# Properties of Dilute Solution

**Dr. Md. Mahbub Alam**
**Department of Chemistry**
**BUET, Dhaka-1000**

# Colligative Properties

A *colligative property* is a property of solutions that depends only upon the number of solute particles, not upon their identity.

There are four colligative properties of solutions:

- Lowering of Vapor Pressure
- Elevation of Boiling Point
- Depression of Freezing Point
- Osmosis

# Lowering of Vapour Pressure

- The vapour pressure of a pure solvent is decreased when a non-volatile solute is dissolved in it.

- If p is the vapour pressure of the solvent and ps that of the solution, the lowering of vapour pressure is (p – $p_s$).

- This lowering of vapour pressure relative to the vapour pressure of the pure solvent is termed the Relative lowering of Vapour pressure.

- Relative Lowering of Vapour Pressure -

$$Relative\ lowring\ of\ vapour\ pressure = \frac{p - ps}{p}$$

Solvent molecules
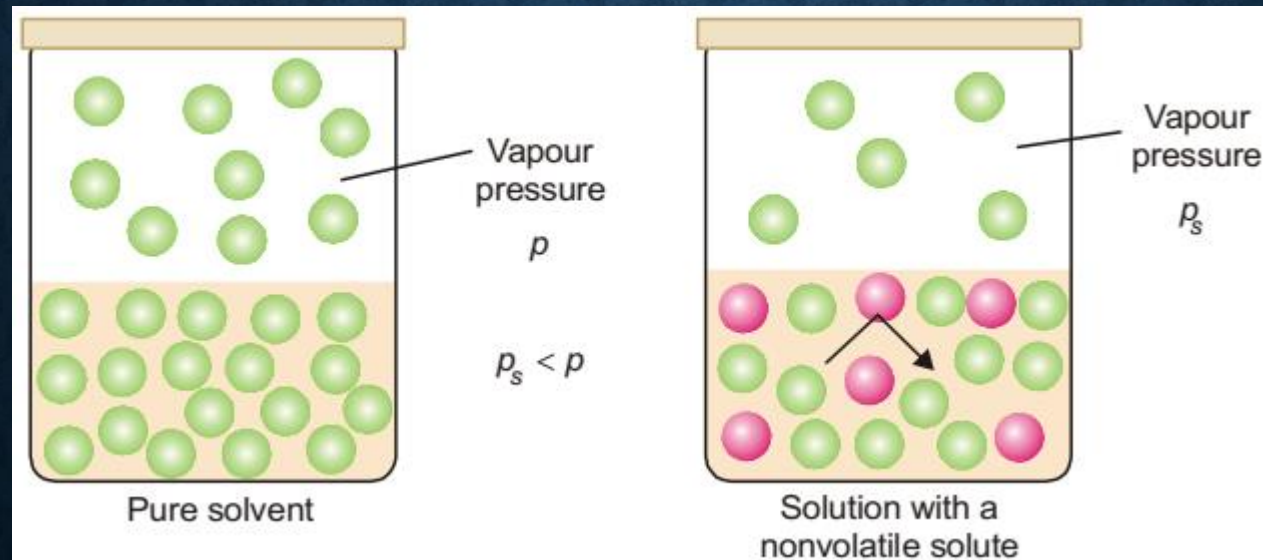
Nonvolatile solute molecules
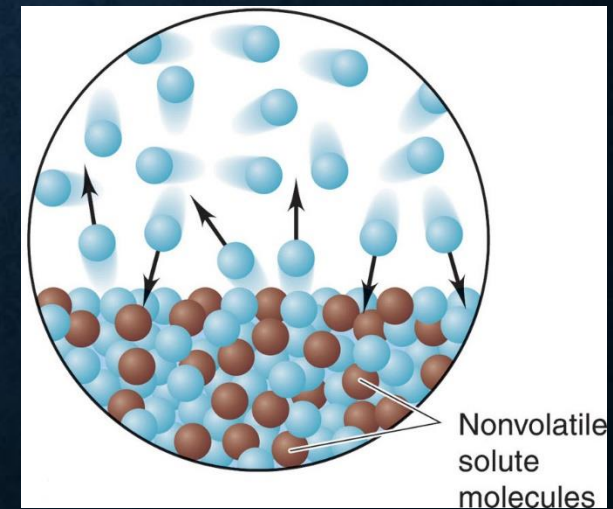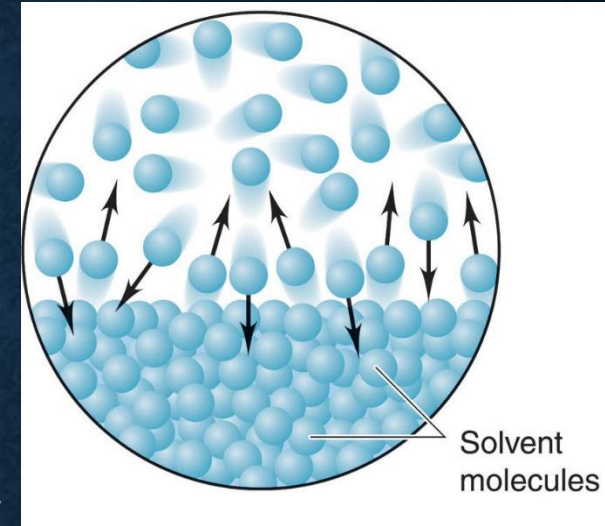
# Lowering of Vapour Pressure: Raoult's Law

*'The relative lowering of the vapour pressure of a dilute solution is equal to the mole fraction of the solute present in dilute solution.'*

$$\frac{p - ps}{p} = \frac{n}{n+N}$$

$n$ = number of moles of solute
$N$ = number of moles of solvent



Vapour pressure $p$

$p_s < p$

Pure solvent

Vapour pressure $p_s$

Solution with a nonvolatile solute

# Derivation of Raoult's Law

- When a non-volatile solute is dissolved in solution, the presence of solute molecules in the surface blocks a fraction of the surface where no evaporation can take place.

- The vapour pressure of the solution is, therefore, determined by the number of molecules of the solvent present at any time in the surface which is proportional to the mole fraction.

$$p_s \ \alpha \ \frac{N}{n + N}$$

$$or \ \ p_s \ _= \ k \ \frac{N}{n+N} \ \ldots\ldots (1)$$

In case of pure solvent, $n = 0$, and $p_s = p$

$$mole \ fraction \ of \ solvent = \ \frac{N}{n+N} = \frac{N}{0+N} = 1$$

Therefore, from (1), $p = k$

**Equation (1) can now be written as -**

$$or \ \ p_s \ _= \ p \ \frac{N}{n + N}$$

$$or \ \ \frac{p_s}{p} = \frac{N}{n + N}$$

$$or \ \ 1 - \frac{p_s}{p} = 1 - \frac{N}{n + N}$$

$$or \ \frac{p - p_s}{p} = \frac{n}{n+N} \ ; \text{Raoutl's Law}$$

# Determination of Molecular weight from Lowering of Vapour Pressure

- **The molecular mass of a nonvolatile solute can be determined by measuring the lowering of vapour pressure ($p - p_s$) produced by dissolving a known weight of it in a known weight of the solvent.**

- **If w grams of solute is dissolved in W grams of the solvent, m and M are molecular masses of the solute and solvent respectively, we have –**

- **No. of moles of solute (n) = w/m**

- **No. of moles of solvent (N) = W/M**

- **Substituting these values in the Raoult's Law equation –**

$$\frac{p - p_s}{p} = \frac{n}{n + N}$$

- *Since for very dilute solution, the number of moles (molecules) of solute (w/m), is very small, it can be neglected in the denominator. Then,*

$$\frac{p - p_s}{p} = \frac{wM}{Wm}$$

$$or, \quad \frac{p - p_s}{p} = \frac{w/m}{w/m + W/M}$$

- *Knowing the experimental value of (p – ps)/p, and the molecular mass of the solvent (M), the molecular weight of solute (m) can be calculated.*

**SOLVED PROBLEM.** Calculate the vapour pressure lowering caused by the addition of 100 g of sucrose (mol mass = 342) to 1000 g of water if the vapour pressure of pure water at 25°C is 23.8 mm Hg.

Using Raoult's Law Equation

$$\frac{p - p_s}{p} = \frac{\Delta p}{p} = \frac{n}{n + N}$$

where

$\Delta p$ = lowering of vapour pressure

$p$ = vapour pressure of water = 23.8 mm Hg

$n$ = moles of sucrose = $\frac{100}{342}$ = 0.292 mole

$N$ = moles of water = $\frac{1000}{18}$ = 55.5 moles

Substituting values in equation (1)

$$\frac{\Delta p}{23.8} = \frac{0.292}{0.292 + 55.5}$$

$$\Delta p = 23.8 \times \frac{0.292}{55.792} = \textbf{0.125 mm}$$

Thus the lowering of vapour pressure = **0.125 mm Hg**

**SOLVED PROBLEM 1.** The vapour pressure of ether (mol mass = 74) is 442 mm Hg at 293 K. If 3g of a compound A are dissolved in 50 g of ether at this temperature, the vapour pressure falls to 426 mm Hg. Calculate the molecular mass of A. Assume that the solution of A in ether is very dilute.

Here the approximate form of the Raoult's law Equation will be used.

$$\frac{p - p_s}{p} = \frac{w}{\dfrac{m}{W / M}} = \frac{wM}{mW}$$

In this case :

| | |
|---|---|
| $w$, the mass of solute (A) | = 3 g |
| $W$, the mass of solvent (ether) | = 50 g |
| $m$, the mol mass of solute A | = ? |
| $M$, the mol mass of solvent (ether) | = 74 |
| $p$, the vapour pressure of solvent (ether) | = 442 mm |
| $p_s$, the vapour pressure of solution | = 426 mm |

Substituting the values in equation (1),

$$\frac{442 - 426}{442} = \frac{3 \times 74}{m \times 50} \quad \text{or} \quad m = \frac{3 \times 74 \times 442}{50 \times 16}$$

Hence $\qquad\qquad m = \mathbf{122.6}$

Thus **the molecular weight of A is 123**

**SOLVED PROBLEM 2.** 18.2 g of urea is dissolved in 100 g of water at 50°C. The lowering of vapour pressure produced is 5 mm Hg. Calculate the molecular mass of urea. The vapour pressure of water at 50°C is 92 mm Hg.

Since the solution is not very dilute, the complete Raoult's Law Equation applied is

$$\frac{p - p_s}{p} = \frac{w/m}{W/M + w/m} \qquad ...(1)$$

In this case :

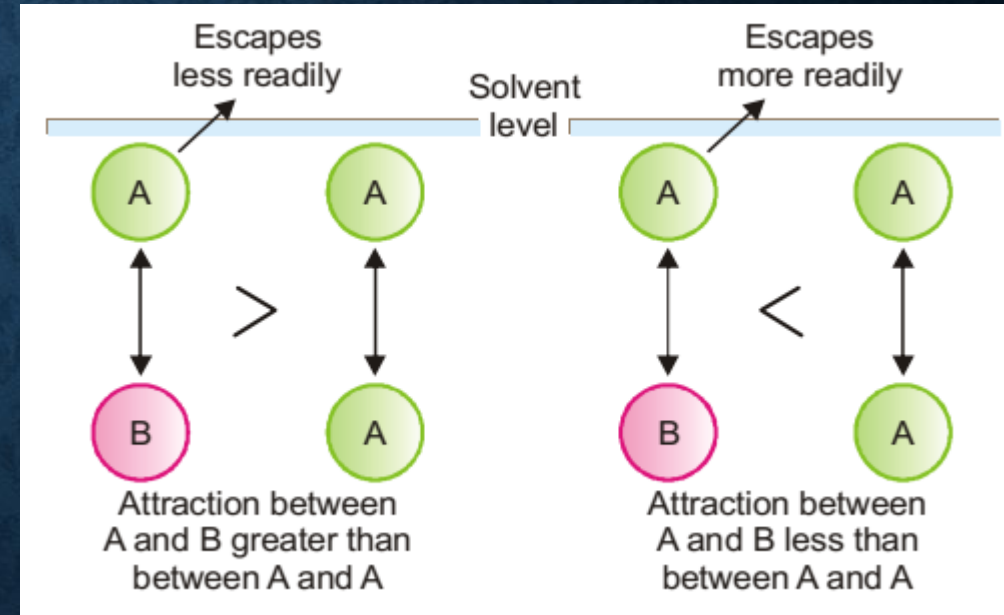| | |
|---|---|
| $w$, the mass of solute (urea) | = 18.2 g |
| $W$, *the* mass of solvent (water) | = 100 g |
| $m$, the mol mass of solute (urea) | = ? |
| $M$, the mol mass of solvent (water) | = 18 |
| $p - p_s$, the lowering of vapour pressure | = 5 mm |
| $p$, the vapour pressure of solvent (water) | = 92 mm |

Substituting these values in equation (1),
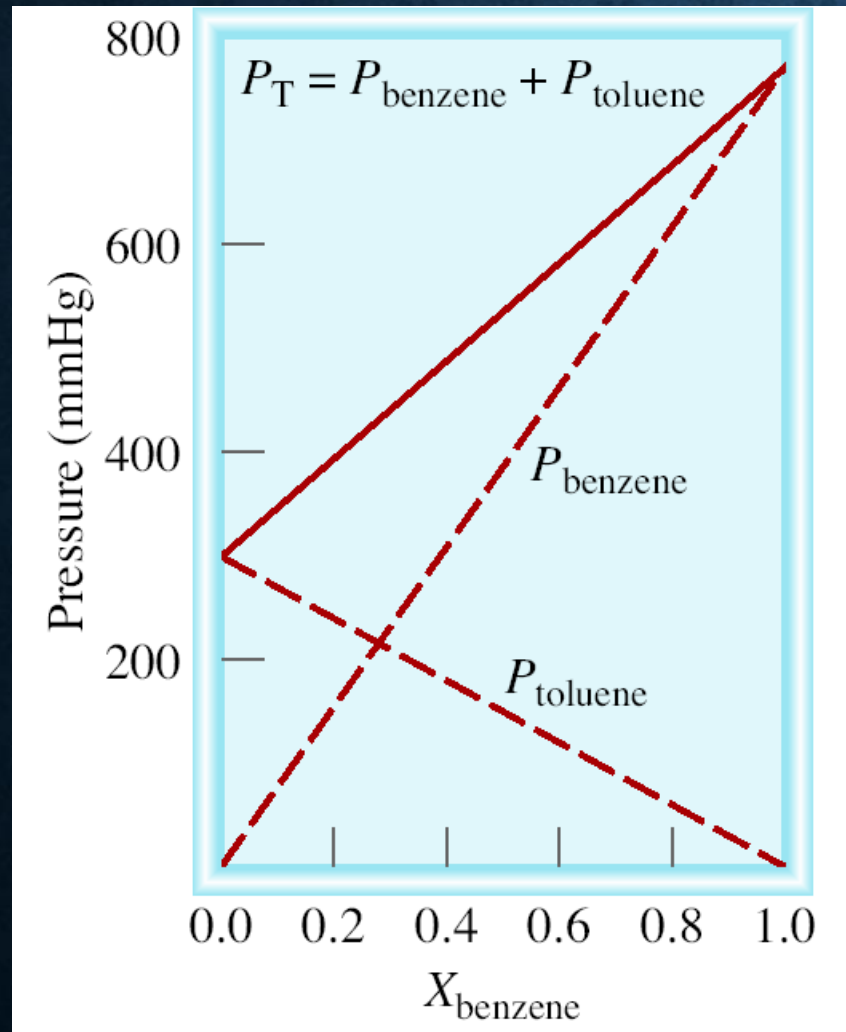
$$\frac{5}{92} = \frac{18.2/m}{18.2/m + 100/18}$$

Hence $m$, the molecular mass of urea = **57.05**

# Ideal Solutions and Deviations from Raoult's Law

- A solution which obeys Raoult's law strictly is called an Ideal solution.

- A solution which shows deviations from Raoult's law is called a Non-ideal or Real solution.

- Suppose the molecules of the solvent and solute are represented by A and B respectively.

- Now let $\delta_{AB}$ be the attractive force between A and B, and $\delta_{AA}$ between A and A.

- If $\delta_{AB} = \delta_{AA}$, the solution will show the same vapour pressure as predicted by Raoult's law and it is an ideal solution.



Escapes less readily

Escapes more readily

Solvent level

A  A      A  A

\>           <

B  A      B  A

Attraction between A and B greater than between A and A

Attraction between A and B less than between A and A

# Ideal Solutions and Deviations from Raoult's Law


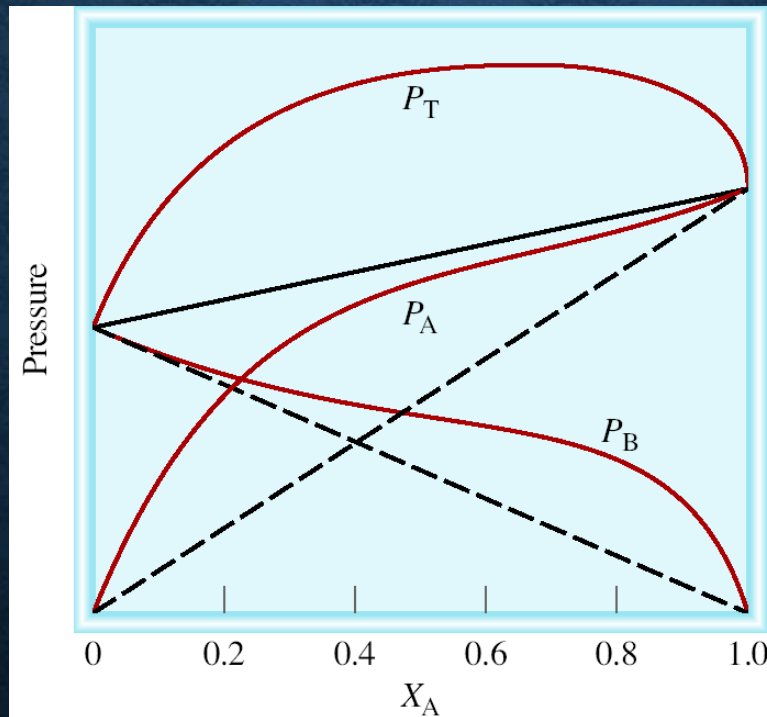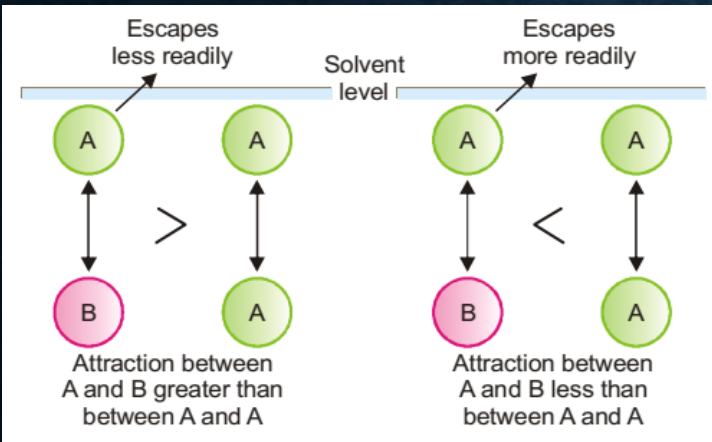
$$P_A = X_A P_A^0$$

$$P_B = X_B P_B^0$$

$$P_s = P_A + P_B$$

$$P_s = X_A P_A^0 + X_B P_B^0$$

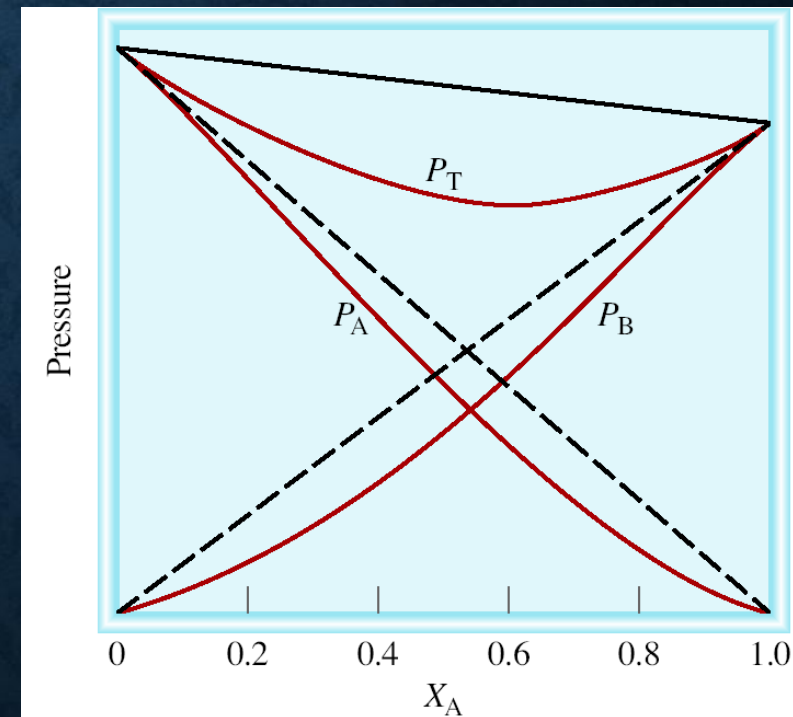# Ideal Solutions and Deviations from Raoult's Law

## Positive Deviation

$P_s$ is greater than predicted by Raoults's law



Force A-B  <  Force A-A  &  Force B-B

## Negative Deviation

$P_s$ is less than predicted by Raoults's law



Force A-B  >  Force A-A  &  Force B-B

# Elevation of Boiling Point

If $T_b$ is the boiling point of the solvent and $T$ is the boiling point of the solution, the difference in the boiling points ($\Delta T$) is called the elevation of boiling point.
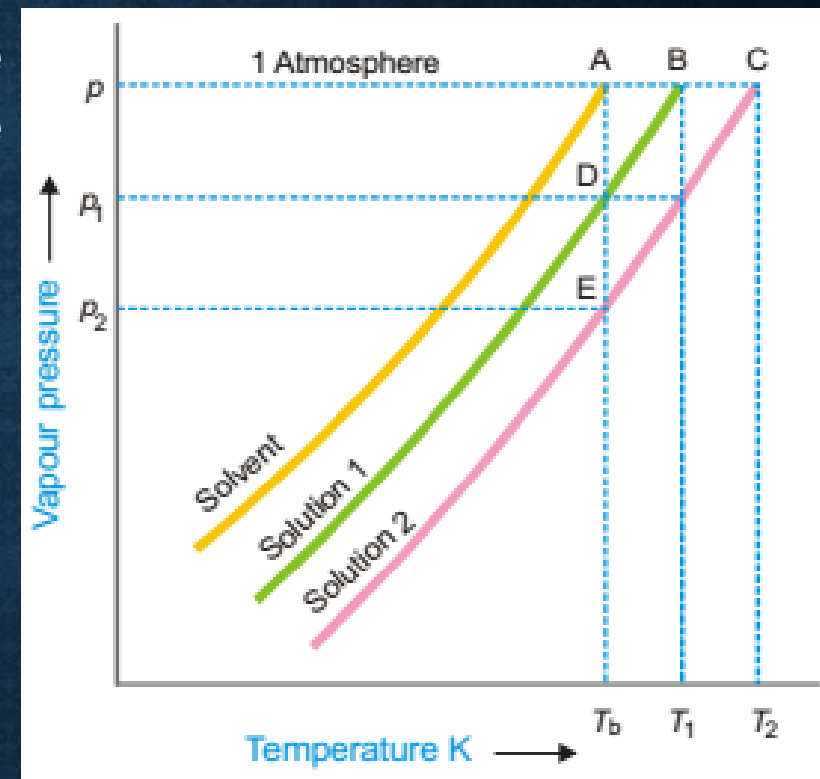
$$T - T_b = \Delta T$$

From triangles ABD and ACE,

$$\frac{AB}{AC} = \frac{AD}{AE}$$

$$\frac{T_1 - T_b}{T_2 - T_b} = \frac{p - p_1}{p - p_2}$$



where $p - p_1$ and $p - p_2$ are lowering of vapour pressure for solution 1 and solution 2 respectively. Hence the elevation of boiling point is directly proportional to the lowering of vapour pressure.
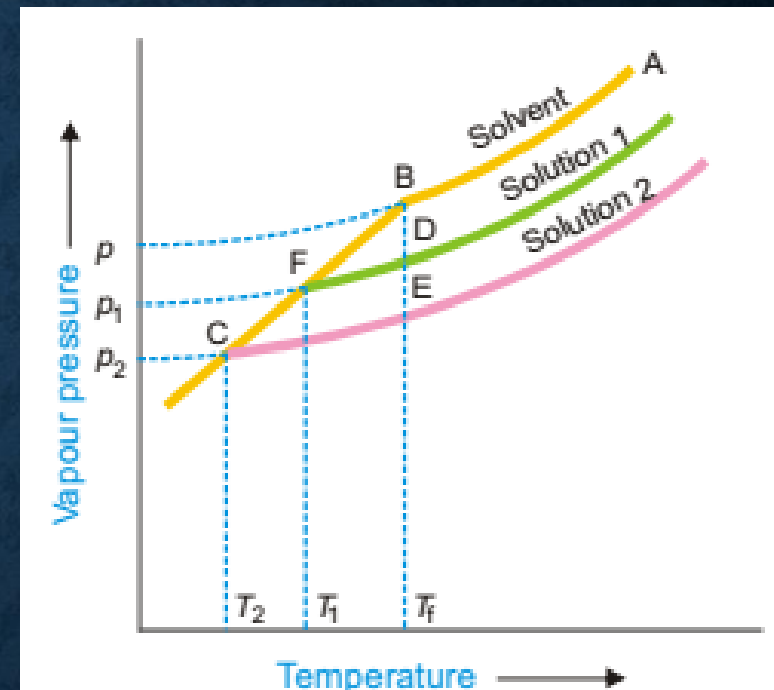
$$\Delta T \, \alpha \, p - p_s$$

# Depression of Freezing Point

- The difference of the freezing point of the pure solvent and the solution is referred to as the Depression of freezing point. It is represented by the symbol $\Delta T$ or $\Delta T_f$.
- From triangles BDF and BEC,

$$\frac{DF}{EC} = \frac{BD}{BE}$$

$$\frac{T_f - T_1}{T_f - T_2} = \frac{p - p_1}{p - p_2}$$



where $p_1$ and $p_2$ are vapour pressure of *solution* 1 and *solution* 2 respectively. Hence depression of freezing point is directly proportional to the lowering of vapour pressure.

$$\Delta T \, \alpha \, p - p_s$$

# Osmosis and Osmotic Pressure

## What is Osmosis?

- **The movement of solvent molecules through a semipermeable membrane from a region of low solute concentration to a region of high solute concentration.**
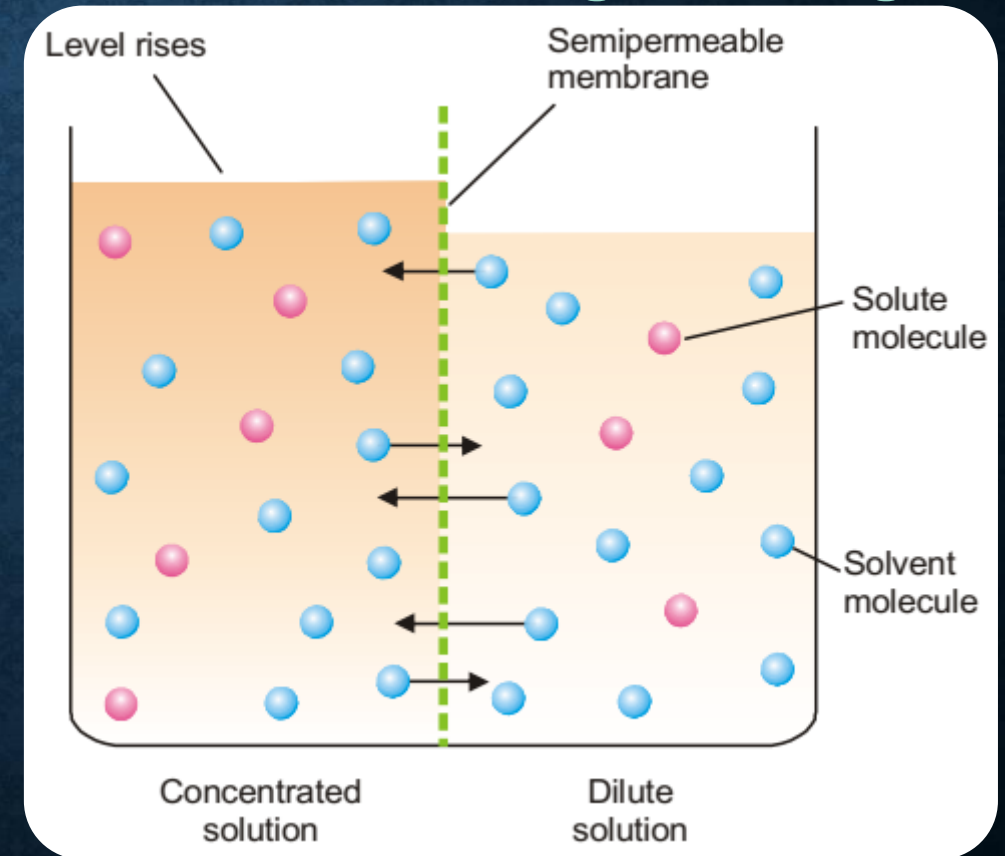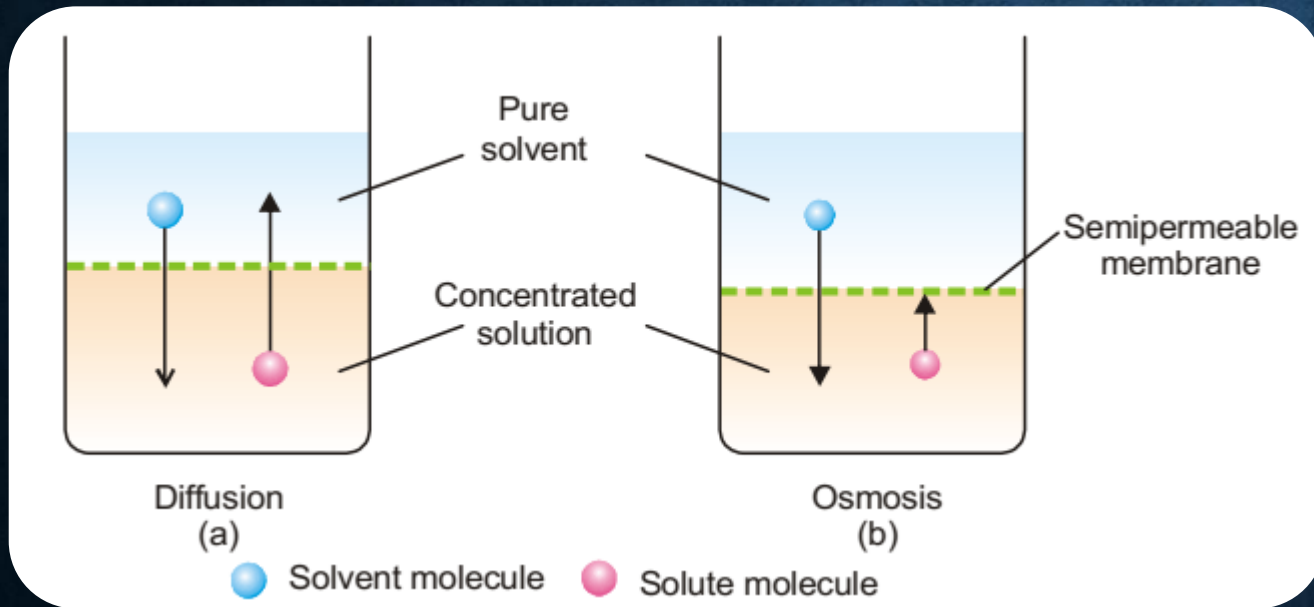
# Osmotic Pressure

Osmotic Pressure: The amount of pressure necessary to stop Osmosis.

## Laws of Osmotic Pressure

(a) The osmotic pressure of a solution at a given temperature is directly proportional to its concentration.

(b) The osmotic pressure of a solution of a given concentration is directly proportional to the absolute temperature.

*Boyle – van't Hoff Law*

If $\pi$ is the osmotic pressure and C its concentration,

then $\pi \propto C$, or $\pi \propto 1/V$ ---------- (1); at constant temperature

*Charles – van't Hoff Law*

If T is absolute temperature,

then $\pi \propto T$ ----------- (2) ; at constant concentration

Combining (1) and (2): $\pi \propto T/V$, or $\pi V = RT$; for 1 mole of solute

For n mole of solute, $\pi V = nRT$ --------- (3)

**SOLVED PROBLEM 1.** Calculate the osmotic pressure of a 5% solution of glucose (mol wt = 180) at 18°C.

**SOLUTION**

$$\pi V = nRT \qquad \text{...van't Hoff Equation}$$

where $\pi$ = osmotic pressure in atmospheres; $V$ = volume in litres; $n$ = number of moles of solute ($w/M$), $w$ being the weight in grams and $M$ its molecular weight; $R$ = gas constant.

In this case :

$$\pi = ?$$

$$V = 100\,ml = \frac{1}{10}\,litre$$

$$n = \frac{5}{M} = \frac{5}{180}$$

$$R = 0.0821 \text{ litre-atmosphere deg}^{-1}\text{ mole}^{-1}$$

$$T = 273 + 18 = 291\,K$$

Substituting the values in van't Hoff Equation

$$\pi \times \frac{1}{10} = \frac{5}{180} \times 0.0821 \times 291$$

$$\pi = 6.64 \text{ atm}$$

**SOLVED PROBLEM 2.** Find the osmotic pressure in millimetres of mercury at 15°C of a solution of naphthalene ($C_{10}H_8$) in benzene containing 14 g of naphthalene per litre of solution.

**SOLUTION**

$$\pi V = nRT \qquad \text{...vant Hoff equation}$$

Here,
$$\pi = ? \text{ atmosphere}$$
$$V = 1 \text{ litre}$$
$$n = \frac{14}{128} \text{ (mol mass of naphthalene} = 128)$$
$$R = 0.0821 \text{ litre-atmosphere } K^{-1} \text{ mol}^{-1}$$
$$T = 15 + 273 = 288 \text{ K}$$

Substituting values in van't Hoff equation,

$$\pi \times 1 = \frac{14}{128} \times 0.0821 \times 288$$
$$\pi = 2.586 \text{ atm}$$
$$= 2.586 \times 760 = \mathbf{1965 \text{ mm}}$$

**SOLVED PROBLEM 1.** Morse and Frazer observed that a solution of glucose containing 18 grams per litre had an osmotic pressure of 2.39 atmospheres at 23°C. Find the molecular weight of glucose.

### SOLUTION

We know that:

$$M = \frac{wRT}{\pi V} \quad \quad \dots(1)$$

Here,

$$w = 18 \text{ g}$$

$$R = 0.0821 \text{ litre-atmosphere}$$

$$T = 23 + 273 = 296 \text{ K}$$

$$\pi = 2.39 \text{ atmospheres}$$

$$V = 1 \text{ litre}$$

Substituting these values in relation (1)

$$M = \frac{18 \times 0.0821 \times 296}{2.39 \times 1}$$

$$= \textbf{183.0}$$

**SOLVED PROBLEM 2.** A solution of glycol containing 1.821 g per litre has an osmotic pressure of 51.8 cm of mercury at 10°C. What is the molecular mass of glycol?

**SOLUTION**

We know that from van't Hoff equation

$$M = \frac{wRT}{\pi V} \qquad \qquad ...(1)$$

In this case,

$$w = 1.821g$$

$$R = 0.0821 \text{ litre-atmosphere}$$

$$T = 10 + 273 = 283 \text{ K}$$

$$\pi = \frac{51.8}{76} \text{ atmosphere}$$

$$V = 1 \text{ litre}$$

Substituting these values in expression (1),

$$M = \frac{1.821 \times 0.0821 \times 283 \times 76}{51.8 \times 1}$$

$$= \mathbf{62.07}$$

# Reverse Osmosis

- If the external pressure to the solution is greater than the osmotic pressure, solvent flows from the more concentrated side to the other one. This is known as reverse osmosis.

- This process is used to obtain pure water from salt water.



© 2003 Thomson - Brooks/Cole
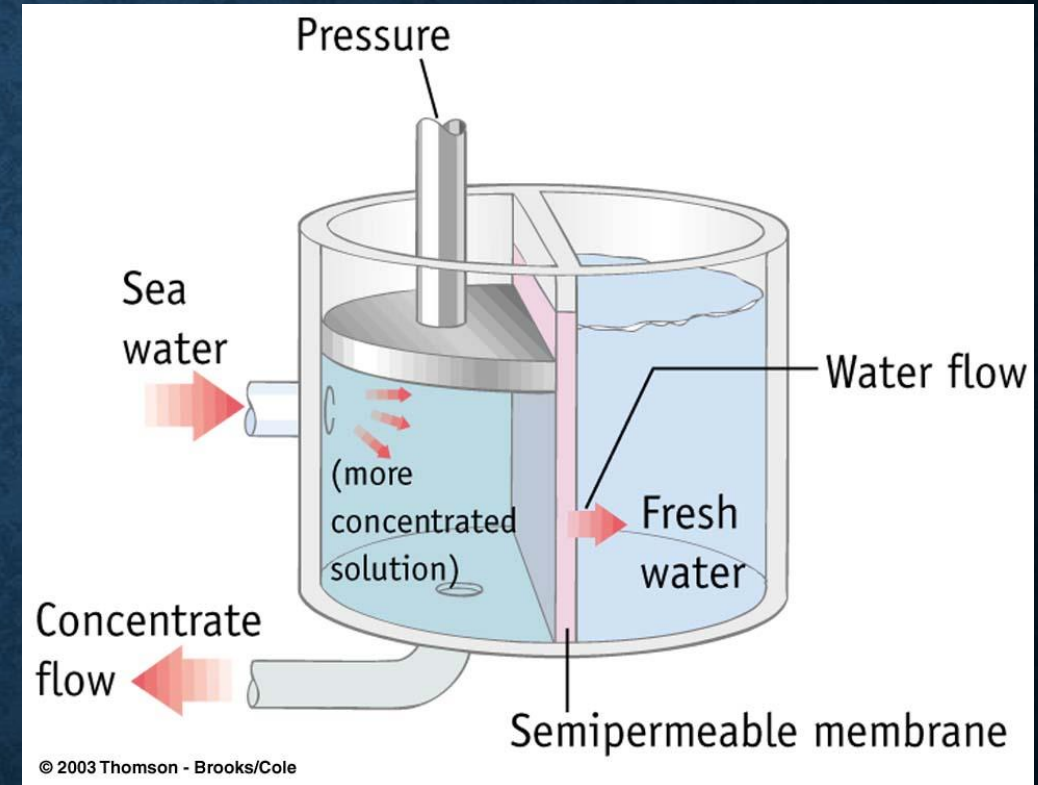
# Hypotonic, Isotonic and Hypertonic Medium
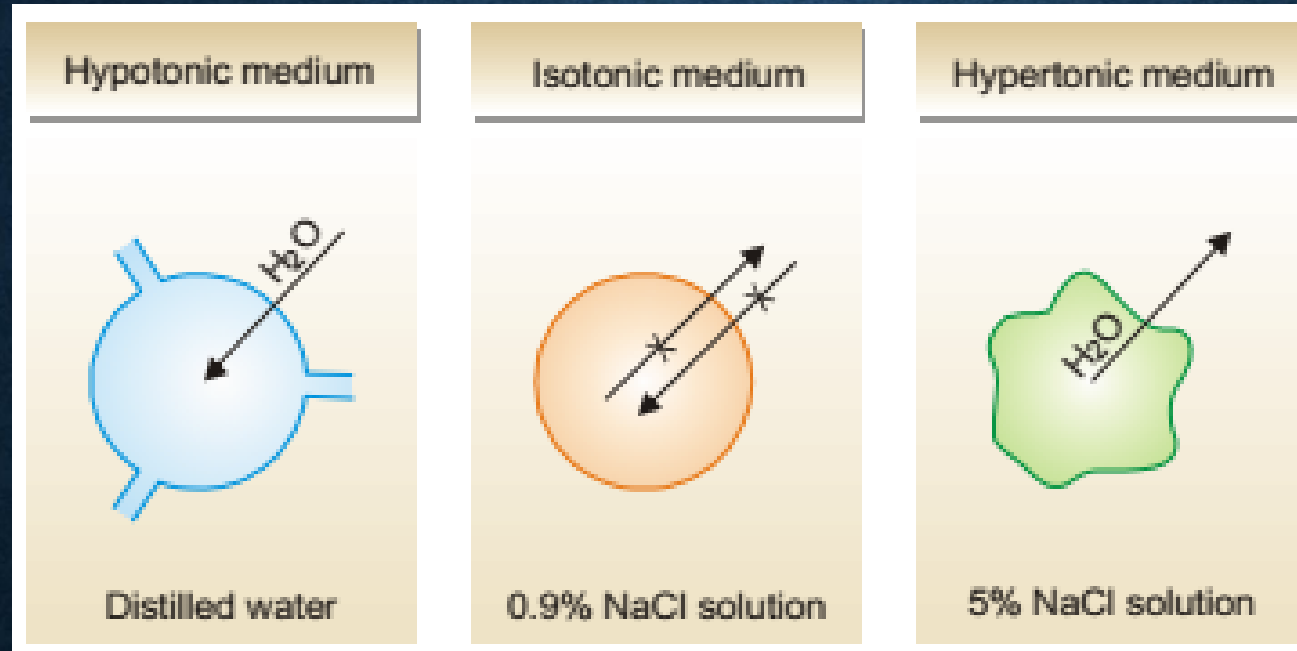
# Dialysis

- In a dialysis machine, blood from the patient runs through tubes made of a semi-porous membrane. Outside the tubes is a sterile solution made up of water, sugars and other components.

- Red and white blood cells and other important blood components are too large to fit through the pores in the membranes, but urea and salt flow through membranes into the sterile solution and are removed.
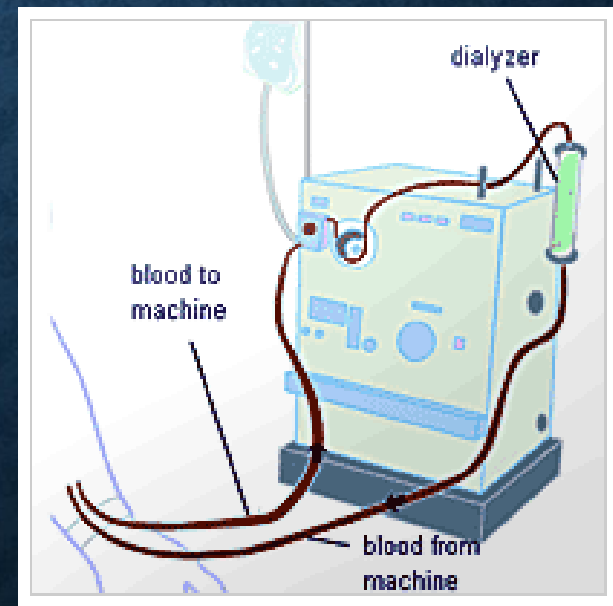
# How Does Dialysis Work?



*Blood from body*

→
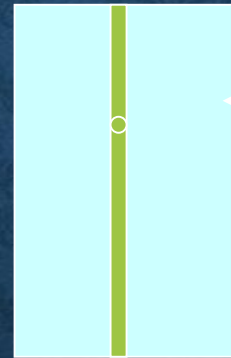
*Solution is isotonic in Ions that the blood needs But lacks waste*

*Therefore, waste dialyzes out!*

←

*Blood returned To body*

- *Dialysis acts as a kidney*
- *Bloods is "purified" of waste by this process*

Thank you