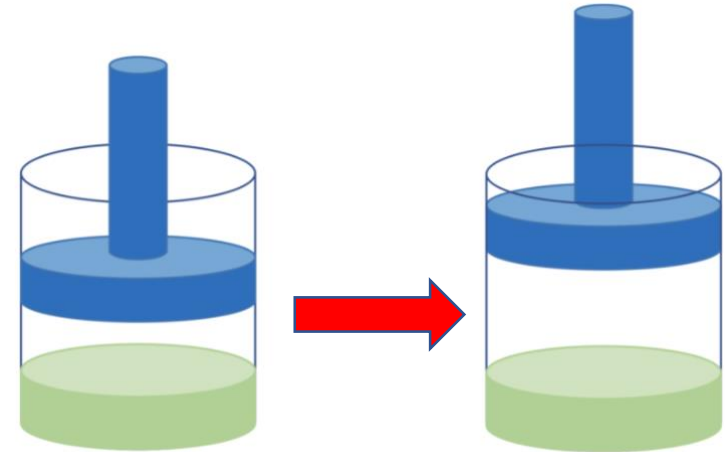
- Some **molecules on the surface of liquid** in the vessel would have **enough kinetic energy to overcome the attractive forces** (binding force) and **escape into the vapor**.
 - In the open vessel, the **vapor molecules are swept away** and **evaporation continues until no liquid is left**.
 - In a closed evacuated vessel, the liquid molecules on the surface start to evaporate immediately, Initially, **the rate of condensation = zero** (no molecules in the vapors).
 - As long as '**T**' remains constant, **evaporation will continue** at a **constant rate** and the number of **molecules in the vapor phase increase**.
 - When **large vapor molecules be in contact with liquid**, they *collide* to each other and come back to liquid surface. i.e. **condensation process** starts which **changes vapor molecules into liquid**.

Contd...

- As the **condensation rate increases**, it eventually becomes equal to the **rate of evaporation**. At this time ,
 - *The number of vapor molecules which enter into liquid per unit time = The number of liquid molecules which escape into vapor per unit time .*
- Then, the **pressure of the vapor stops increasing and remains constant**.
- If the system is allowed **without any disturbance at fixed temperature**, evaporation and condensation **continue at equal rates** and **pressure of the vapor remains unchanged**.
- This is **a state of equilibrium** which is known as **liquid-vapor equilibrium**. (i.e. *equilibrium between two- phases*)
- At **equilibrium**, **evaporation and condensation processes do not stop** but **the constancy of the equilibrium vapor pressure** is a consequence of two opposing tendencies **proceeding at equal rates**. Thus, we can say that **phase equilibrium is dynamic in nature**.

Illustrate the *liquid-vapor equilibrium* in a cylinder closed by movable piston

- **Case I:** Volume of cylinder increased (by raising piston) at const. tempr. (i.e. eqm. disturbed).
 - Results lowering vapor molecule/unit volume due to lowering no. of collision /unit time with liquid surface
 - Decreases rate of condensation (no change in rate of evap.)
 - Now, **rate of evap. > cond.**
 - Ultimately, cond. will inevitably cause to increase in **no. of vapor molecules** so that both opposing processes proceed equally and **restores the phase equilibrium.**



Case II: If system initially at eqm. is disturbed by decrease in volume, what happens?

Useful generalizations from liquid-vapor equilibrium:

From liquid-vapor equilibrium, we can draw some important features of all equilibrium which are as follows:

- Equilibrium in molecular system is *dynamic in nature* and is the consequences of equality of the rates of opposing processes.
- A system always moves spontaneously toward a *state of equilibrium* if any stress is applied on it.
- The *nature and properties of an equilibrium* state are the same regardless of how it is reached.
- The condition of a system at equilibrium represents a **compromise between two opposing tendencies**, one drives for the molecules to assume the **state of lowest energy** and another urges toward **molecular chaos** or maximum entropy.

Temperature dependence of vapor pressure:

- *Vapor pressure:-* Vapor pressure of a liquid is defined as **the pressure exerted by its vapor when it is at equilibrium with the liquid at a given temperature.**
- *Different liquids have different vapor pressure at particular temperature.* **Greater escaping tendency, greater is its vapor pressure.** So, the *liquid with high vapor pressure* will be more **volatile**.
- For example, *volatile nature* of **diethyl ether** and **water**?
- The ***equilibrium vapor pressure*** of a liquid **depends upon the *temperature*.**

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- Experimental measurements show that the **equilibrium vapor pressure of a liquid increases as the temperature raising.**
- **Diethyl ether** (B.pt. 34.6°C); **n-hexane** (B.pt. 68.95°C); **Ethanol** (B.pt. 78.3°C); **Benzene** (B.pt. 80.19°C); Water (B.pt. 100°C) etc.
- **Boiling point:-** The temperature at which the equilibrium vapor pressure becomes equal to 1 atm. is called **normal boiling temperature** or **the boiling point**.

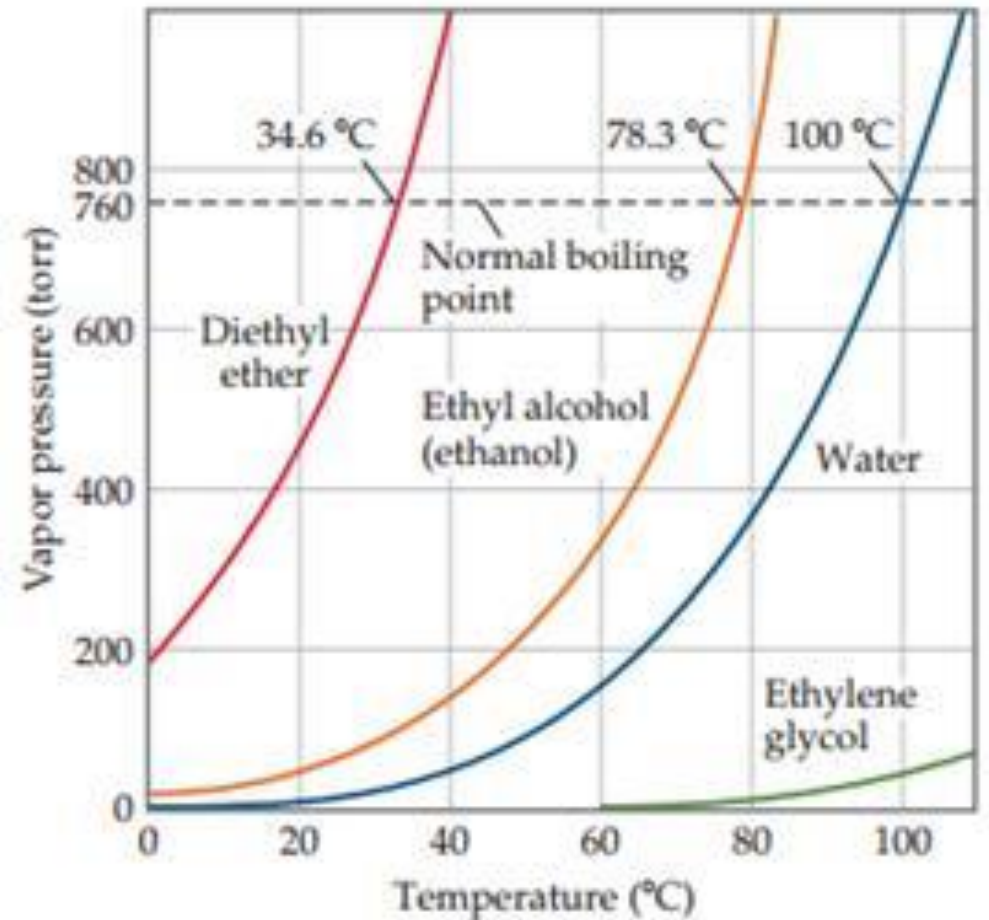
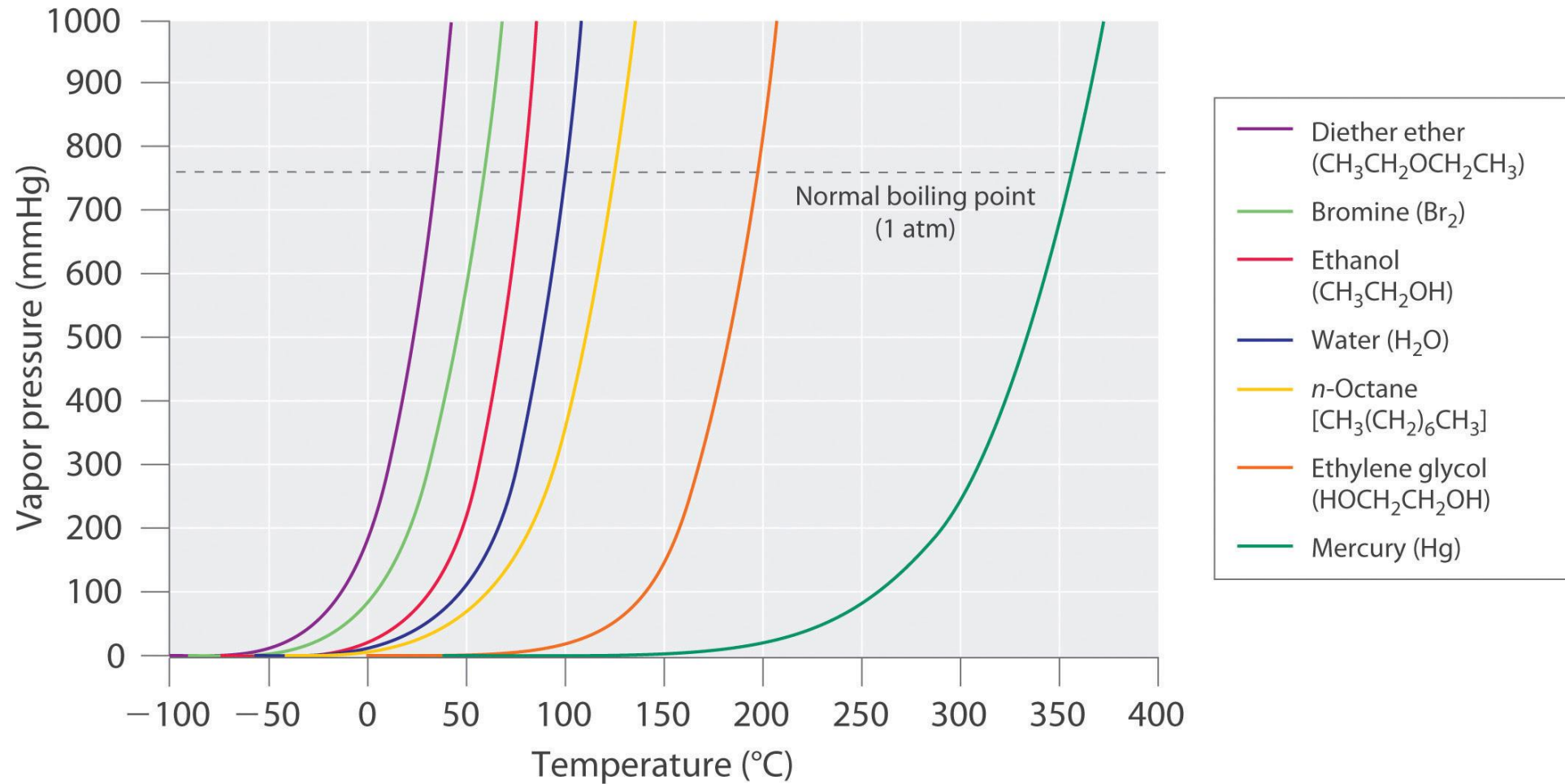


Fig. A plot shows that how the vapor pressure of liquid varies with temperature

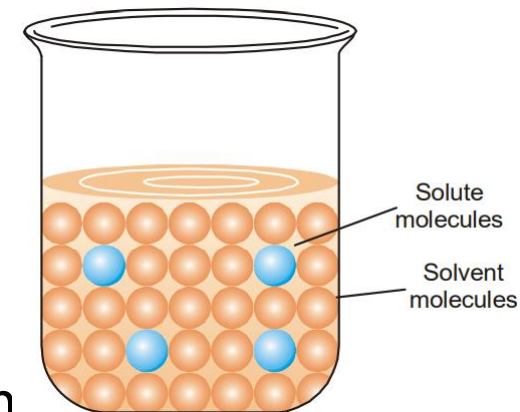
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- **Bubble formation and boiling of liquid:** In the boiling process, *bubbles of vapor* form throughout the bulk of the liquid. i.e. evaporation occurs at anywhere in the liquid. Because, this happens only when *the vapor pressure equals the atmospheric pressure*.
- **In order to form and grow bubbles**, the **pressure of vapor inside it must be at least equal to the pressure exerted on it by the liquid**. Thus, *bubble formation and boiling* occur **only when vapor pressure of the liquid is equal to the pressure of the atmosphere**.
- **Bumping:** When bubble formation in a **superheated liquid** (i.e. reaching a tempr. greater than its boiling point) occurs, it produces almost ***explosive violence***. Because the vapor pressure in any bubble formed greatly exceeds atmospheric pressure and bubbles tend to expand rapidly. Such violent boiling, *is called bumping*. It can be avoided by adding ***porous pieces of ceramic materials*** (can initiate bubbles in the liquid as soon boiling tempr. is reached)

Solution and types of Solution:



Molecular model
of a solution

- **Solution:** It is a *homogeneous mixture* of two or more substances on molecular or ionic level. i.e. **Solution = Solute + Solvent**.
- The constituent of the mixture present in a **smaller amount** is called the **Solute** and the one present in a **larger amount** is called the **Solvent**.
- For example, when a smaller amount of **sugar** (solute) is mixed with **water** (solvent), a **homogeneous solution in water** is obtained. In this solution, sugar molecules are uniformly dispersed in molecules of water.
- Similarly, a **solution of salt ($\text{Na}^+ \text{Cl}^-$) in water** consists of **ions of salt (Na^+, Cl^-)** dispersed in water.

Types of solution: (many possible types of solute –solvent pairs depending on state of solute and solvent resulting following types of solution)

State of Solute	State of Solvent	Example
1. Gas	Gas	Air
2. Gas	Liquid (Carbonated drinks)	Oxygen in water, CO ₂ in water
3. Gas	Solid	Adsorption of H ₂ by palladium
4. Liquid	Liquid	Alcohol in water
5. Liquid	Solid	Mercury in silver
6. Solid	Liquid	Sugar, Salt
7. Solid	Solid (Steel)	Metal alloys : Carbon in iron

Different Ways of Expressing Concentration

- **Concentration of a solution:** It is the amount of solute present in a given amount of solution. i.e. $\text{Concentration} = \frac{\text{Quantity of solute}}{\text{Volume of solution}}$
- Dilute solution??
- Concentrated solution??
- *There are several ways of expressing concentration (i.e. units) of a solution.*
 - Per cent by weight
 - Mole fraction
 - Molarity
 - Molality
 - Formality and Normality

Contd...

- **Per cent by Weight:**

$$\% \text{ by weight of solute} = \frac{\text{Wt.of solute}}{\text{Wt.of solution}} \times 100$$

- **Mole fraction:**

$$X_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute} + \text{Moles of solvent}}$$

$$X_{\text{solvent}} = \frac{\text{Moles of solvent}}{\text{Moles of solute} + \text{Moles of solvent}}$$

Mole fraction is **unitless** and $X_{\text{solute}} + X_{\text{solvent}} = 1$

It is useful to emphasize the *relation between some concentration –dependent property of a solution and relative numbers of molecules of solute and solvent.*

Contd...

- **Molarity:**

$$\text{Molarity(M)} = \frac{\text{Moles of solute}}{\text{Volume in litres}} \text{ or } (M) = \frac{\text{Moles of solute}}{\text{Volume solution in ml}} \times 1000$$

- **Molarity is a very convenient unit for lab. work** because aqueous solution of known molarity can be prepared easily by weighing out definite amount of solutes and dissolving in known volume of solution in calibrated vessel.
- As the ***volume of a solution depends on temperature***, concentration expressed in unit of molarity also depends on temperature. This is a disadvantage which the mole fraction and molarity units do not have.

Contd...

- **Molality:**

$$\text{Molality}(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent in kilograms}} \quad \text{or} \quad (M) = \frac{\text{Moles of solute}}{\text{Mass of solvent in grams}} \times 1000$$

- *Molality is a useful unit in calculation of **freezing and boiling points** but it is difficult to weigh out liquid and this makes molality an inconvenient unit.*
- **Formality:-** The number of gram-formula weights of solute per litre. (F)
 - 1 F solution of NaCl refers to the solution containing 58.5 gm of NaCl in 1 litre of solution.
- **Normality:-** The number of gram-equivalent weight of solute in one litre of solution
 - 1 N solution of NaOH refers to the solution containing **one gram equivalent of solute in one litre of solution. i.e.** (40 gm= eq. wt.) of NaOH in one litre of solution.

Colligative properties:

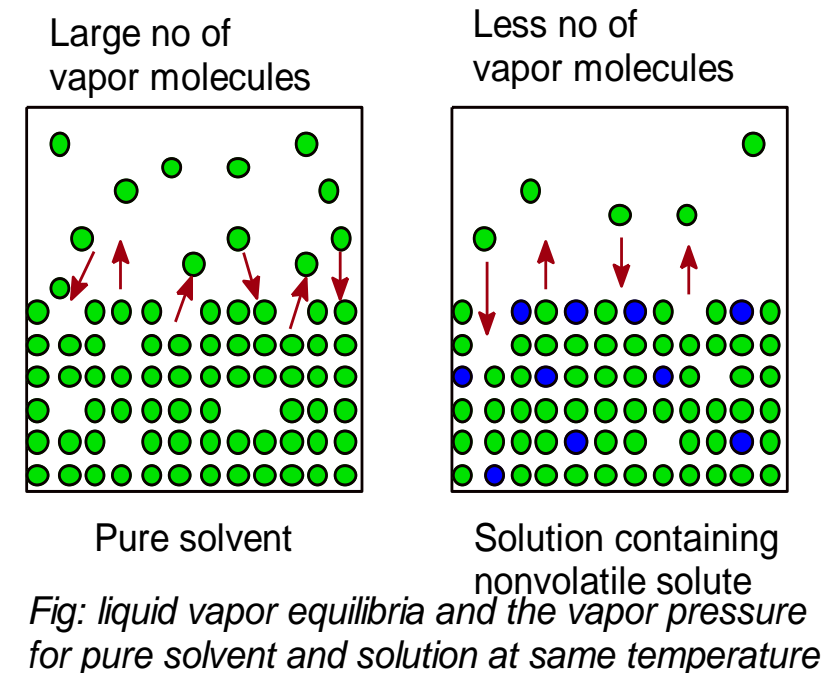
- A ***dilute solution*** of **non-volatile solutes** in **volatile solvent** show the major properties which depend only on the number of solute particles present in the solution. i.e. on the **concentration** (molality) of solution **but not on the nature and size of the particles**.
- These properties are collectively known as colligative properties. (Gr. Colligatus = collected together)
- A ***colligative property*** may be defined as one which depends ***on the number of particles in solution and not in any way on the size or chemical nature of the particles***.

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- A dilute solution containing non-volatile solutes exhibits the following properties:
 - *Lowering of the vapor pressure(or relative lowering of vapor pressure)*
 - *Elevation of the boiling point*
 - *Depression of the freezing point*
 - *Osmotic pressure*

Lowering of the vapor pressure (Raoult's law):

- *The vapor pressure of the pure solvent depends on the number of molecules evaporating from its surface.*
- *If we consider a solution composed of non-volatile solute in volatile solvent, the presence of solute molecules in the surface blocks a fraction of the surface where no evaporation can take place.*
- *This results the lowering of vapor pressure. Now, the vapor pressure of the solution is ultimately determined by the number of molecule of the solvent present at any time in the surface. i.e. Vapor pressure of solution is directly proportional to the mole fraction of solvent*



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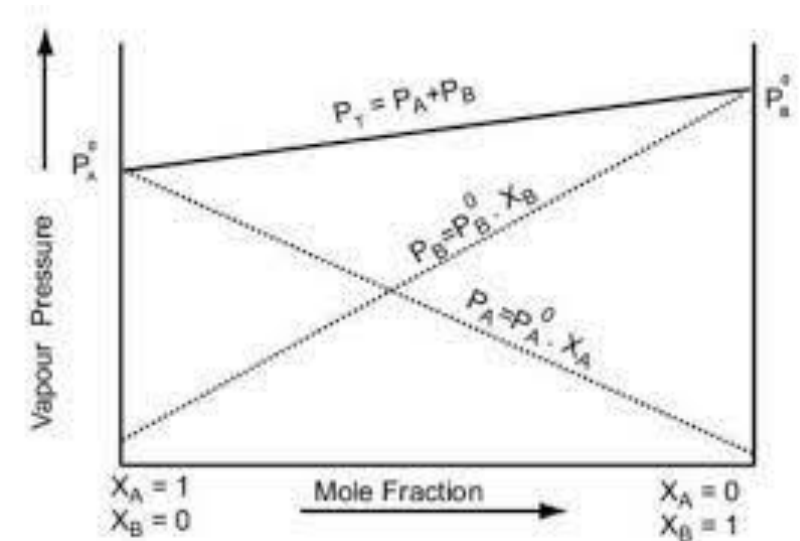
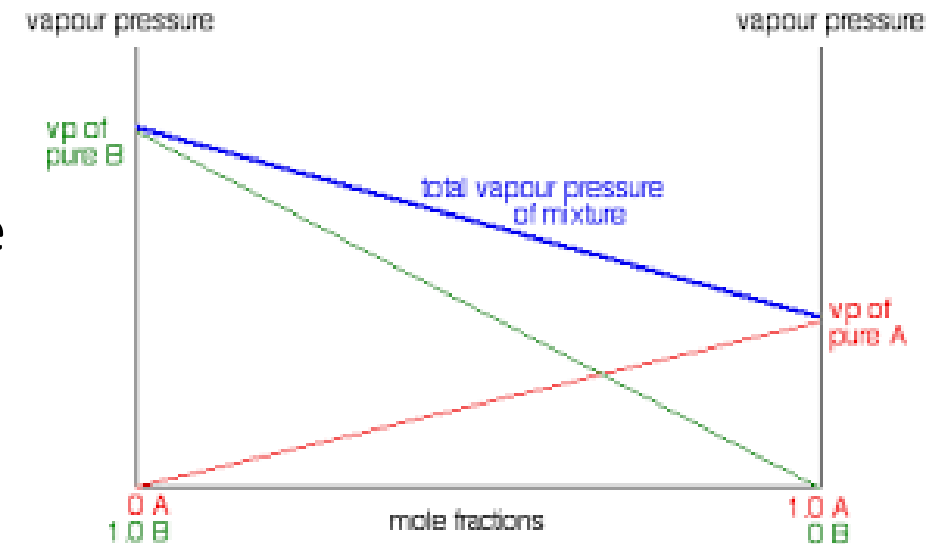
- If P_s be vapor pressure of solution (solvent component in solution) and X_1 be mole fraction of solvent.
- Then, $P_s \propto X_1$ **or** $P_s = k \cdot X_1$ **or** $P_s = k \cdot \frac{n_1}{n_1 + n_2}$ (i)
- Here, k is **proportionality constant**.
- In case of **pure solvent**, $n_2 = 0$ and hence,
- Mole fraction of solvent $= \frac{n_1}{n_1 + n_2} = \frac{n_1}{n_1 + 0} = 1$
- Now from eqn. (i), $P_s = k = P^0$ (**vapor pressure of pure solvent**)
- Then, eqn. (i) becomes, $P_s = P^0 \cdot \frac{n_1}{n_1 + n_2}$ **or** $P_s / P^0 = \frac{n_1}{n_1 + n_2}$ (ii)

Contd...

- As we know that, mole fraction of solute is; $X_2 = 1 - X_1$ or $X_2 = 1 - \frac{n_1}{n_1 + n_2}$ or $1 - X_2 = \frac{n_1}{n_1 + n_2}$
- Now, eqn.(ii) can be written as; $P_s / P^0 = 1 - X_2$ or $1 - P_s / P^0 = X_2$
- Or $(P^0 - P_s) / P^0 = X_2$ or $\frac{\Delta P}{P^0} = X_2$ (iii)
- $$[\Delta P = P^0 \cdot \frac{W_2 / MW_2}{W_1 / MW_1 + W_2 / MW_2}]$$
- Where, $(P - P_s)$ represents *lowering of vapor pressure* and $(P - P_s) / P$ represents *relative lowering of vapor pressure*. Here, eqn.(iii) is known as **Raoult's Law**.
 - **Raoult's law states** that, the relative lowering of vapor pressure of a dilute solution is equal to the mole fraction of the non-volatile component (i.e. solute) present in the dilute solution.
- This is a useful to study the **effect of solute on boiling point and freezing point of the solution**. This also helps in determining the **molecular weight of dissolved solute**.

Ideal Solution:

- Any solution whose vapor pressure depends on the concentration according to the relation $P = P^0 \cdot X_1$ is known as **ideal solution**.
- Simply, a solution which obeys Raoult's law strictly is called **an Ideal solution**. While a solution showing deviation from Raoult's law is called **Non-ideal or Real solution**.
- For example**; a mixture of **n-hexane and n-heptane** behaves almost as an ideal solution. Likewise, **Benzene and Toluene; Chloroform and Bromoform** etc.



Contd...

- **Characteristics features of Ideal solution:**

- It should obey *Raoult's law under all conditions of temperature, pressure and concentration.*
- There should be no change in volume on mixing i.e. $\Delta V_{\text{mixing}} = 0$.
- There should be no change in enthalpy on mixing i.e. $\Delta H_{\text{mixing}} = 0$.
- The solute shows **neither dissociation nor association** during its dissolution.
- For ideal solution, **like forces must be similar to the unlike forces.** (i.e. A-B molecular interaction force = A-A, B-B interaction force.)
- Compounds having **similar structure and polarity** form ideal solution.
- **No perfect ideal solution** but many of them behave *ideally in dilute solution.*

Colligative Properties contd.....

2. *Elevation of the boiling point:* (i.e. Relation between boiling point elevation and lowering of V.P.)

- **Boiling point-**

The intersection of the solution vapor-pressure curve with the line corresponding to 760 mm atmospheric pressure

- The **addition of a non-volatile solute lowers vapor pressure** and elevates boiling point of the solution.
- Thus, **the lowering of vapor pressure will increase boiling point of the solution.** i.e. boiling point of the solution > pure solvent.
- Let ' T_b ' = boiling point of the pure solvent, ' T ' = boiling point of the solution, then boiling point elevation $\Delta T_b = T - T_b$

- **Elevation of boiling point-**

The temperature by which the boiling point of a solution rises than that of its pure solvent to make its vapor pressure equilibrium with the atmospheric pressure.

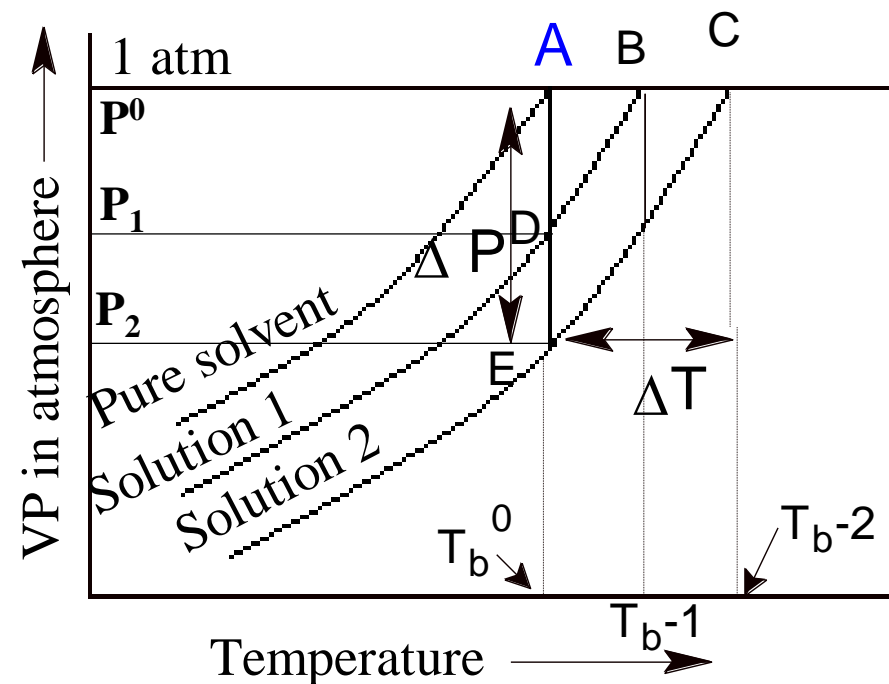


Fig: Relation between elevation of BP and lowering of VP

- The figure clearly shows the **vapor pressure curves of the pure solvent and solution (1) and (2)** with different concentrations of solute.
- For the **dilute solutions**, the curves **BD || CE** & **straight lines** approximately. Then, we have the **similar triangles**, **ACE** and **ABD**. For the **similar triangles**, we may write,

$$AB/AC = AD/AE \text{ or, } T_1 - T_b / T_2 - T_b = P^0 - P_1 / P^0 - P_2$$

- Hence, **the elevation of boiling point is directly proportional to the lowering of vapor pressure. i.e.**

$$\text{Or, } \Delta T_b \propto \Delta P \dots\dots\dots(i)$$

- According to Raoult's law,

$$\Delta P \propto X_2 \dots\dots\dots(ii)$$

From eqn. (i) and(ii), we may write, $\Delta T_b \propto X_2 \dots\dots\dots(iii)$

If K_b ' be proportionality constant ,then

$$\Delta T_b = K'_b X_2 = \Delta T_b = K_b' \cdot (n_2 / n_1 + n_2) \dots\dots\dots(iv)$$

- For a **dilute solution**, $n_2 \ll n_1$. Then, we can make approximation that

$(n_2 / n_1 + n_2) = (n_2 / n_1)$ or $(n_2 / n_1) = (W_2 / MW_2) / (W_1 / MW_1)$ where W_1 and W_2 are weights of solvent and solute in solution , and MW_1 , and MW_2 are *their molecular weights* .

Now eqn.(iv) becomes $\Delta T_b = K_b' \cdot (W_2/MW_2)/(W_1/MW_1) \dots \dots \dots (v)$

- For *ideal solution*, the value of the constant **K_b' depends only on the identity of the solvent and not at all on the solute.** The quantity MW_1 is also a **property of the solvent only**, and a *new constant* is introduced by combining MW_1 with K_b' .

- Here, we define **boiling point constant** K_b by the equation, **$1000 \cdot K_b = K_b' \cdot MW_1$**

Or, $\Delta T_b = K_b \{ (W_2/MW_2)/ W_1 \} \cdot 1000$. From definition.of **molality**, **$\{m = (W_2/MW_2)/ W_1 \} \cdot 1000$**

Or, $\Delta T_b = K_b m \dots \dots \dots (vi)$ where K_b called **molal boiling point constant** (or **molal elevation constant**). It is equal to boiling point elevation when conc. of solution is 1-molal. So, it is defined as **boiling point elevation produced when 1-mol of solute is dissolved in 1kg of solvent.**

- The eqn. (vi) shows that **how boiling point of a solution elevate with concentration or simply shows dependency of elevation of boiling point with concentration.**

Table: Molal boiling point constant for different liquids.

Solvents	Boiling point	K_b
Acetic acid	118.1	2.93
Benzene	80.2	2.53
Chloroform	61.2	3.63
water	100	0.51 ³⁴

3. Depression of the freezing point: (Relation between freezing point depression and V.P. lowering)

- **Freezing point of the solution**

The intersection of the vapor-pressure curve of the solution with the vapor pressure of the pure solid solvent i.e. *temperature* at which the first crystals of the solvent appear when a solution is cooled.

- Therefore, the temperature at which crystals first appear is defined as the **freezing point of a solution** of a given concentration.
- **Upon addition of non-volatile solute**, the **vapor pressure of solution decreases** and hence freezing point will also be lowered.
- Let ' T_f ' = freezing point of the pure solvent, ' T ' be freezing point of the solution, then *depression of freezing point* $\Delta T_f = (T_f - T)$
- **Depression of freezing point-**

The temperature by which the freezing point of a solution drops than that of its pure solvent.

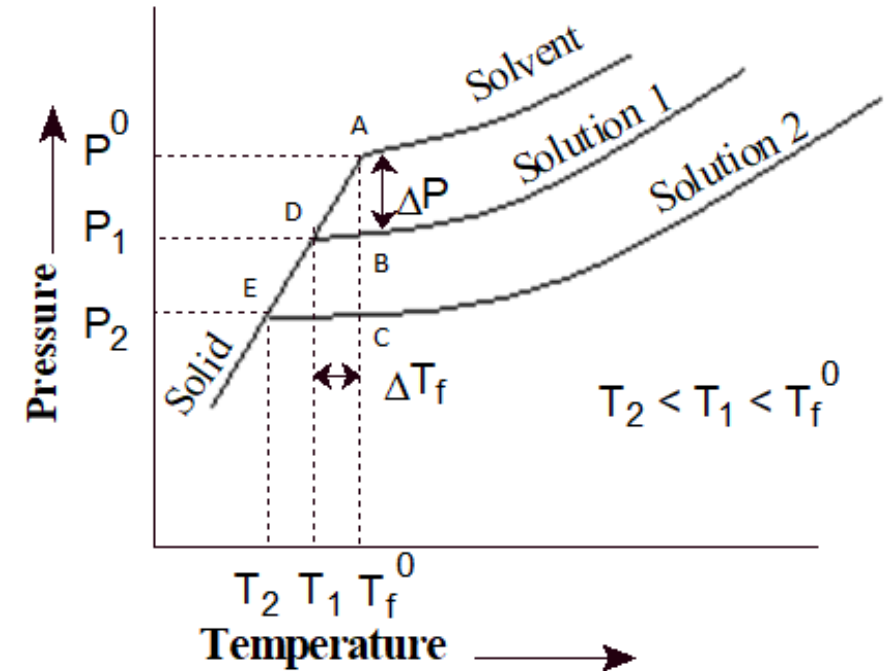


Fig: Relation between depression of freezing point and V.P. lowering

- The figure clearly shows the **vapor pressure curves of the pure solvent and solution (1) and (2)** with different concentrations of solute.
- For the **dilute solutions**, the curves **BD || CE** & **straight lines** approximately. Then, we have the **similar triangles**, **ACE** and **ABD**. For the **similar triangles**, we may write,

$$\text{BD/CE} = \text{AB/AC} \text{ or, } T_f - T_1 / T_f - T_2 = P^0 - P_1 / P^0 - P_2$$

- Hence, **the depression of freezing point is directly proportional to the lowering of vapor pressure. i.e.**

$$\text{Or, } \Delta T_f \propto \Delta P \dots\dots\dots(\text{i})$$

- According to Raoult's law,

$$\Delta P \propto X_2 \dots\dots\dots(\text{ii})$$

From eqn. (i) and(ii),we may write, $\Delta T_f \propto X_2 \dots\dots\dots(\text{iii})$

If K_f' be proportionality constant ,then

$$\Delta T_f = K_f' X_2 = \Delta T_f = K_f' \cdot (n_2 / n_{1+n_2}) \dots\dots\dots(\text{iv})$$

- For a **dilute solution**, $n_2 \ll n_1$. Then, we can make approximation that

$(n_2 / n_{1+n_2}) = (n_2 / n_1)$ or $(n_2 / n_1) = (W_2 / MW_2) / (W_1 / MW_1)$ where W_1 and W_2 are weights of solute and solvent in solution , and MW_2 , and MW_1 are their molecular weights .

Now eqn.(iv) becomes $\Delta T_f = K_f' \cdot (W_2/MW_2)/(W_1/MW_1) \dots\dots\dots(v)$

- For *ideal solution*, the value of the constant **K_f' depends only on the identity of the solvent and not at all on the solute.** The quantity MW_1 is also a **property of the solvent only**, and a *new constant* is introduced by combining MW_1 with K_b' .
 - Here, we define *freezing point constant* K_f by the equation, **$1000 \cdot K_f = K_f' \cdot MW_1$**
- Or, $\Delta T_f = K_f \{ (W_2/MW_2)/ W_1 \} \cdot 1000$. From definition.of **molality**, **$\{m = (W_2/MW_2)/ W_1 \} \cdot 1000$**
- Or, $\Delta T_f = K_f m \dots\dots\dots(vi)$ where K_b called ***molal freezing point constant (or molal depression constant)***. It is equal to freezing point depression when conc. of solution is 1-molal. So, it is defined as **freezing point depression produced when 1-mol of solute is dissolved in 1kg of solvent.**

Table: Molal depression constant for different liquids.

- The eqn. (vi) shows that **how freezing point of a solution drops with concentration or simply shows dependency of depression of freezing point with concentration.**

Solvents	freezing point	K_f
Acetic acid	17	3.9
Benzene	5.4	5.12
Naphthalene	80	6.8
water	0	1.86

4. Osmotic pressure:

- When a solution is separated from its pure solvent by a semi-permeable membrane, pure solvent molecules pass through the membrane into solution.

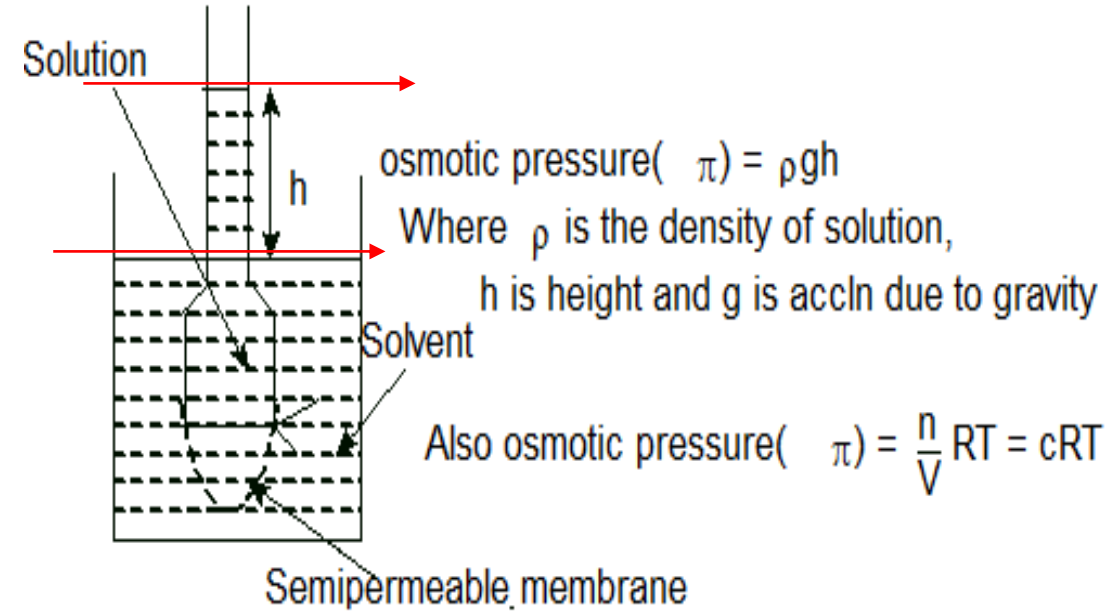
- **Osmosis:**

The spontaneous flow of the solvent molecules from pure solvent to the solution, or from a dilute solution to concentrated solution through a semi-permeable membrane.

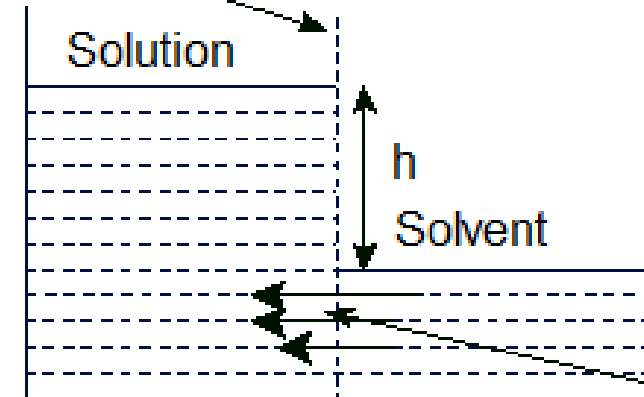
- The process of osmosis remains continued until osmotic pressure becomes equal to hydrostatic pressure (i.e. external pressure). i.e. the flow of solvent molecules stops and system reaches at equilibrium by raising a certain level of solution.

- **Semi permeable membrane:**

Porous membrane that permits only solvent molecules (small) but not the solute molecules (large) are called semi permeable membrane



Semipermeable membrane



- **Osmotic pressure(π):**

It is defined as the hydrostatic pressure built upon the solution or external pressure applied to the solution in order to just stop the osmosis of pure solvent into solution through semi permeable membrane.

- **Vant hoff equation for solution**

1. BoylesVant Hoff law: Osmotic pressure of any ideal solution at constant temperature is directly proportional to the molar concentration of the solution.

$$\pi \propto C \text{ Or, } \pi \propto n/V \dots\dots\dots(i)$$

2. Charles Vant Hoff law: Osmotic pressure of any ideal solution at constant pressure is directly proportional to the absolute temperature of the solution.

$$\pi \propto T \dots\dots\dots(ii)$$

Combining above equations,

$$\pi \propto (n/V)/ T \text{ Or, } \pi V = nRT \dots\dots\dots(iii)$$

• Determination of molecular weight from osmotic pressure:

$$\text{we have } n = \frac{W_2 \text{ (weight of solute dissolved)}}{MW_2 \text{ (molecular weight of solute)}}$$

$$\text{or, } MW_2 = \frac{W_2 R T}{\pi V} \dots\dots\dots(4)$$

- The ideal gas equation can be expressed in terms of colligative properties. On account of osmotic pressure, ideal gas equation can be written as,

$$\pi V = n RT$$

or, $\pi = n/V \cdot RT$ or, $\pi = C \cdot RT$(i) where, $C = n/V = \text{molar conc.}$

- Here, π = osmotic pressure, C = molar concentration, R = gas constant, and T = temperature in Kelvin. If C is mol/lit.
- then the value of R should 0.082 lit-atm /vol, π should be in atm.
- From above eqn.
 $\pi \propto C$ at a tempr.
- This means that osmotic pressure is also **colligative property**.

Solutions of two volatile components:

- Consider an ideal solution of two volatile liquids (Benzene and Toluene). Then both components follow Raoult's law at any concentration.i.e. $P_1 = P_1^0 X_1$ and $P_2 = P_2^0 X_2$

- Now, total vapor pressure of solution is;

$$P_T = P_1 + P_2 = P_1^0 X_1 + P_2^0 X_2$$

- *The composition of a vapor in mole-fraction units is not the same as the composition of the liquid solution at equilibrium*
- Given, Let a liquid mixture of benzene and toluene.

$$P_B^0 = 75 \text{ mm and } X_B = 0.33 ; P_T^0 = 22 \text{ mm and } X_T = 0.67$$

- Then, $P_B = 0.33 \times 75 = 24.75 \text{ mm}$
 $P_T = 0.67 \times 22 = 14.74 \text{ mm}$
- Now, $P_T = P_1 + P_2 = 24.75 + 14.74 = 39.49 \text{ mm}$

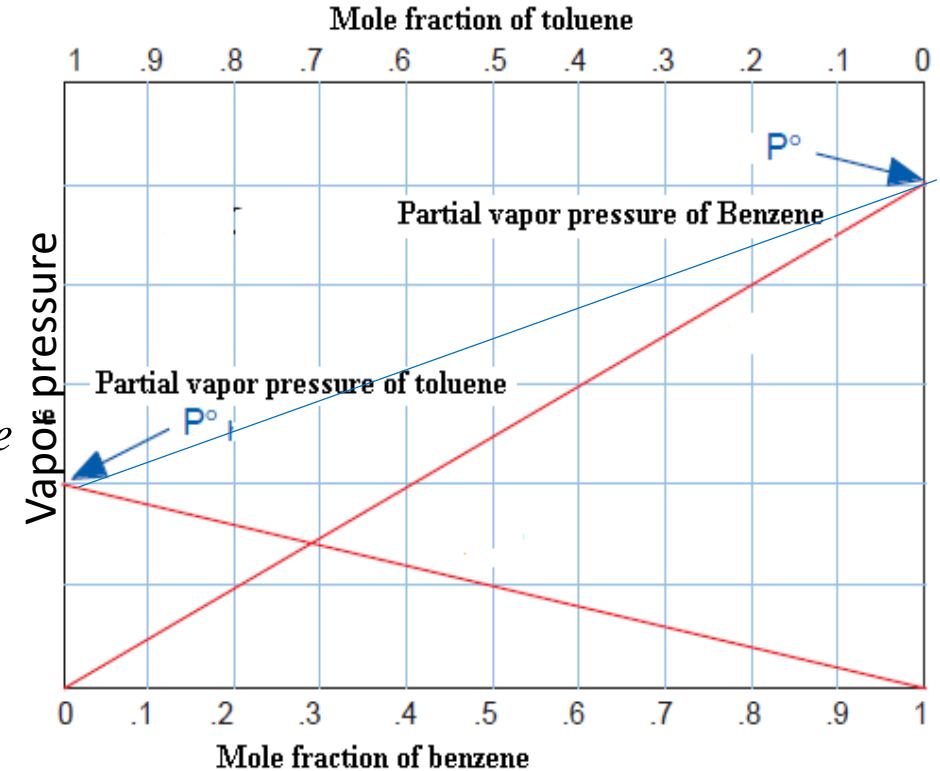


Fig. Vapor pressure as a function of the composition for an ideal solution of benzene and toluene

Contd...

- The **composition of the vapor** in mole-fraction units can be obtained by using Dalton's law.
- Then, $X'_B = P_B / P_T = 24.75/39.49 = 0.63$
- $X'_T = P_T / P_T = 14.74/39.49 = 0.37$
- Then, **condensed the vapor of benzene and toluene to liquid** and **allowed to evaporate so as to come into eqm. with its vapor.**
- Determine the *composition of two components in new the vapor.*
- $P_B^0 = 75 \text{ mm}$ and $X_B = 0.63$; $P_T^0 = 22 \text{ mm}$ and $X_T = 0.37$
- Now, $P_T = P_1 + P_2 = P_1^0 X_1 + P_2^0 X_2 = 47.25 + 8.1 = 55.35 \text{ mm}$.
- $X''_B = P_B / P''_T = 47.25/55.35 = 0.854$ and $X''_T = P_T / P''_T = 8.1/55.35 = 0.146$
- The repetition of two processes tends to produce **vapor nearly pure benzene** and **a liquid that is very nearly pure toluene.**

Non-ideal solutions: Types of non-ideal solutions

1. Negative deviation from Raoult's law:

- The components in the solution are found to have **lower energy than in their pure states**.
- This kind of behavior occurs when there are **stronger attractive forces between unlike molecules than between molecules of the same kind**.
- **A strong hydrogen bond** is easily formed between CHCl_3 and $(\text{CH}_3)_2\text{CO}$ but **this does not occur in pure** CHCl_3 or pure $(\text{CH}_3)_2\text{CO}$ due to lacking O-atom in CHCl_3 and H-atom in $(\text{CH}_3)_2\text{CO}$.
- The **vapor pressure of solution is less** than that of **an ideal solution of the same components**.

Example: $\text{CH}_3\text{COOH} + \text{C}_5\text{H}_5\text{N}$ (pyridine); $\text{H}_2\text{O} + \text{HCl}$;
Acetone + Aniline, $\text{H}_2\text{O} + \text{HNO}_3$

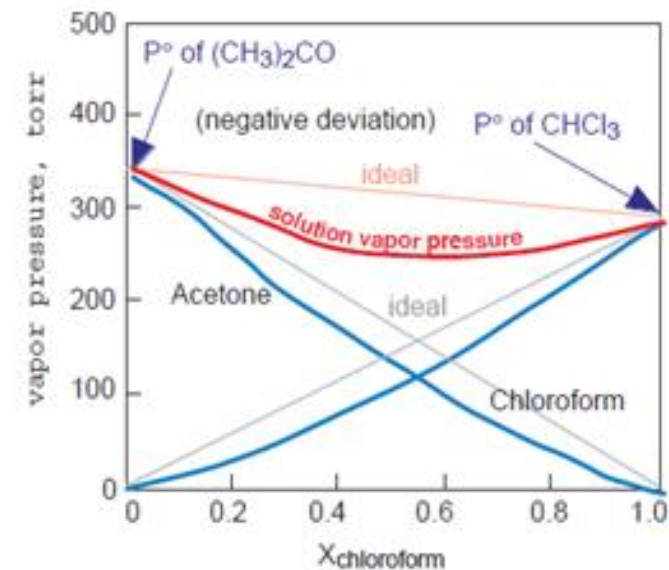


Fig. Vapor pressure as a function of composition for acetone -chloroform solution

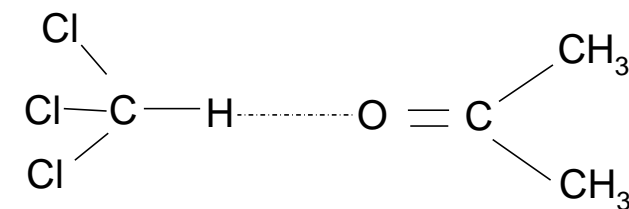


Fig. Hydrogen bond interaction between chloroform and acetone

Contd...

2. Positive deviation from Raoult's law:

- The components in the solution are found to have **higher energy than in their pure states**.
- This kind of behavior occurs when **attractive forces between unlike molecules are weaker than between molecules of the same kind**.
- There is **weak interaction** between $(\text{CH}_3)_2\text{CO}$ and CS_2 because there is **no any hydrogen bond interaction or anything else between them**.
- The **vapor pressure of solution is greater** than that of **an ideal solution of the same components**

Examples: $\text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{OH}$; $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{OH}$
; $\text{CCl}_4 + \text{CHCl}_3$.

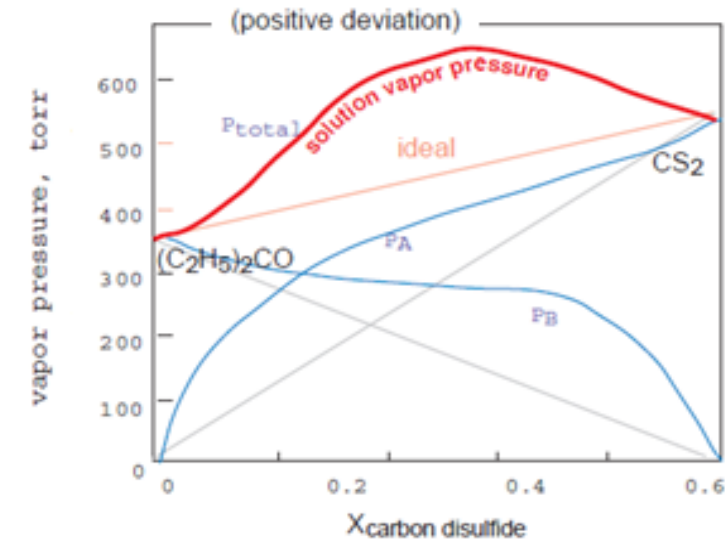


Fig. Vapor pressure as a function of composition for acetone-carbon disulfide solution

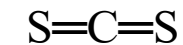


Fig. linear molecule (not polar in nature)

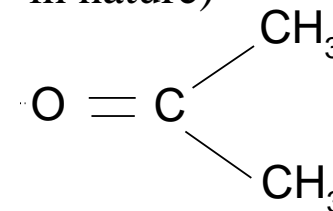


Fig. Dipole moment

Azeotropic mixture:

- A mixture of two liquids that boils at **constant composition**
- Deviation from Raoult's law leading to **maximum or minimum in the boiling point composition**
- Azeotropic mixture can not be separated into its constituents by distillation

Components		Composition By % Mass	Boiling Point, ⁰ c		Azeotrope	Deviation from
A	B	B	A	B		
H ₂ O	C ₂ H ₅ OH	95.6	100	78.37	78.1	Positive deviation from Raoult's law
(CH ₃) ₂ CO		67	56.2	46.3	39.2	
H ₂ O	HCl	20.3	100	-85.05	110	Negative deviation from Raoult's law
H ₂ O	HNO ₃	68	100	83	127	

Solubility

- Each solvent has limited capacity to dissolve solute forming homogeneous mixture.
- A solution always attains a constant concentration i.e. *solute and solution is at equilibrium* and it is said to be **saturated**.
- **The solubility of a substance in a particular solvent at a given temperature is the concentration of solute in saturated solution.**
- **The solubility of a substance in a particular solvent is controlled by;**
 - Nature of solvent and solute themselves.
 - Condition of temperature and pressure.
- If we consider an **ideal solution of two liquids**, we may observe **two facts**;
 - Limited solubility and a saturated solution result only when a solute and its solution reach equilibrium
 - The equilibrium state is a compromise between a natural tendency toward minimum energy and maximum molecular chaos.

Temperature effects on solubility:

- If dissolution of a solute is accompanied by change in enthalpy, there is sharp effects of a change in temperature on the solubility.
- The solubility of the most of the substances increases with rise in temperature but the effect of temperature is not same for all.
 - For ΔH_{sol} is positive (endothermic process, Solute + Solvent \rightarrow Solution) then solubility of the solute increases.
 - While, if ΔH_{sol} is negative, then solubility of the solute decreases as temperature increases.
- The ΔH_{sol} for KNO_3 , NaCl , and Na_2SO_4 are +8.5, +1.3 and -5.5 kcal/mole

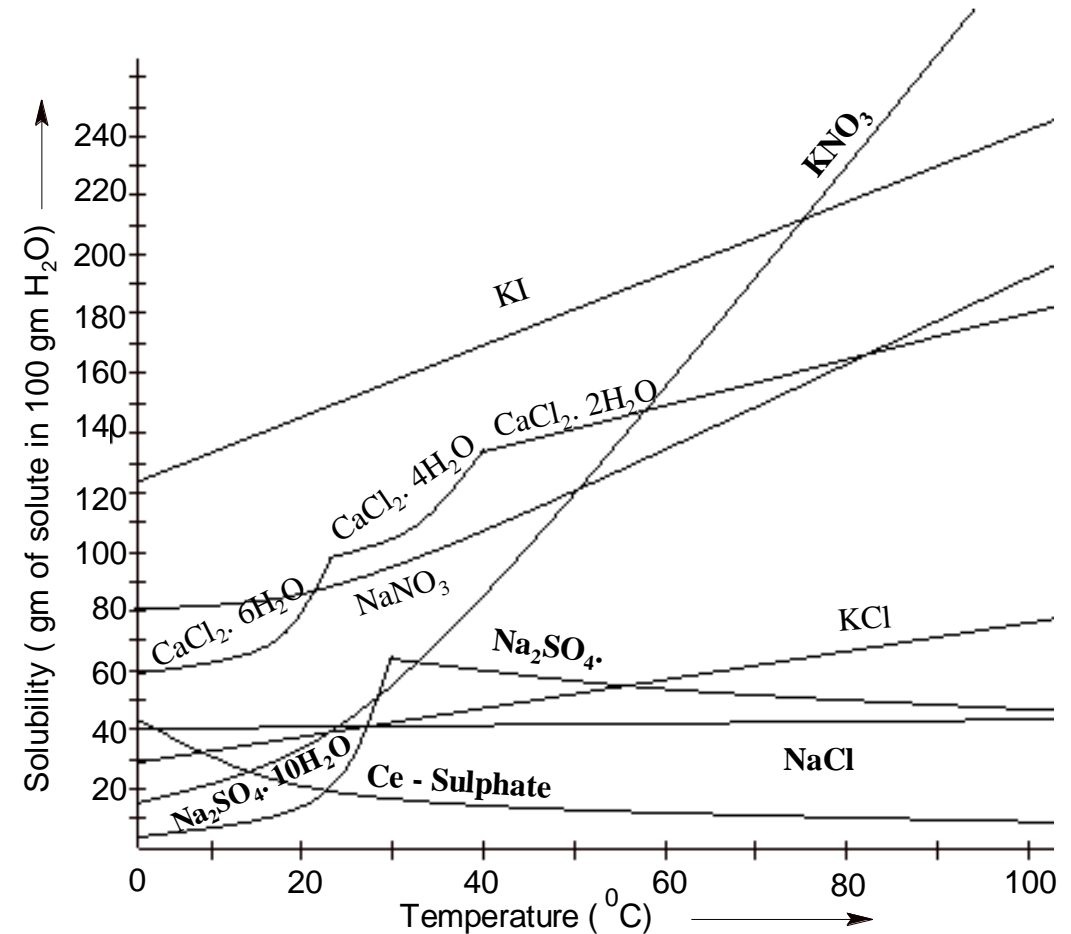


Fig: Solubility curves of common salts in water

Numerical Problems (Properties of solution)- Practice Session

4.1 What are the molality and the molarity of a solution of ethanol, C_2H_5OH , in water if the mole fraction of ethanol is 0.05? Assume that the density of the solution is 0.997gm/ml.

Solution:

- Let, wt. of solvent (H_2O) = 1000 gm
- Then, $X_{C_2H_5OH} = n_2 / [(1000/18) + n_2]$ or $(1000/18) \times 0.05 + 0.05 n_2 = n_2$
- or $n_2 = 2.92$
- **Now, molality of solution = 2.92m**
- **Weight of solution = wt. of solute (ethanol) + wt. of solvent (water)**
- Or Weight of solution = $n_2 \times \text{mol. Wt. of ethanol} + 1000\text{gm} = 1134.32$
- **Then, $D = M/V$ or $V \text{ of solution} = 1134.32/0.997 = 1137.73 \text{ ml solution.}$**
- **Molarity (M) = $(2.92/1137.73) \times 1000 = 2.57M$**

4.2 Concentrated nitric acid is 69% by weight HNO_3 and has a density of 1.41gm/ml at 20°C. What volume and what weight of concentrated nitric acid are needed to prepare 100 ml of 6-M acid?

Solution:

- Original Molar conc. of nitric acid = **(density x % purity x10)/Mol.wt**
- $= (1.41 \times 69 \times 10) / 63$ or, = **15.44 M**
- Then, use, $S_1 V_1 = S_2 V_2$ formula for dilution.
- $V_1 =$ **38.86 ml**
- Then, wt. of 38.86 ml of original $\text{HNO}_3 = 38.86 \times 1.41 =$ **54.79 gm**

4.4 Exactly 100 gm of a certain solution contain 10 gm of NaCl. The density of the solution is 1.071gm/ml. What is the molality and the molarity of NaCl?

Ans. Molarity (M) = $(n_2 / 93.37) \times 1000 = [(10 / 58.5) / 93.37] \times 1000 =$ **1.83M**

Molality(m) = $(n_2 / \text{wt. of solvent}) \times 1000 = [(10 / 58.5) / 90] \times 1000 =$ **1.899m**

- **4.5** The boiling point of a solution of 0.402gm of Naphthalene, $C_{10}H_8$, in 26.6gm of chloroform is $0.455^\circ C$ higher than that of pure chloroform. What is the molal boiling point elevation constant for chloroform?
- Solution:
- Now, $\Delta T_b = K_b \times m$ or, $0.455 = K_b \times (n_{2/w1}) \times 1000$
- or, $0.455 = K_b \times [(0.402/128)/26.6] \times 1000$ or, $K_b = 3.855$
- **4.6** The vapor pressure of a dilute aqueous solution is 23.45mm at $25^\circ C$, where as the vapor pressure of pure water at this temperature is 23.76mm. Calculate the molal concentration of solute, and use the tabulated value of K_b for water (0.51) to predict the boiling point of the solution.
- We have, $\Delta P = P^0 \times X_2$ or $X_2 = 0.013$ or $X_2 = (n_2 / n_1 + n_2)$
- If $n_2 \ll n_1$, then $X_2 = (n_2 / n_1)$. let, solvent wt. = 1000gm. Then, $n_1 = 55.55$
- $n_2 = 0.722 m$ Then, $\Delta T_b = 0.368$
- Boiling point of solution (T_b') = $100 + 0.368 = 100.368^\circ C$

4.10 Ten liters of dry air were bubbled slowly through liquid water at 20°C, and the observed weight loss of the liquid was 0.172gm. By assuming that 10 liters of saturated water vapor were formed in the experiment, calculate the vapor pressure of water at 20°C.

- Solution:
- The observed weight loss of the liquid = **0.172gm**
- Saturated water vapor formed in the experiment = **10 liters**
- Now, $PV = nRT$
- $P = 2.2958 \times 10^{-2}$ atm. Or **17.448 mm**

4.12 At 20°C, the vapor pressure of pure benzene is 22mm, and that of pure toluene is 75 mm. What is the composition of the solution of these two components that has a vapor pressure of 50 mm at this temperature? What is the composition of the vapor in equilibrium with this solution?

- $P_T = P_1 + P_2 = P_1^0 X_1 + P_2^0 X_2$
- $X_B = 0.47$ Then, $X_T = ???$ Then, $P_T = 39.75\text{mm}$ and $P_B = 10.34\text{mm}$ Vapor????

Exercise Problems (Properties of solution)

8. **What** are the molality and the molarity of a solution of ethanol, C_2H_5OH , in water if the mole fraction of ethanol is 0.05? Assume that the density of the solution is 0.997gm/ml.
[m=2.92m; M=2.57M]
9. Concentrated nitric acid is 69% by weight HNO_3 and has a density of 1.41gm/ml at 20°C. What volume and what weight of concentrated nitric acid are needed to prepare 100 ml of 6-M acid?
[38.853ml; 54.78gm]
10. Calculate how many milliliters of 0.10-M $KMnO_4$ are required to react completely with 0.01 mole of oxalate ion, $C_2O_4^{2-}$, according to the reaction
[40ml]
$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ = 2Mn^{2+} + 10CO_2 + 8H_2O$$
11. Exactly 100 gm of a certain solution contain 10 gm of $NaCl$. The density of the solution is 1.071gm/ml. What is the molality and the molarity of $NaCl$?
[1.9m; 1.82M]
12. The boiling point of a solution of 0.402gm of Naphthalene, $C_{10}H_8$, in 26.6gm of chloroform is 0.455° C higher than that of pure chloroform. What is the molal boiling point elevation constant for chloroform?
[3.85]
13. The vapor pressure of a dilute aqueous solution is 23.45mm at 25°C, whereas the vapor pressure of pure water at this temperature is 23.76mm. Calculate the molal concentration of solute, and use the tabulated value of K_b for water (0.51) to predict the boiling point of the solution.
[0.731m; $\Delta T=0.3731^\circ C$; $T_b=100.3731^\circ C$]

14. What weight of ethylene glycol, $C_2H_6O_2$, must be included in each 1000gm of aqueous solvent to lower the freezing point to $-10^\circ C$? [333gm]
15. When 1 gm of sulfur is dissolved in 20 gm of naphthalene, the resulting solution freezes at a temperature $1.28^\circ C$ lower than pure naphthalene does. What is the molecular weight of sulfur? [265.62]
16. The freezing point depression constant for mercuric chloride, $HgCl_2$, is 34.3. For a solution of 0.849 gm of mercurous chloride (empirical formula $HgCl$) in 50gm of $HgCl_2$, the freezing point depression is $1.24^\circ C$. What is the molecular weight of mercurous chloride in this solution? What is its molecular formula? [470, Hg_2Cl_2]
17. Ten liters of dry air were bubbled slowly through liquid water at $20^\circ C$, and the observed weight loss of the liquid was 0.172gm. By assuming that 10 liters of saturated water vapor were formed in the experiment, calculate the vapor pressure of water at $20^\circ C$. [17.35mmHg]
18. Ethanol and methanol form a solution that is very nearly ideal. The vapor pressure of ethanol is 44.5mm and that of methanol is 88.7 at $20^\circ C$. (a) Calculate the mole fractions of methanol and ethanol in a solution obtained by mixing 60 gm of ethanol with 40 gm of methanol. (b) Calculate the partial pressures and the total vapor pressure of this solution and the mole fraction of ethanol in the vapor.
[$X_E=0.51, X_M=0.49; P_E=22.7, P_M=43.5, P_T=66.2; X_E$ in vapour=0.343]
19. At $20^\circ C$, the vapor pressure of pure benzene is 22mm, and that of pure toluene is 75 mm. What is the composition of the solution of these two components that has a vapor pressure of 50 mm at this temperature? What is the composition of the vapor in equilibrium with this solution?
[$X_T=0.53, X_B=0.47; P_B=10.38, P_T=39.6; \text{in vapour } X_B=0.27, X_T=0.79$]
20. The solubility of borax ($Na_2B_4O_7 \cdot 10H_2O$) in water increases as the temperature increases. Is heat evolved or absorbed as this salt dissolves? Is the ΔH of the dissolution process positive or negative? [ΔH =positive, absorbed]
21. At $55^\circ C$, ethanol has a vapor pressure of 168mm, and the vapor pressure of methyl cyclohexane is 280mm. A solution of the two, in which the mole fraction of ethanol is 0.68, has a total vapor pressure of 376mm. Is this solution formed from its components with the evolution or absorption of heat? [Given $P_T=376mm$; calculated $P_T=203.84mm$, solution is formed by absorption of heat]