Lecture 8

Spring 2022

General Chemistry II

Chem 102

Colligative Properties

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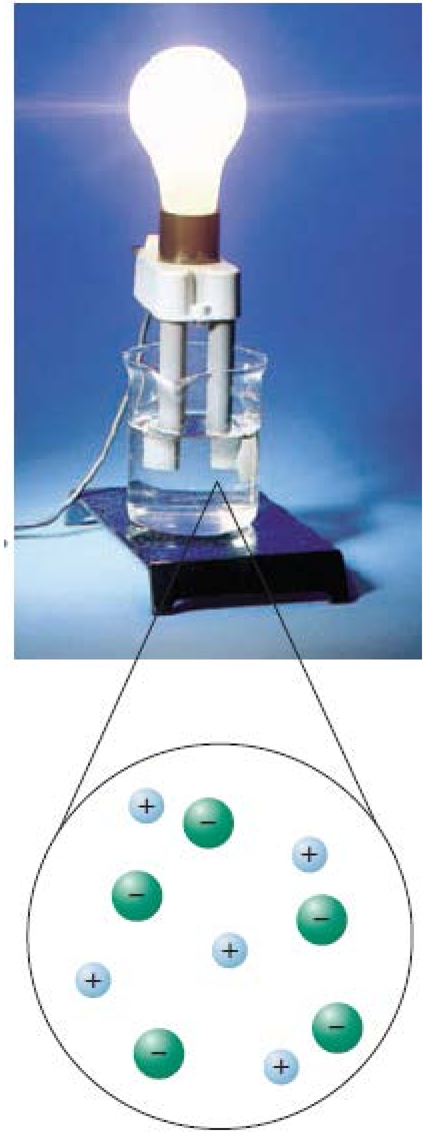
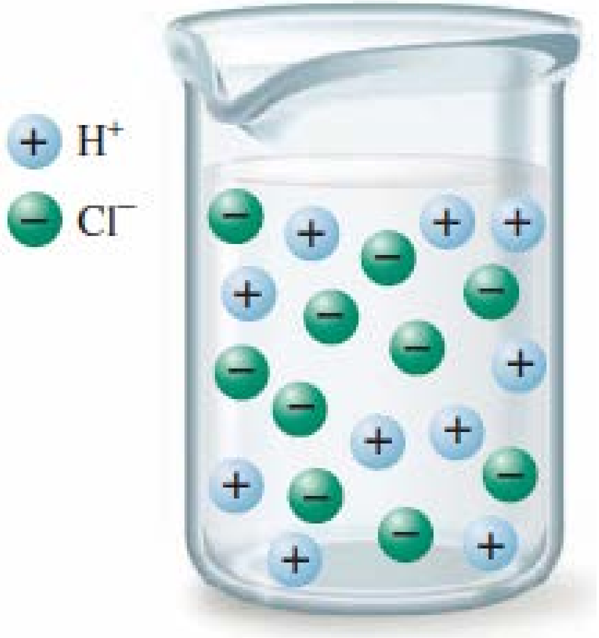
Types of Solutions

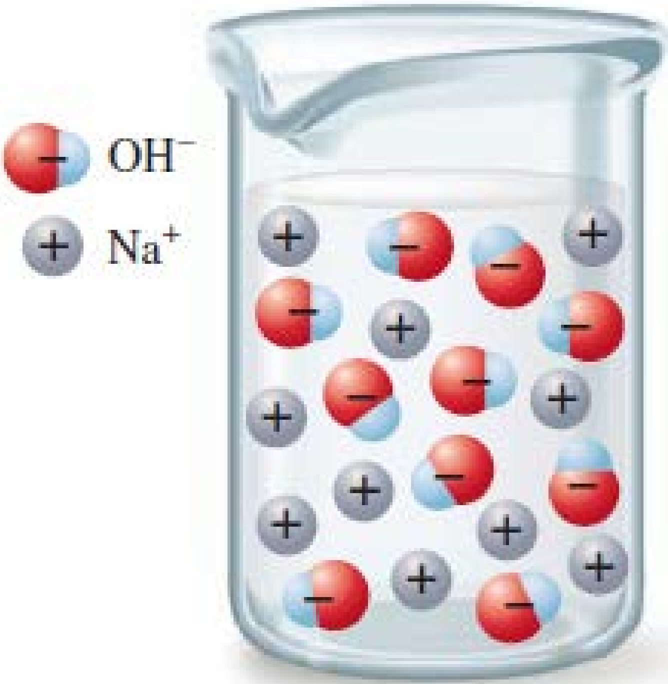
Solute	Solvent	Solution	Example
Gas	Gas	Gas	Air , natural gas
Gas	Liquid	Liquid	O_2 in H_2O, Soda
Gas	Solid	Solid	H_2 in Pt
Liquid	Gas	Gas	Moisture in air
Liquid	Liquid	Liquid	Alcohol in H_2O
Liquid	Solid	Solid	Hg in Ag, Drops f H_2O in sugar
Solid	Gas	Gas	Dust in air
Solid	Liquid	Liquid	NaCl in H_2O, sea water
Solid	Solid	Solid	Alloys (Brass, steel)

Strong Electrolyte

Substances that are completely ionized (i.e., conduct electricity efficiently) when they are dissolved in water. Examples include soluble salts, strong acids, and strong bases.

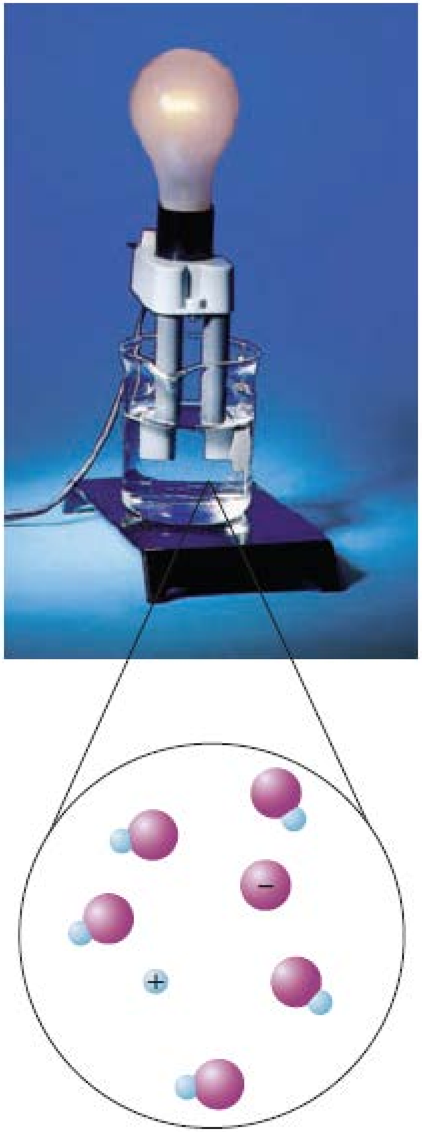






Weak Electrolyte

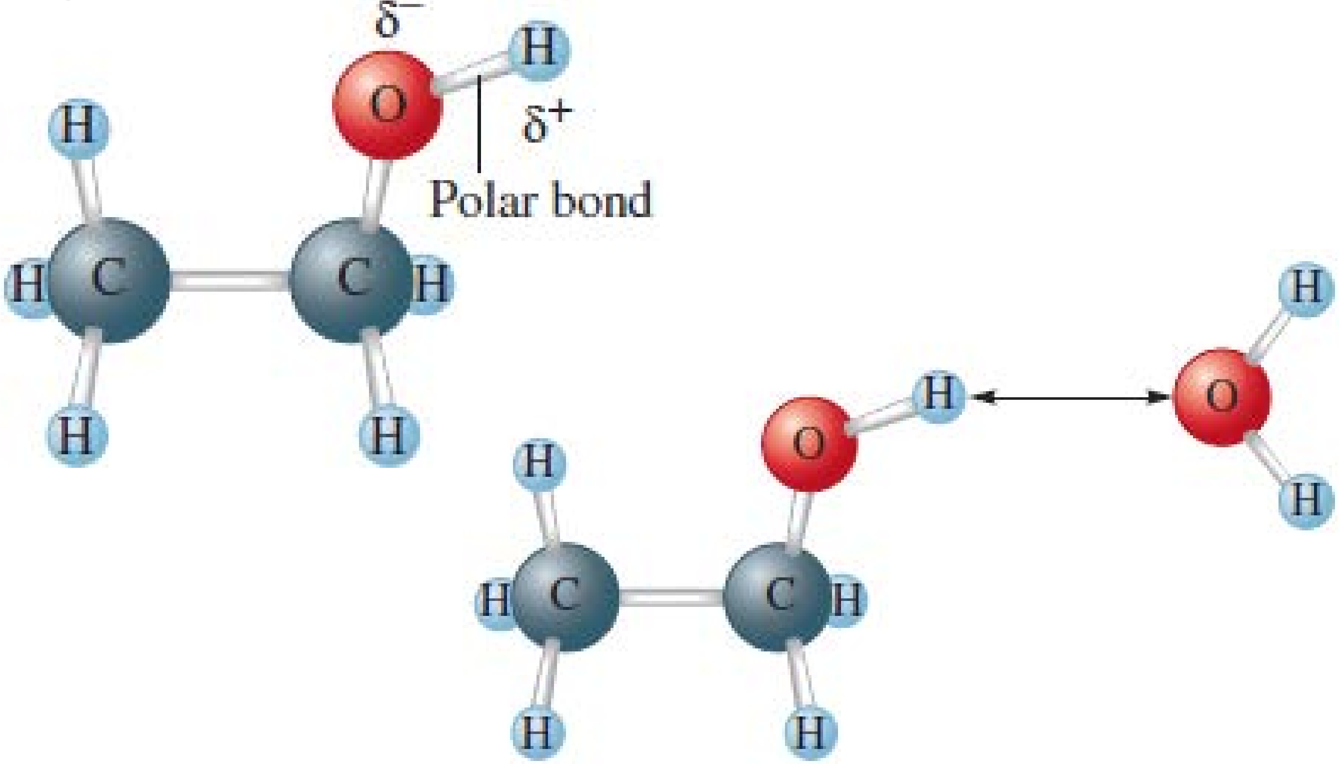
- Substances that exhibit a small degree of ionization in water (i.e., conduct only a small current).
- They produce relatively few ions when dissolved in water.
- Examples include weak acids (acetic acid) and weak bases (ammonia).

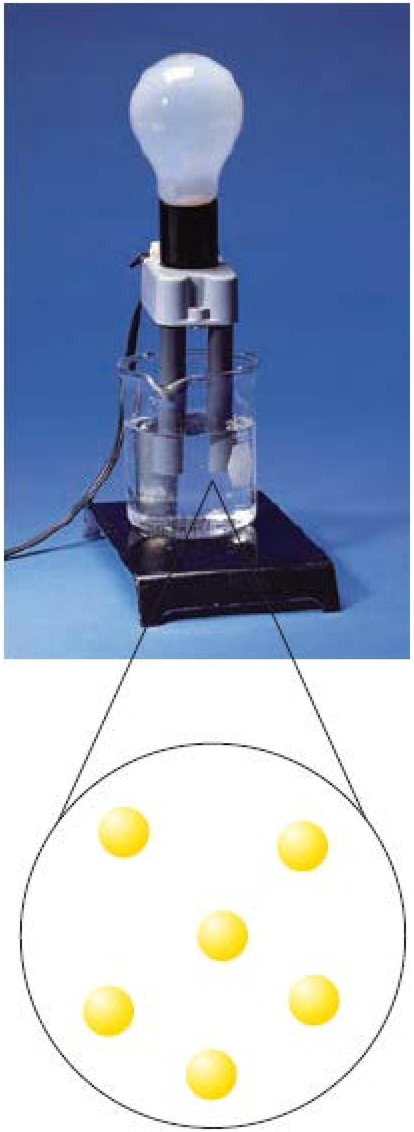


$$HC_2H_3O_2(aq.) + H_2O(l) \leftrightarrow H_3O^+(aq) + C_2H_3O_2^-(aq)$$

Nonelectrolyte

- Substances that dissolve in water but do not produce any ions (i.e., non conductors for electricity).
- Examples include ethanol and glucose





Solutions' VP

Think Why ?

- We add antifreeze to water in a car's cooling system to prevent freezing in winter and boiling in summer.
- We also melt ice on sidewalks and streets by spreading salt.

Think: Solute's **effect** on the solvent's properties

Colligative Properties

- Properties that depend only on the **number** (**concentration**) of solute particles in a solution and **do not** depend on the **identity** of the solute.

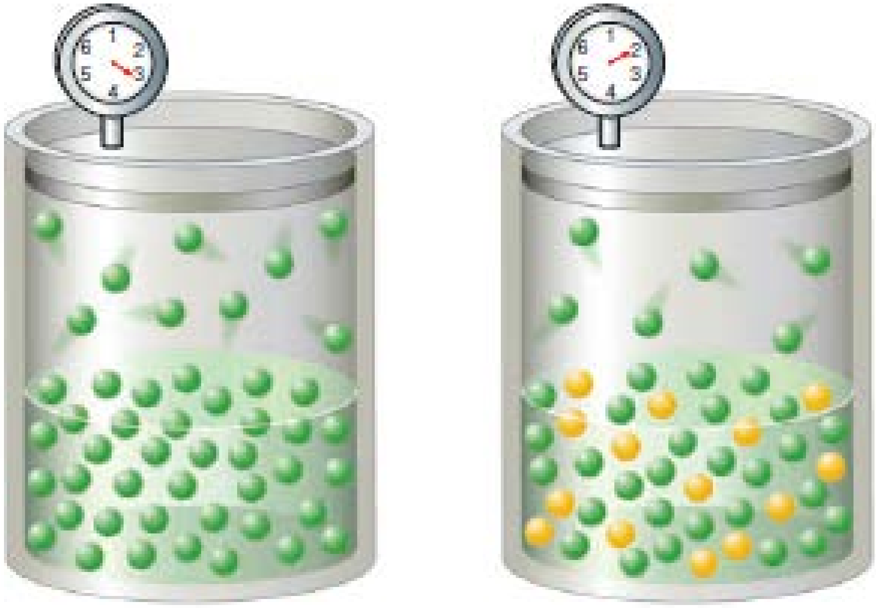
- Consider two aqueous solutions of the same concentration; one containing glucose and the other containing urea.
  - The impact of solute on the solvent's properties is the same for both solutions.

Colligative Properties

- Vapor-pressure **lowering**
- Boiling-point **elevation**
- Freezing-point **depression**
- Osmotic pressure **generation**

VP Lowering

- The dissolution of a nonvolatile solute in a solvent decreases the number of solvent molecules per unit volume.
- It should lower the escaping tendency of the solvent molecules.



Raoult's Law

- The change in vapor pressure is proportional to the **quantity** of the dissolved solute.

$$P_{solution} = X_{solvent} \times P^{o}_{solvent}$$

$P_{solution}$: the vapor pressure of the solution

$X_{solvent}$: the mole fraction of the solvent

$P^{o}_{solvent}$: is the vapor pressure of pure solvent.

Exercise

Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g common table sugar (sucrose, molar mass 342.3 g/mol) in 643.5 cm^3 of water. At 25°C, the density of water is 0.9971 g/cm^3 and its vapor pressure is 23.76 torr.

Solution

$$\text{Number of moles of sucrose} = \frac{158.0\ \text{g}}{342.3\ \text{g / mol}}$$

$$= 0.4616\ \text{mol}$$

Number of moles of H_2O

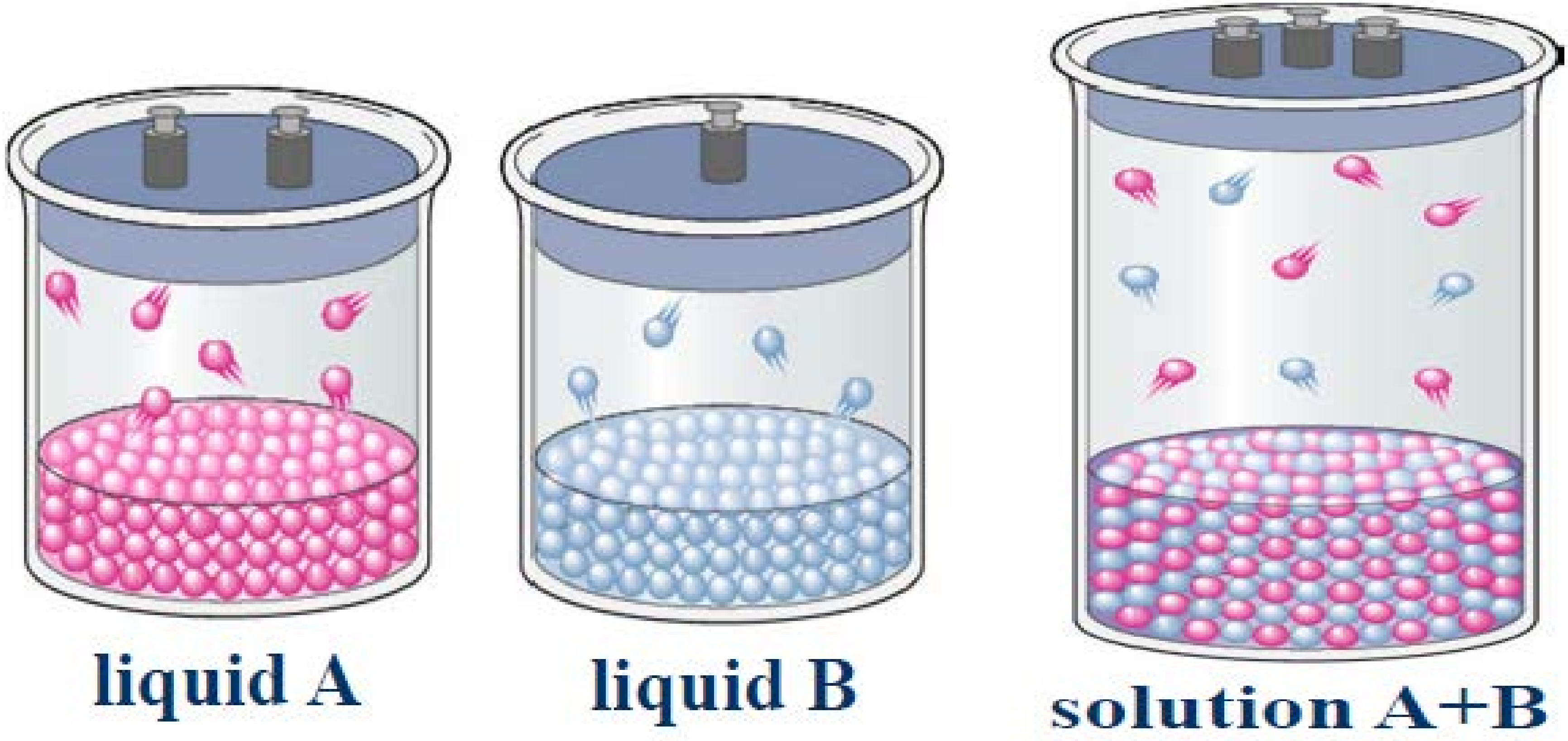
$$= \frac{(643.5\ \text{cm}^3)\ (0.9971\ \text{g/cm}^3)}{18\ \text{g / mol}} = 35.60\ \text{mol}$$

$$\mathbf{P_{solution} = X_{solvent} \times P^{o}_{solvent} =}$$

$$\frac{35.60}{36.06} \times 23.76\ \text{torr} = 23.46\ \text{torr}$$

Ideal (liquid-liquid) solutions

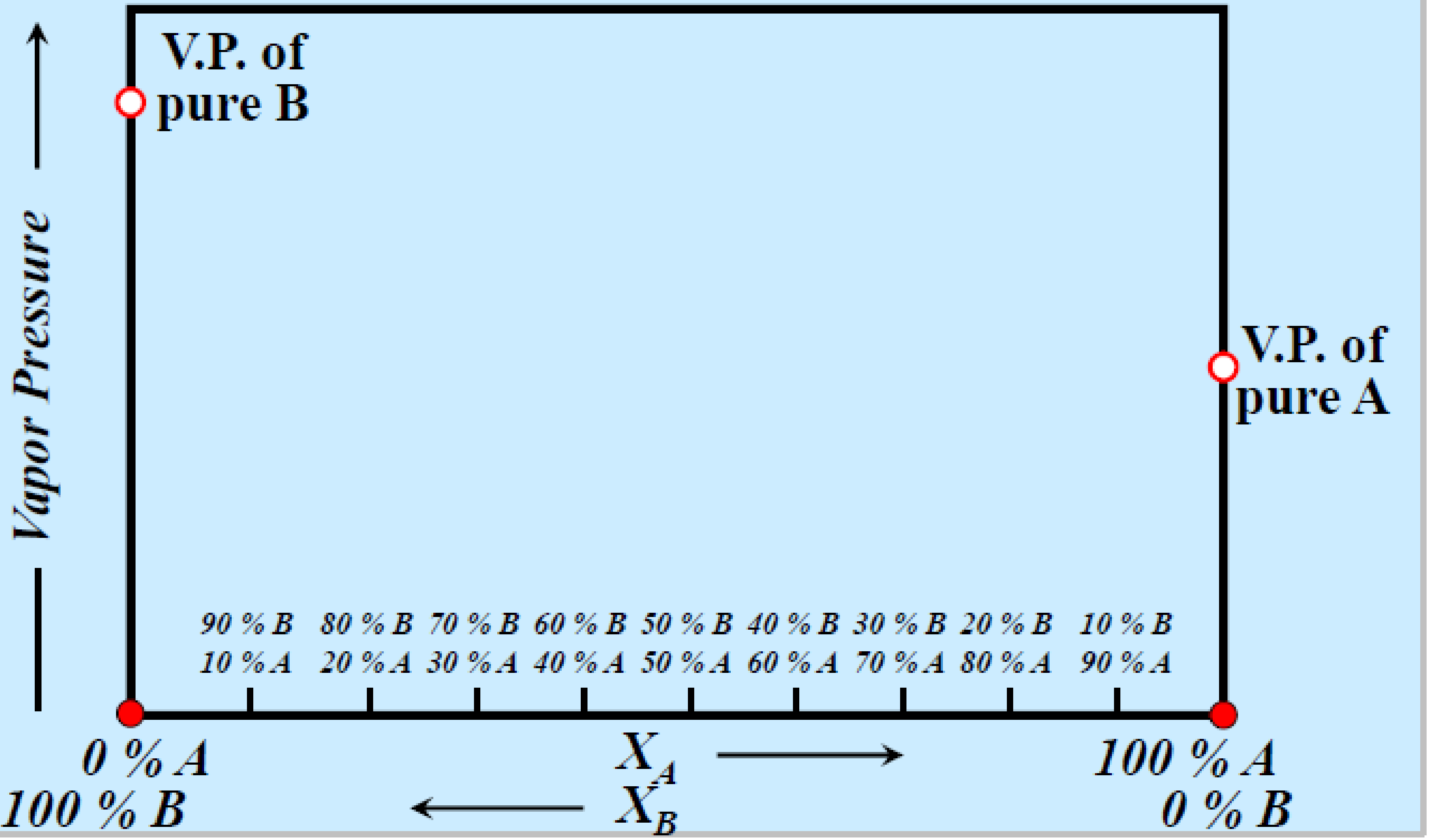
- Both liquids are volatile- Obey **Raoult's Law**



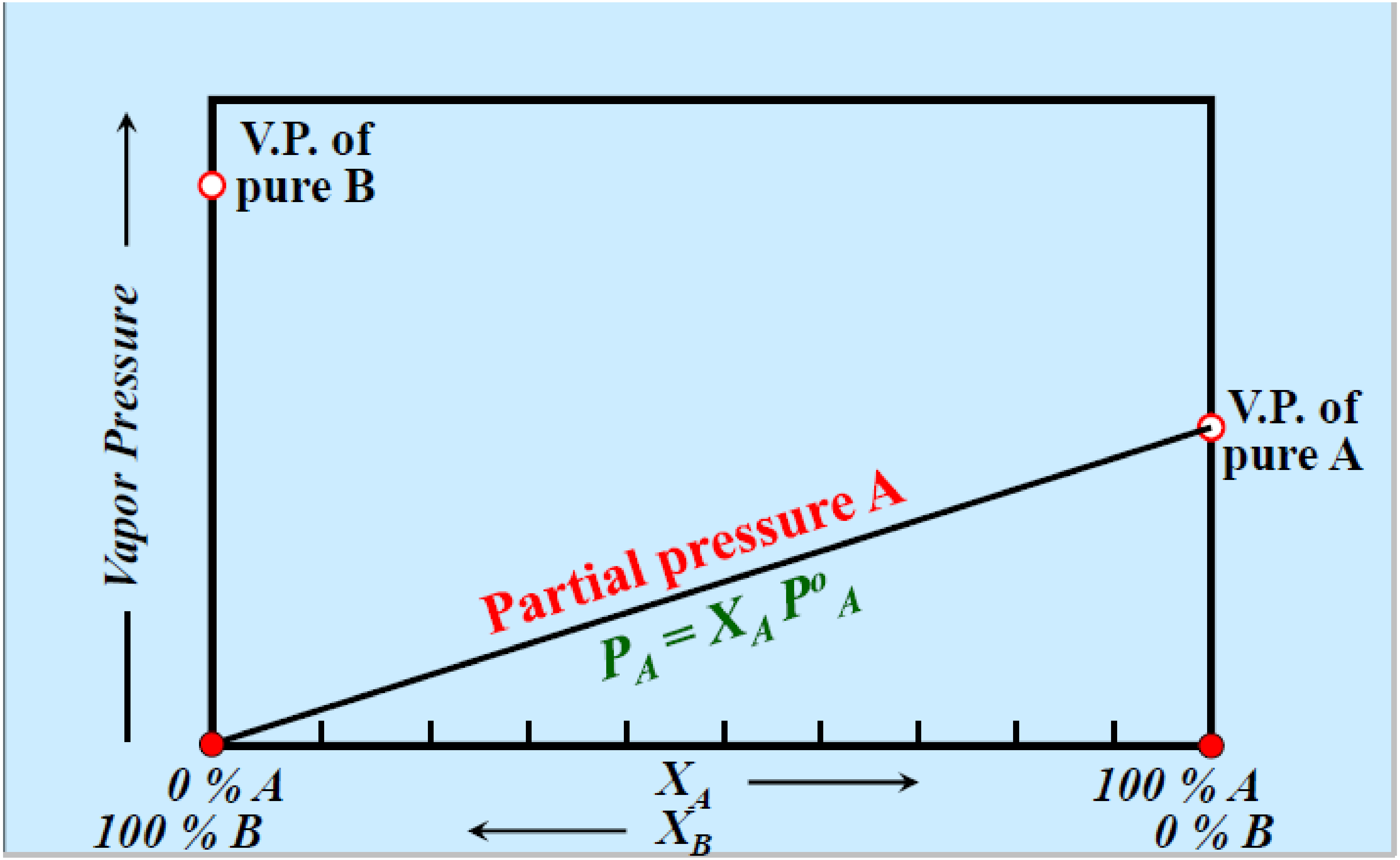
$$P_T = P_A + P_B = X_A\, P_A^o + X_B\, P_B^o$$

Ideal (liquid-liquid) solutions

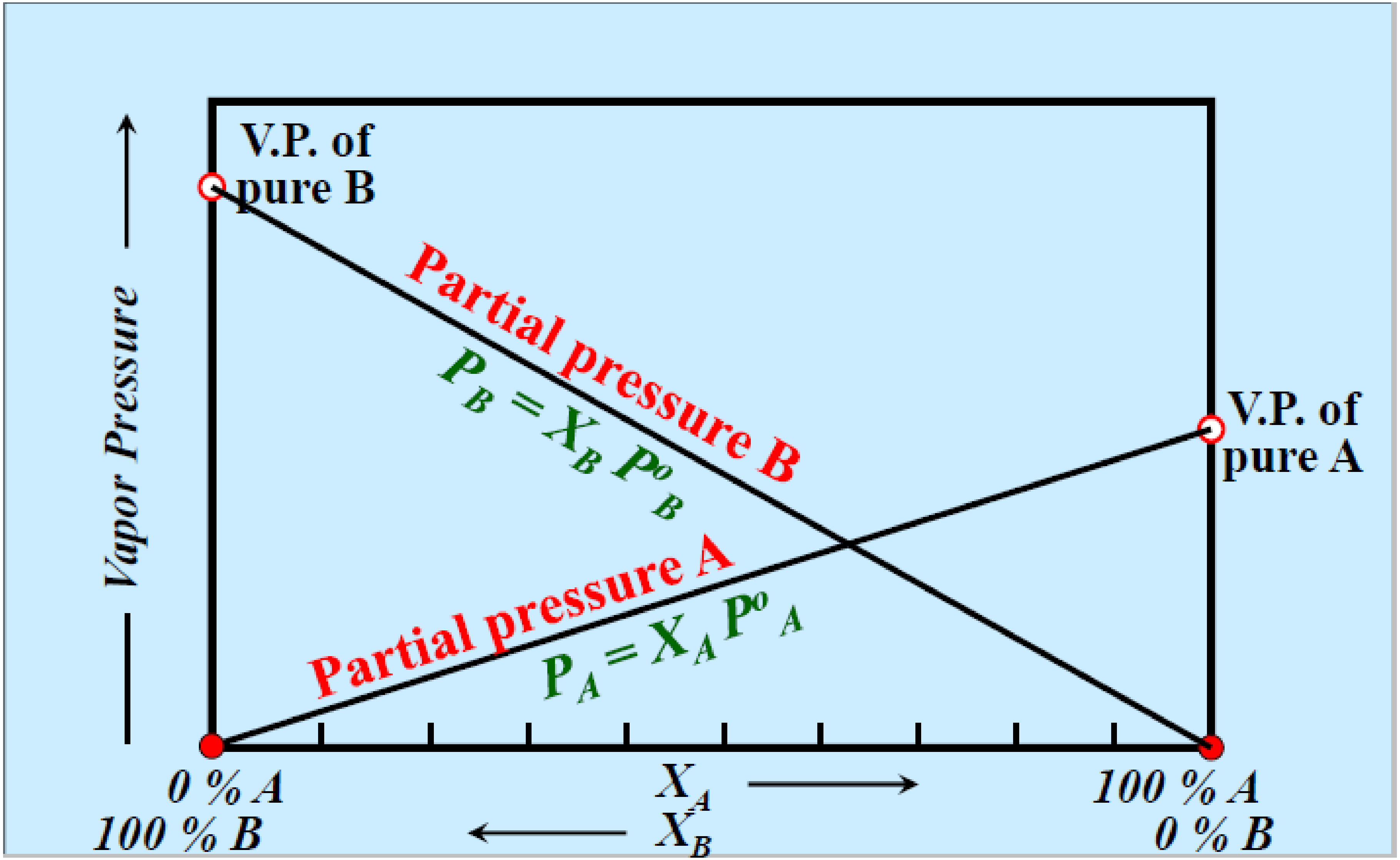
$$P_{soln} = P_A + P_B = X_A P^o_A + X_B P^o_B$$



Ideal (liquid-liquid) solutions

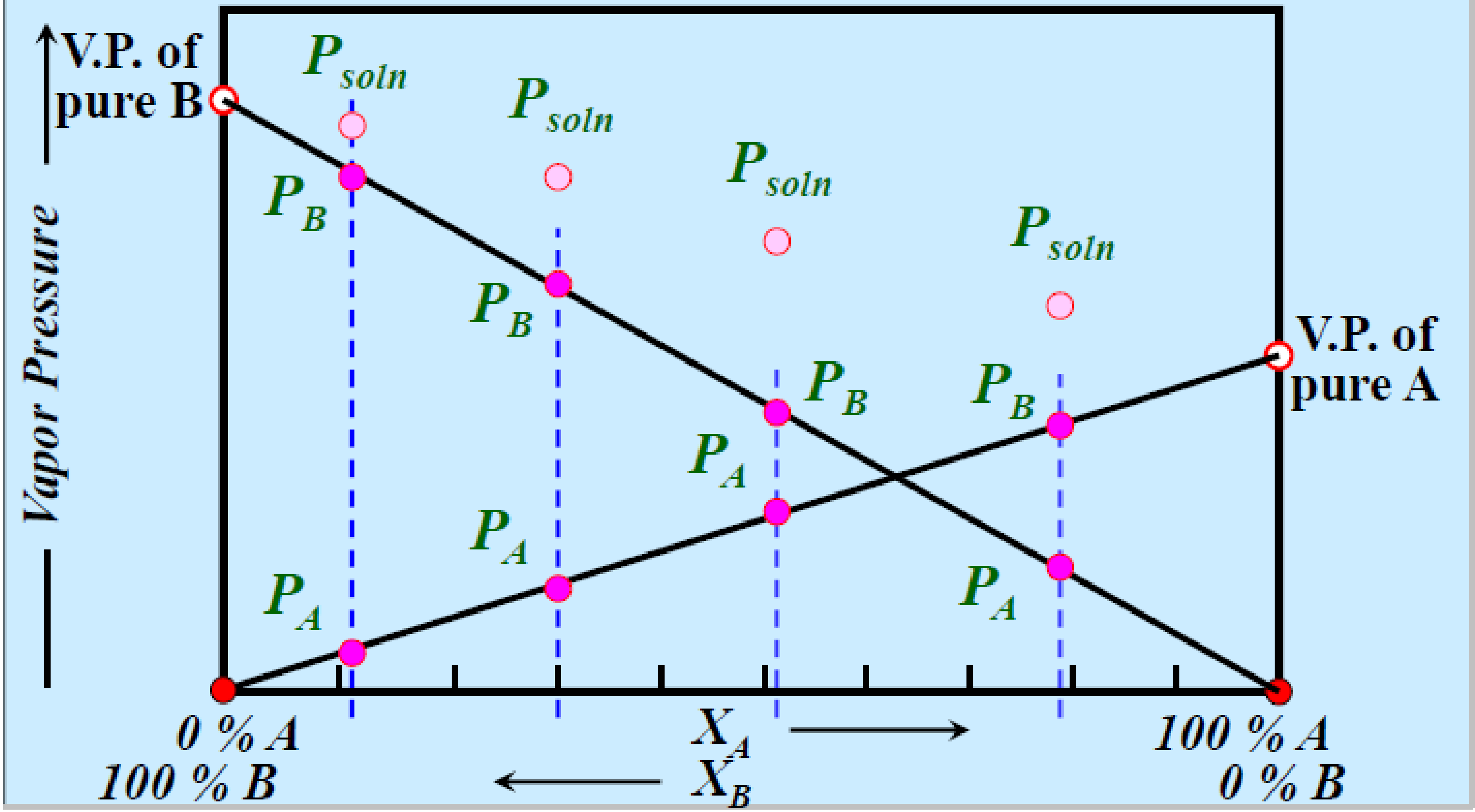


Ideal (liquid-liquid) solutions



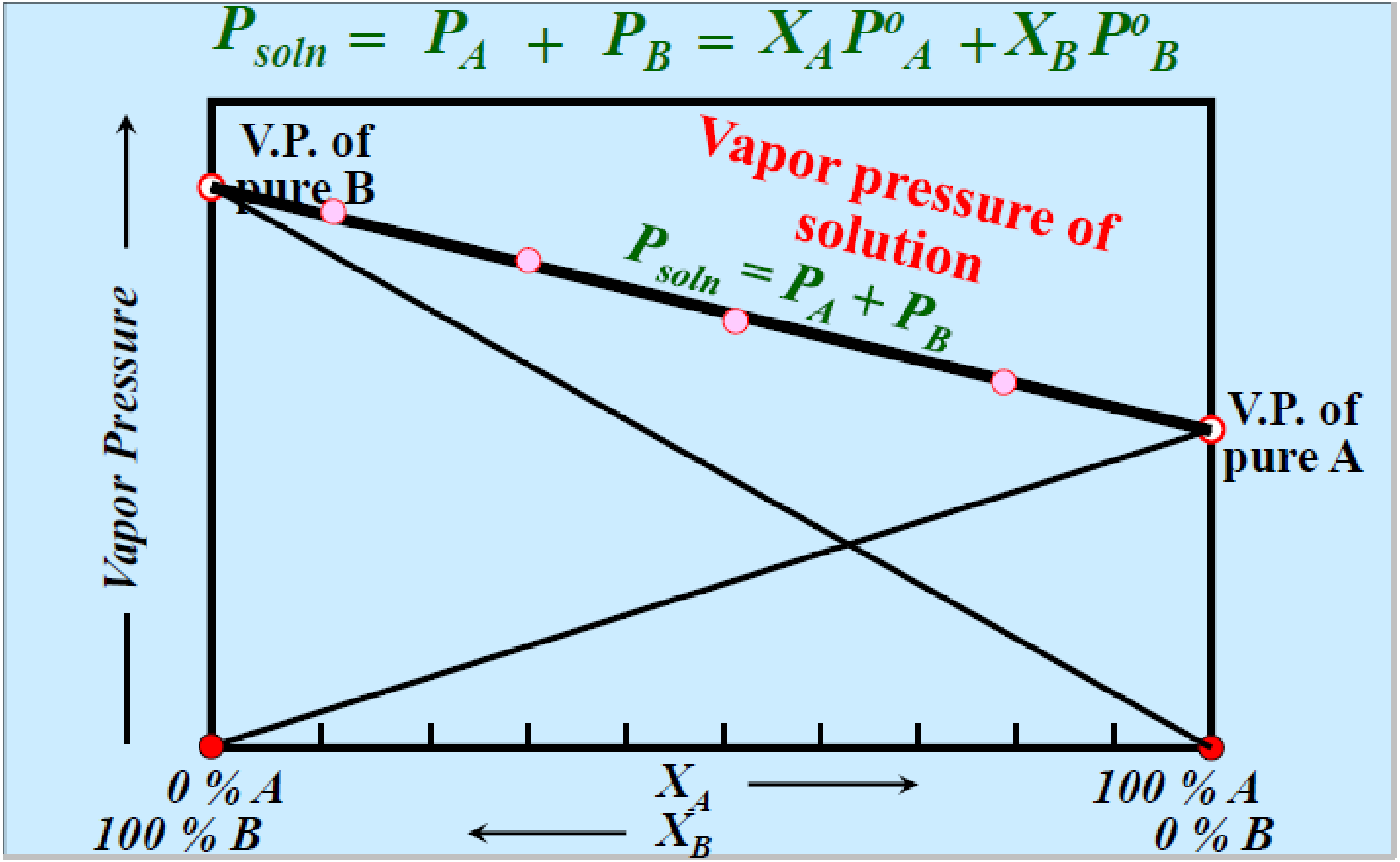
Ideal (liquid-liquid) solutions

$$P_{soln} = P_A + P_B$$



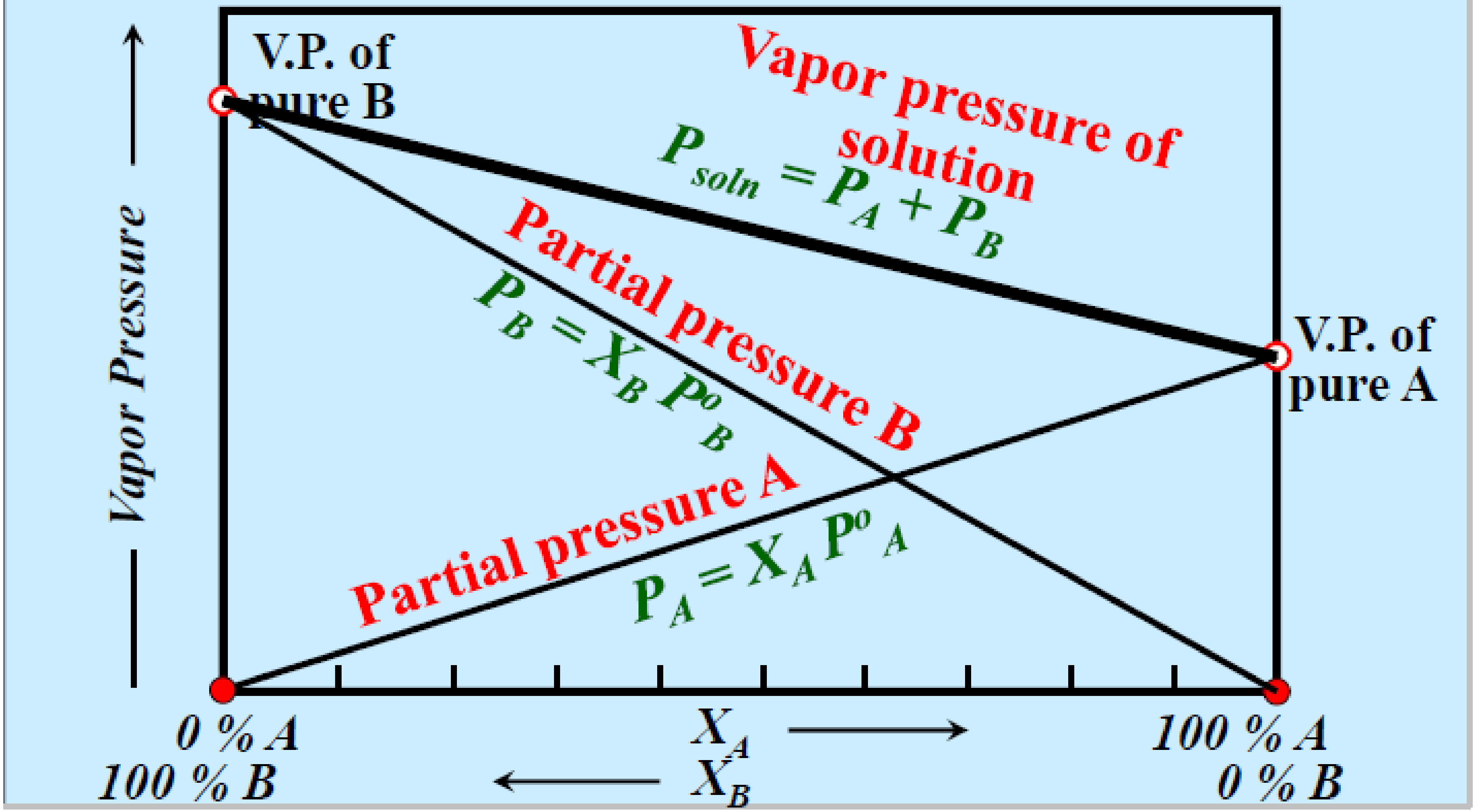
Ideal (liquid-liquid) solutions

$$P_{soln} = P_A + P_B = X_A P^o_A + X_B P^o_B$$



Ideal (liquid-liquid) solutions

$$P_{soln} = P_A + P_B = X_A P^o{}_A + X_B P^o{}_B$$



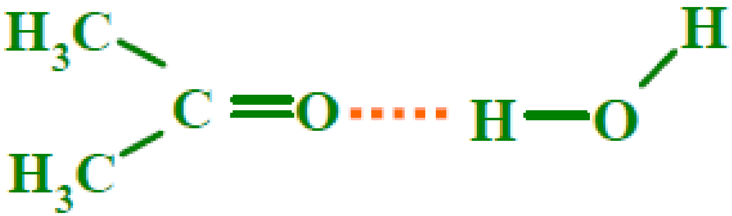
Non-ideal solutions

- Both liquids are volatile but disobey (deviate from) Raoult's Law

Deviation

–Ve

- Solvent has a special affinity to solute e.g., H-bonding



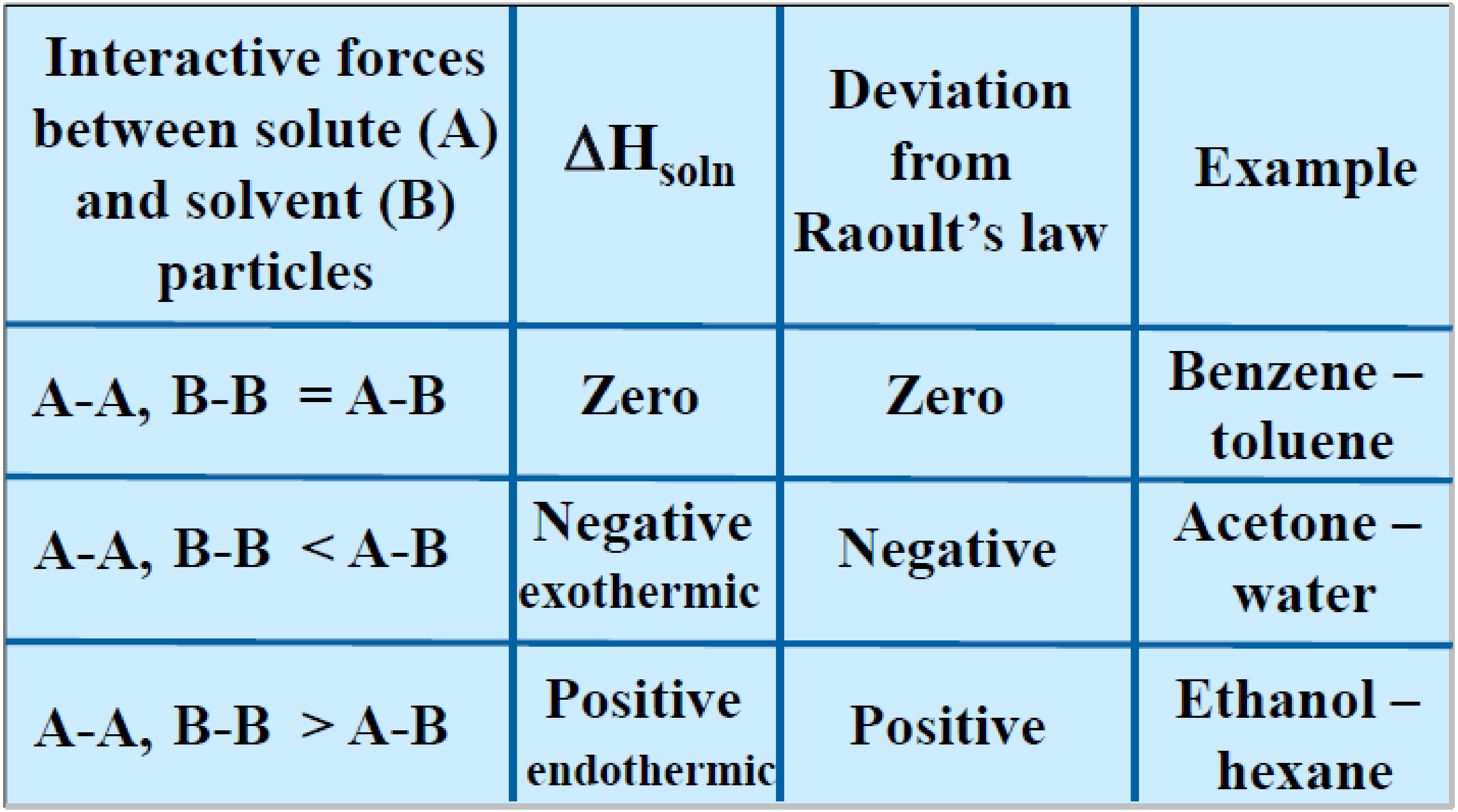
+Ve

- Solvent has no affinity to solute
- Solute-solvent interaction is weaker than in pure liquids

Deviation

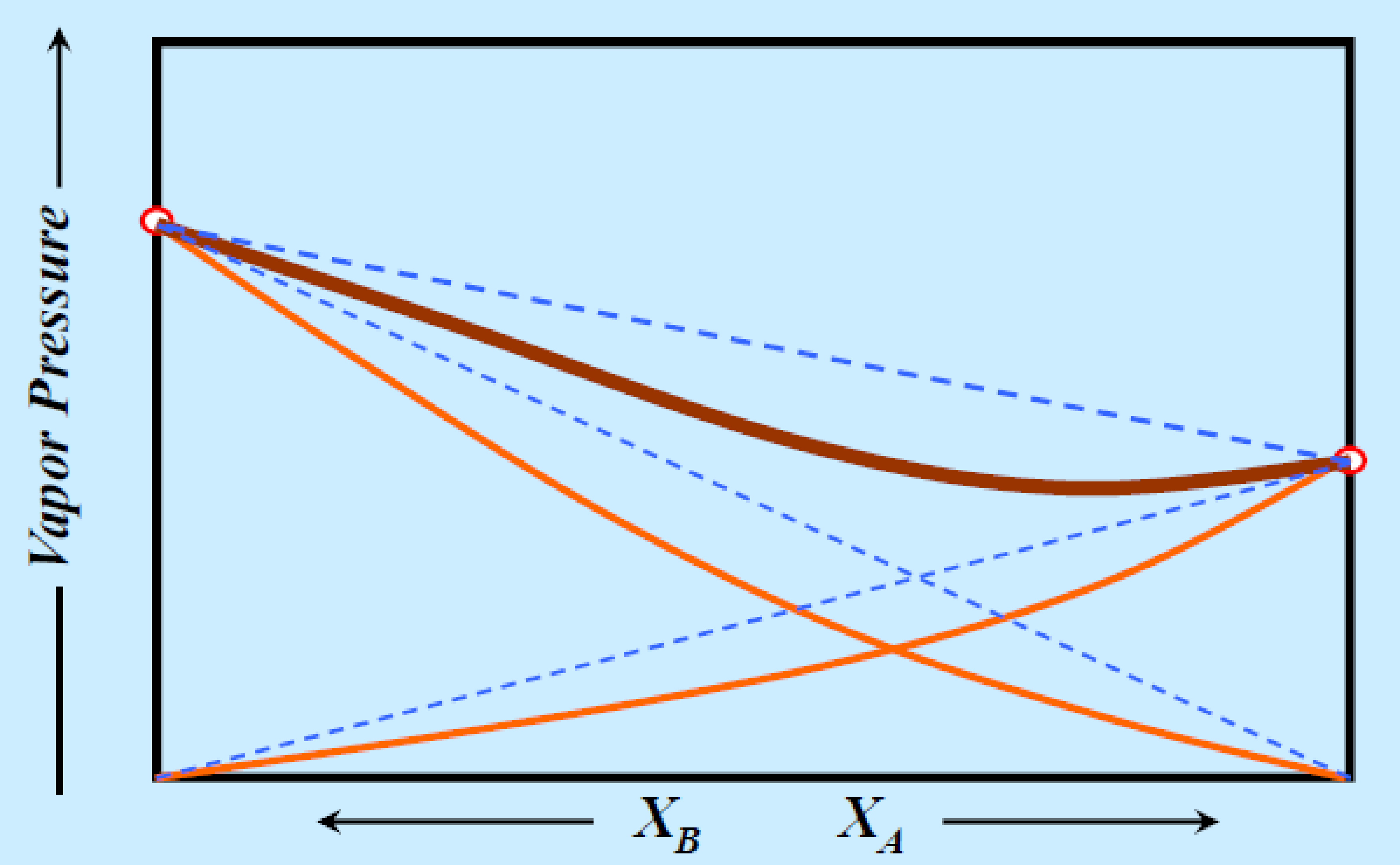
−Ve	+Ve
Observed VP < Predicted VP by Raoult's Law	Observed VP > Predicted VP by Raoult's Law
ΔH_{sol} is −Ve	ΔH_{sol} is +Ve
Exothermic	**Endothermic**

Non-ideal solutions

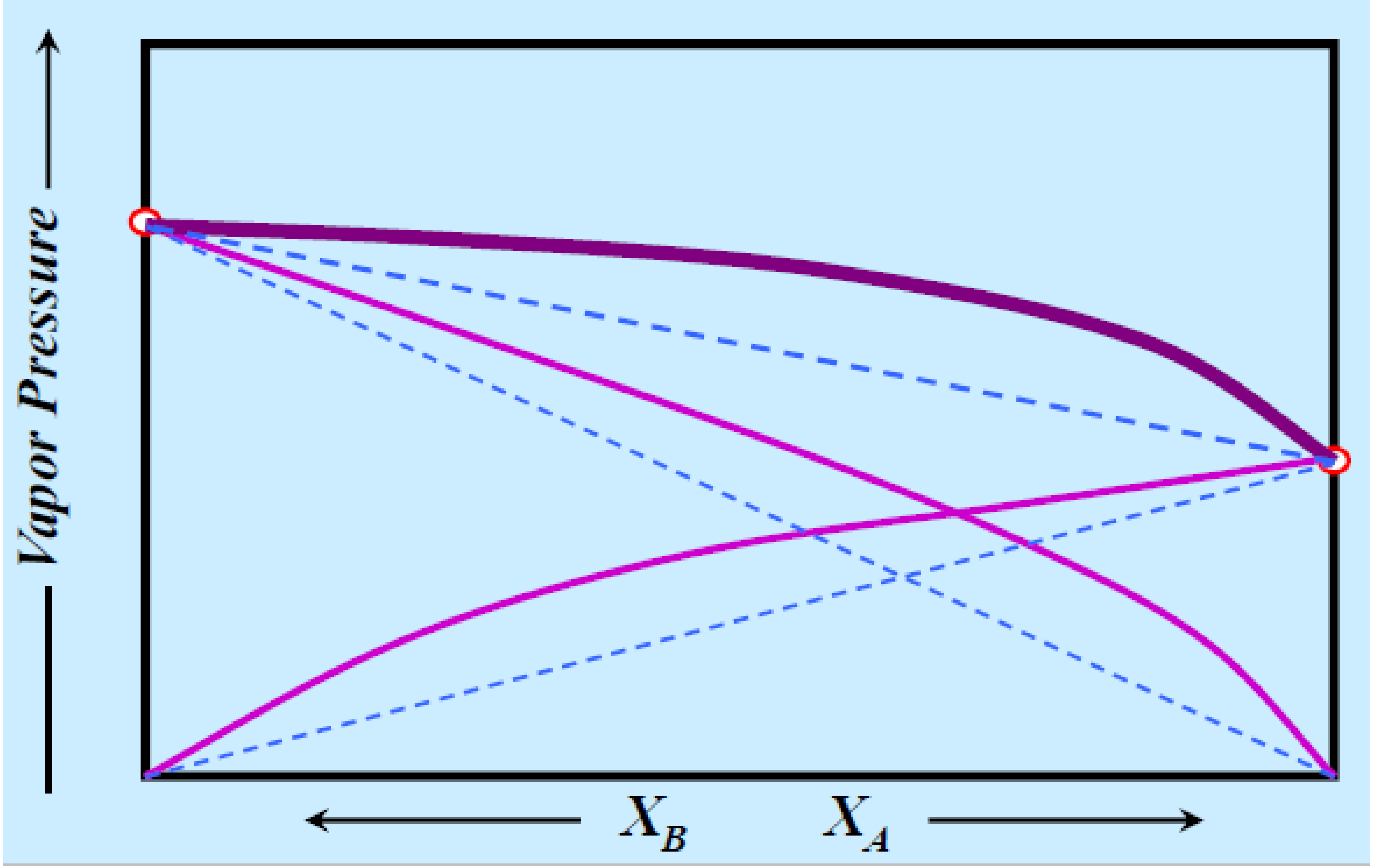


Interactive forces between solute (A) and solvent (B) particles	ΔH_{soln}	Deviation from Raoult's law	Example
A-A, B-B = A-B	Zero	Zero	Benzene – toluene
A-A, B-B < A-B	Negative exothermic	Negative	Acetone – water
A-A, B-B > A-B	Positive endothermic	Positive	Ethanol – hexane

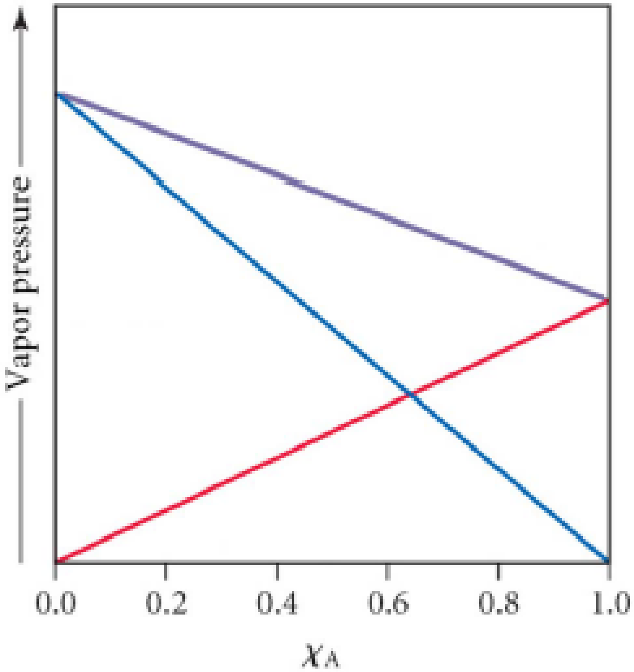
–Ve Deviation



+Ve Deviation

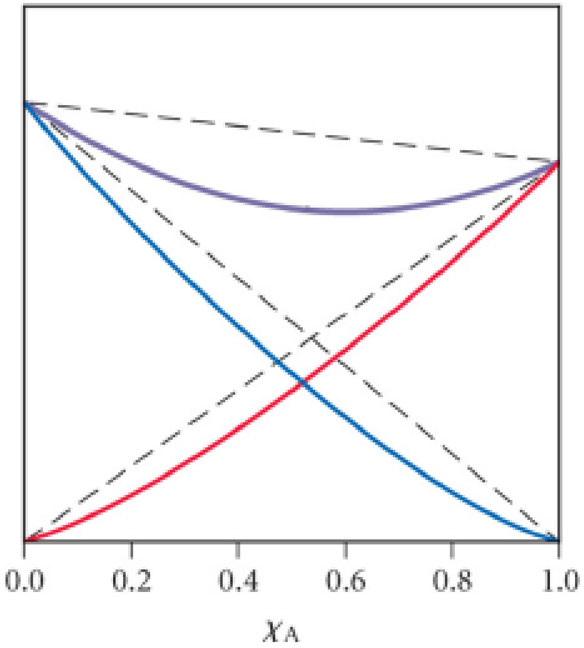


Ideal/Non-ideal



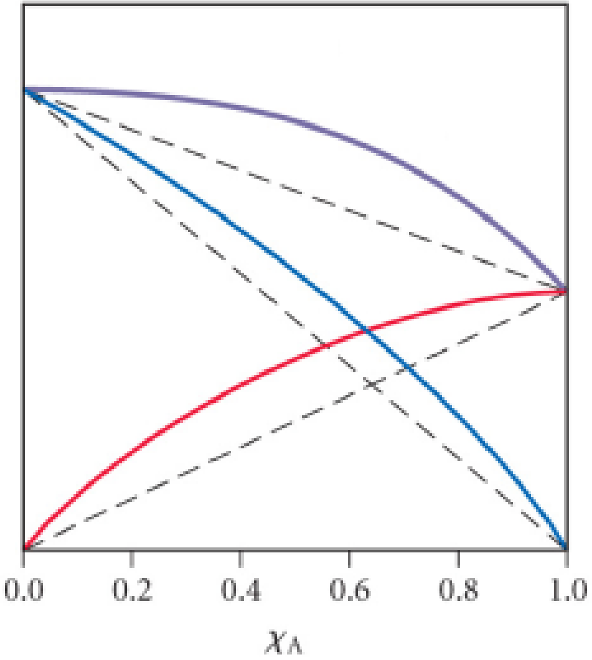
no deviation

Ideal solution



–ve deviation

Strong solute-solvent Interactions



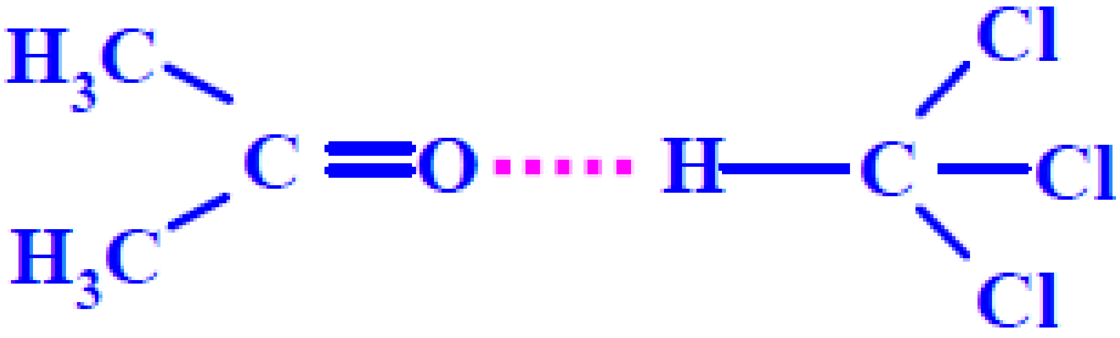
+ve deviation

Weak solute-solvent Interactions

Exercise

- A solution is prepared by mixing 5.81 g acetone (M.wt. = 58.1 g/mol) and 11.9 g chloroform (M.wt. = 119.4 g/mol). At 35°C this solution has a total v.p. of 260 torr. Is this an ideal solution? The v.p. of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.

Solution



- Note H-bonding expect → –Ve Deviation

$$\mathbf{n}_{\mathbf{acetone}} = \frac{5.81\ \text{g}}{58.1\ \text{g/mol}} = 0.1\ \text{mol}$$

$$\mathbf{n}_{\mathbf{chloroform}} = \frac{11.9\ \text{g}}{111.9\ \text{g/mol}} = 0.1\ \text{mol}$$

$$\boxed{\mathbf{X}_{\mathbf{acetone}} = \frac{n_{\text{acetone}}}{n_{\text{acetone}} + n_{\text{chloroform}}} = \frac{0.1}{0.1 + 0.1} = 0.5}$$

$$\mathbf{X}_{\mathbf{chloroform}} = 1 - 0.5 = 0.5$$

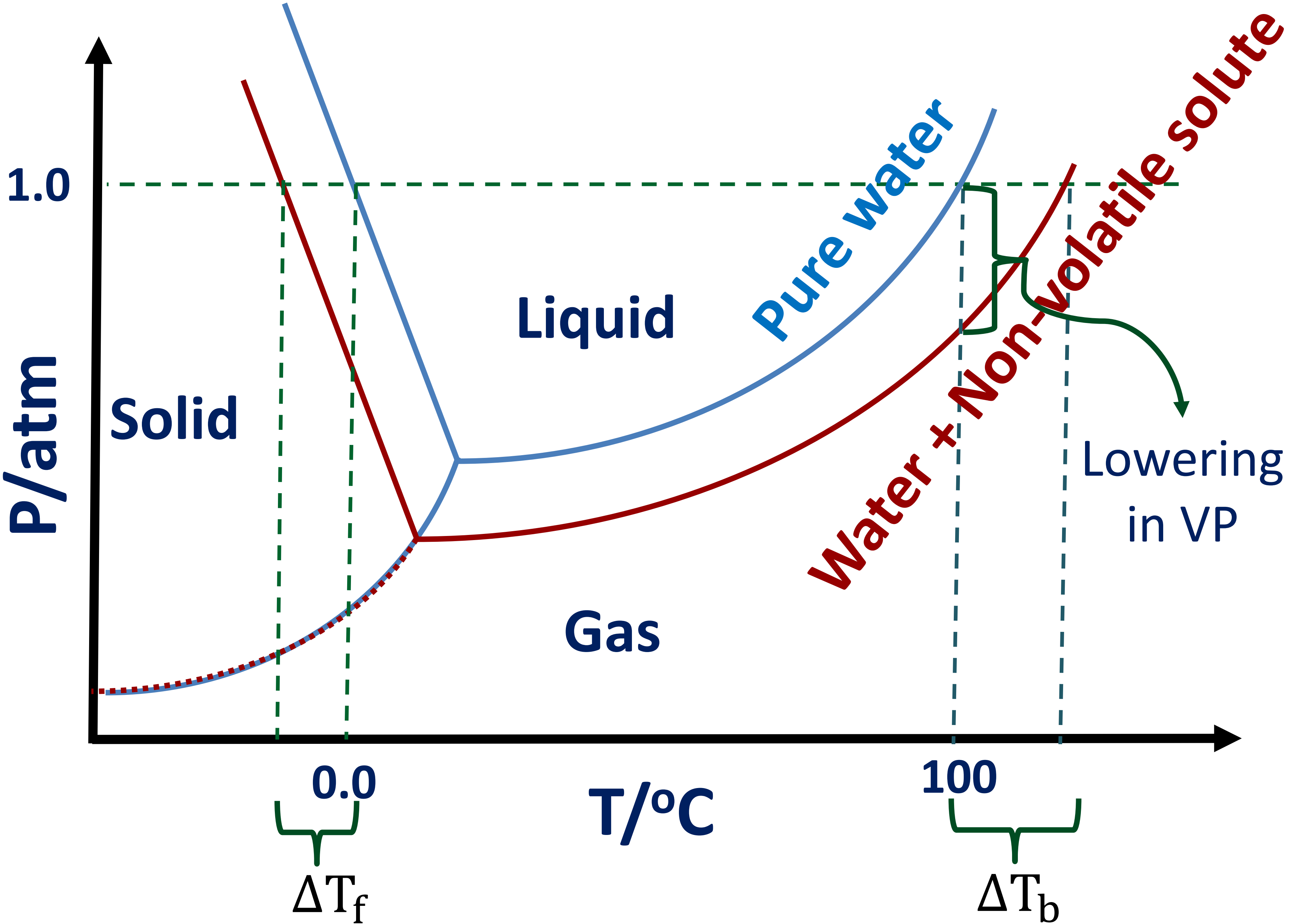
$$P_T = P_A + P_B = X_A\ P_A^o + X_B\ P_B^o$$

$$= (0.5 \times 345) + (0.5 \times 293)$$

$$= 319\ \text{torr} > 260\ \text{torr}$$

–Ve Deviation

Phase diagrams of water and a solution of a nonvolatile solute



- A non-volatile solute lowers the vapor pressure of solution at every T

- The solid-liquid interface moves to left

- Solid-gas interface is not affected

BP elevation

- Normal boiling point of a liquid: the temperature at which its vapor pressure equals 1 atm.

- When a nonvolatile solute is added to a pure solvent, the vapor pressure of the solvent decreases.

- Such a solution must be heated to a **higher temperature** than the boiling point of the pure solvent to reach a vapor pressure of 1 atm, i.e., the boiling point **increases.**

van't Hoff factor i

- Expresses the relation between the moles of solute dissolved and the moles of particles in solution

$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

for $NaCl$ $i = 2$ $NaCl \rightarrow Na^+ + Cl^-$

for K_2SO_4 $i = 3$ $K_2SO_4 \rightarrow 2\,K^+ + SO_4^{2-}$

for $Fe_3(P0_4)_2$ $i = 5$

$$Fe_3(PO_4)_2 \rightarrow 3\,Fe^{3+} + 2\,PO_4^{3-}$$

for Glucose $i = 1$ **Glucose is not dissociate**

- The boiling point elevation is proportional to the number of moles of the solute added to the solvent.

$$\Delta T_b = i\, K_b\, m_{solute}$$

- Here, ΔT_b is the boiling-point elevation, i is the ionization factor, K_b is the boiling-point elevation constant, and m_{solute} is the molal concentration (molality) of the solution.

Exercise

- Calculate the boiling point of 0.2 m aqueous solution of glucose. (K_b of water is 0.5 12^{o}C/m)

Solution

$$\Delta T_b = i\,K_b\,m_{solute}$$
$$= 1 \times 0.512\,{}^oC/m \times o.2\,m = 0.1\,{}^oC$$

- BP of 0.2 m glucose

$$= 100 + 0.1 = 100.1\,°C$$

FP depression

- FP: the temperature at which the vapor pressures of solid and liquid states of a given material become equal.

Liquid ↔ Solid

- The presence of the solute lowers the rate at which molecules in the liquid return to the solid state

water ↔ Ice

Solution ↔ Ice

- The freezing-point depression is proportional to the number of moles of the solute added to the solvent.

$$\Delta T_f = i\, K_f\, m_{solute}$$

- Here, ΔT_f is the freezing-point depression, i is the ionization factor, K_f is the freezing-point depression constant, and m_{solute} is the molal concentration (molality) of the solution.

Exercise

- Calculate the freezing point of 2 m aqueous solution of glucose? (K_f of water is 1.86 $^oC/m$)

Solution

$$\Delta T_f = i\, K_f\, m_{solute}$$

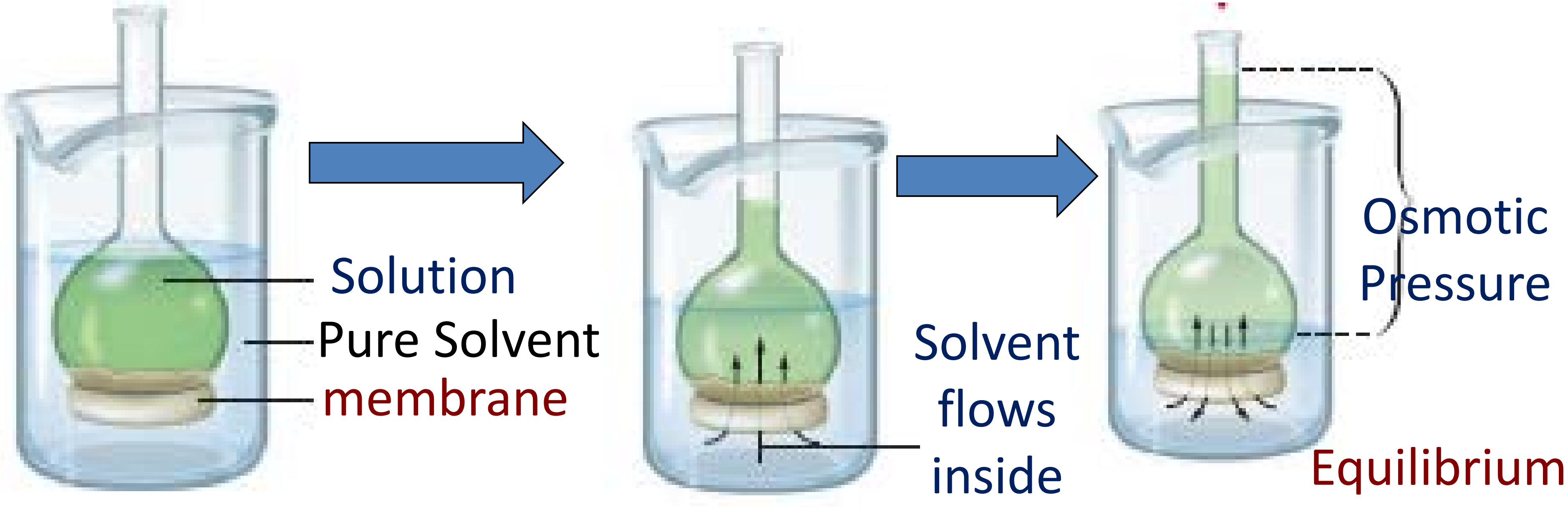
$$= 1 \times 1.86\,^oC/m \times 2\,m = 3.7\,^oC$$

- FP of 2 m glucose

$$= 0 - 3.7 = -3.7°C$$

Osmosis

- Consider a solution and pure solvent are separated by a **semipermeable** membrane, which allows solvent but not solute molecules to pass through.
- As time passes, the volume of the solution increases and that of the solvent decreases.



Solution

Pure Solvent

membrane

Solvent flows inside

Osmotic Pressure

Equilibrium

- **Osmosis**: a phenomenon of flowing a **solvent** into a solution through a semipermeable membrane.

- Eventually the liquid levels stop changing, indicating that the system has reached **equilibrium**.

- Because the liquid levels are different at this point, there is a greater **hydrostatic pressure** on the solution than on the pure solvent.

- This excess pressure is called the **osmotic pressure.**

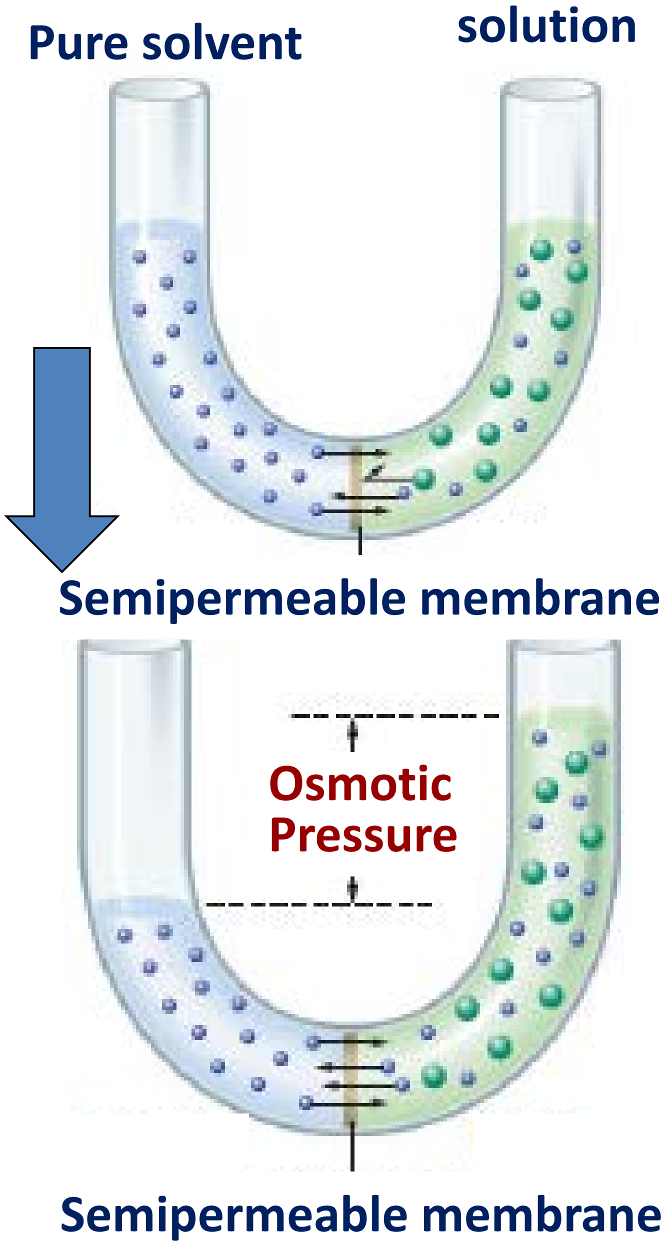
Osmotic Pressure, π

- The pressure required or applied to the solution to stop the flow of the solvent or to stop osmosis.

The osmotic pressure and concentration are related by the following equation:

$$\boxed{\pi = iMRT} \qquad \boxed{\pi V = inRT}$$

M is the molar concentration of the solute, R is the gas constant, and T is the absolute temperature.



Exercise

- To determine the molar mass of a certain protein, 1.00 × 10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution. The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C. Calculate the molar mass of the protein?

Solution

$$\pi = 1.12\ \text{torr} \times \frac{1\ \text{atm}}{760\ \text{torr}} = 1.47 \times 10^{-3}\text{atm}$$

$$\text{M} = \frac{\pi}{\text{RT}} = \frac{1.47 \times 10^{-3}\text{atm}}{(0.08206\ \text{L atm K}^{-1}\ \text{mol}^{-1})\ (298\ \text{K})}$$
$$= 6.01 \times 10^{-5}\text{mol L}^{-1}$$

$$\mathrm{M} = 6.01 \times 10^{-5}\,\mathrm{mol\ L^{-1}} = \frac{\mathrm{n}}{\mathrm{V}} = \frac{\mathrm{m}}{\mathrm{Mwt} \times \mathrm{V}}$$

$$= \frac{1.0 \times 10^{-3}\,\mathrm{g}}{\mathrm{Mwt} \times 1.0 \times 10^{-3}\,\mathrm{L}}$$

$$\mathrm{Mwt}\ (\mathrm{protein\ molar\ mass}) = 1.66 \times 10^{4}\ \mathrm{g}$$

Exercise

- The observed osmotic pressure for a 0.1 M solution of $Fe(NH_4)_2(SO_4)_2$ at 25°C is 10 atm. Compare the expected and experimental values for i ?

Solution

$$\boxed{\pi = \mathrm{iMRT}}$$

$$\mathrm{Fe}(NH_4)_2\,(SO_4)_2 \rightarrow \mathrm{Fe}^{2+} + 2NH_4{}^{+} + 2SO_4{}^{2-}$$

Theoretically, $\mathbf{i}_{exp} = 5$

Experimentally

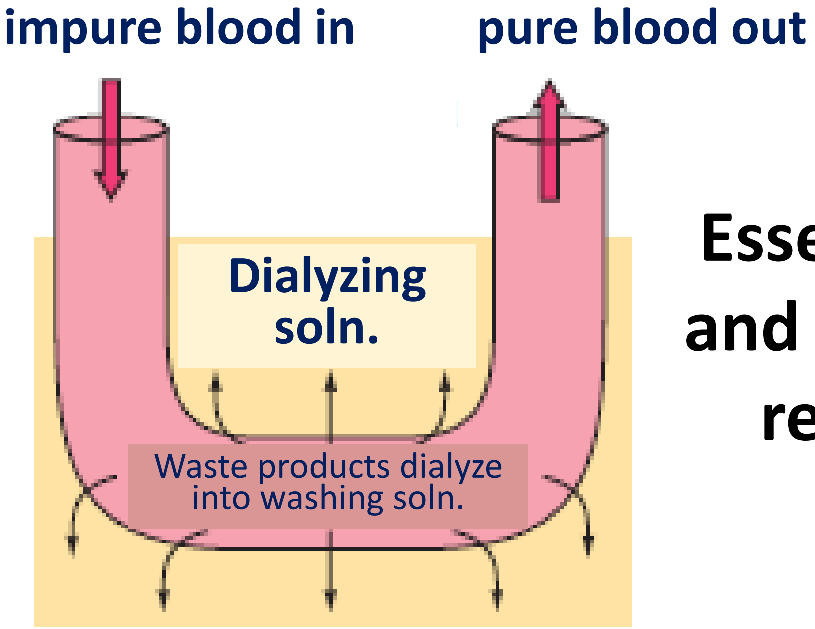
$$\mathrm{i} = \frac{\pi}{\mathrm{MRT}} = \frac{10\ \mathrm{atm}}{(0.1\ \mathrm{mol}\ L^{-1})(0.082\ L\ atm\ K^{-1} mol^{-1})(298\ K)}$$

$$\mathbf{i}_{obs} = 4.42$$

$\mathbf{i}_{obs} < \mathbf{i}_{exp}$ Possibly because of ion pairing

Dialysis

- a similar process to osmosis but the membrane allows transfer of both solvent molecules and small solute molecules and ions.
- occurs at the walls of most plant and animal cells
- **Applications**: **artificial kidney machines** to purify blood



impure blood in

pure blood out

Dialyzing soln.

Waste products dialyze into washing soln.

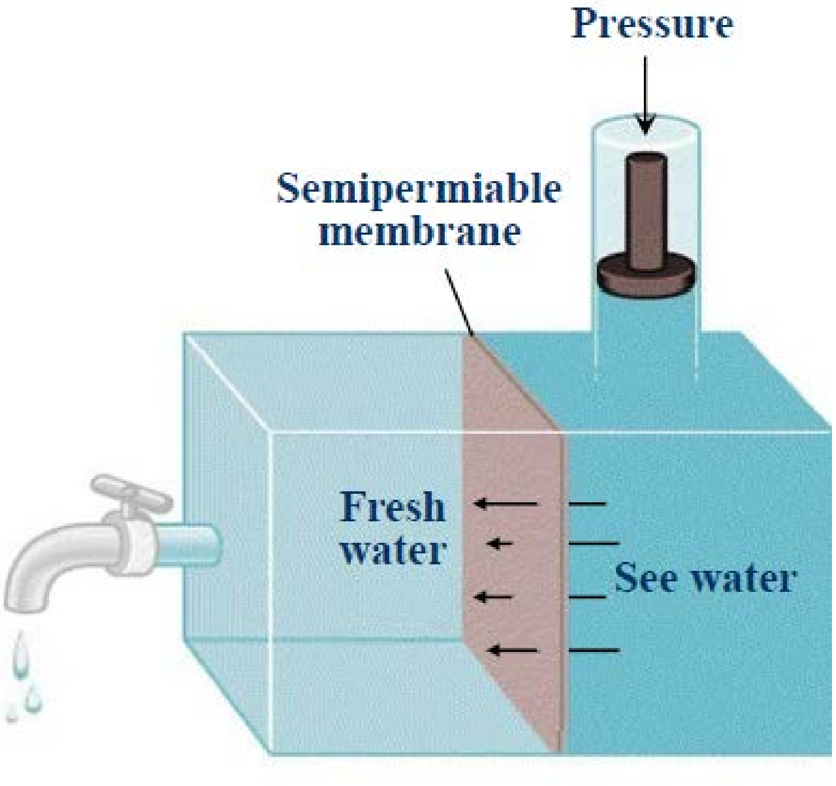
Essential ions and molecules remain in blood

Reverse osmosis/Desalination

- If a solution in contact with pure solvent across a **semipermeable** membrane is subjected to an **external pressure** larger than its osmotic pressure, **reverse osmosis** occurs.

- The pressure will cause a net flow of **solvent** from the solution to the solvent.
- The semipermeable membrane acts as a "**molecular filter**" to remove solute particles.

The process of removing dissolved salts from seawater



Solar Desalination