General Chemistry II

Chem 102

Lecture 8

Colligative Properties

Ahmad Alakraa

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 about: 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.

Pure Solvent

Solution

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

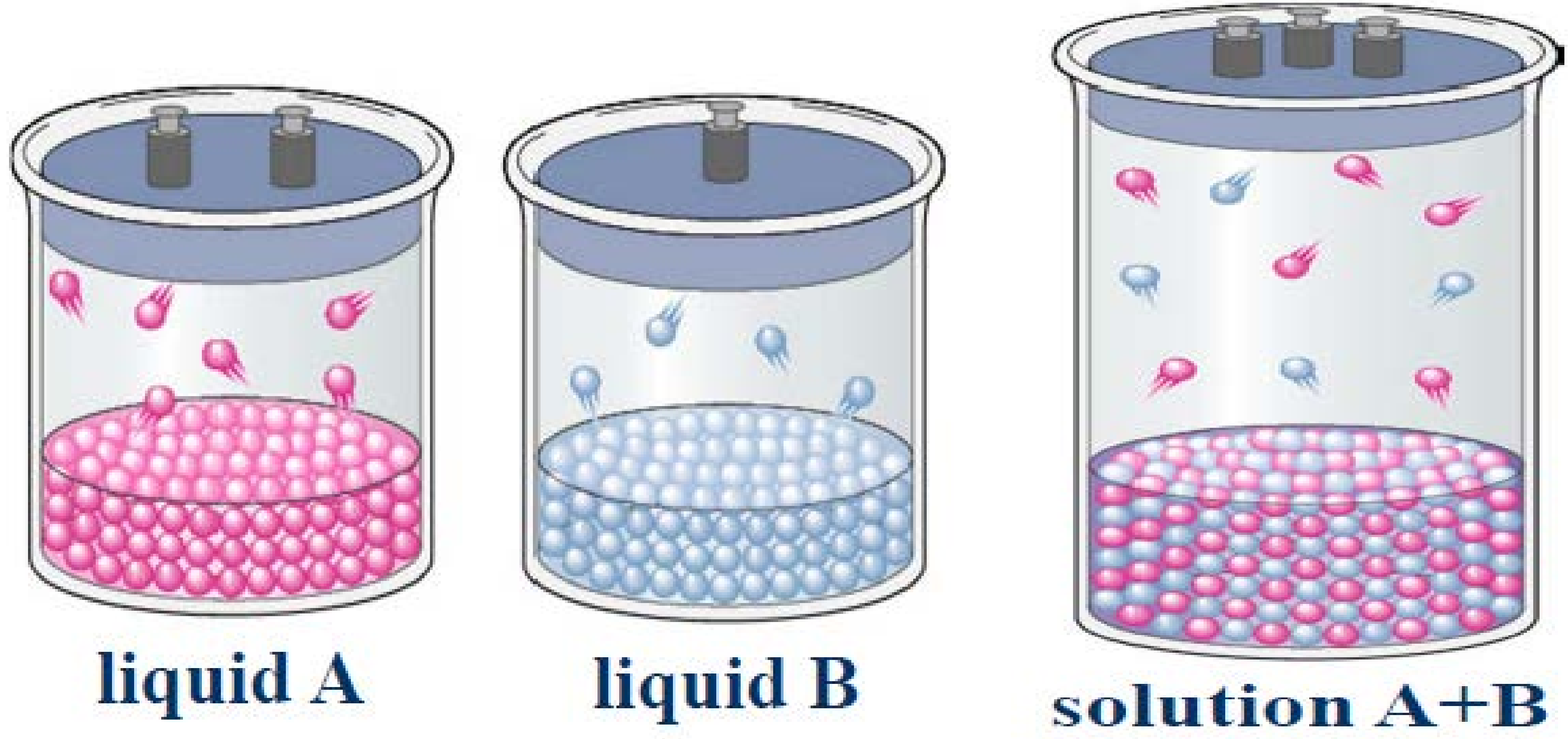
$$= \frac{(643.5\ \mathrm{cm}^3)\ (0.9971\ \mathrm{g/cm}^3)}{18\ \mathrm{g\ /\ mol}} = 35.60\ \mathrm{mol}$$

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

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

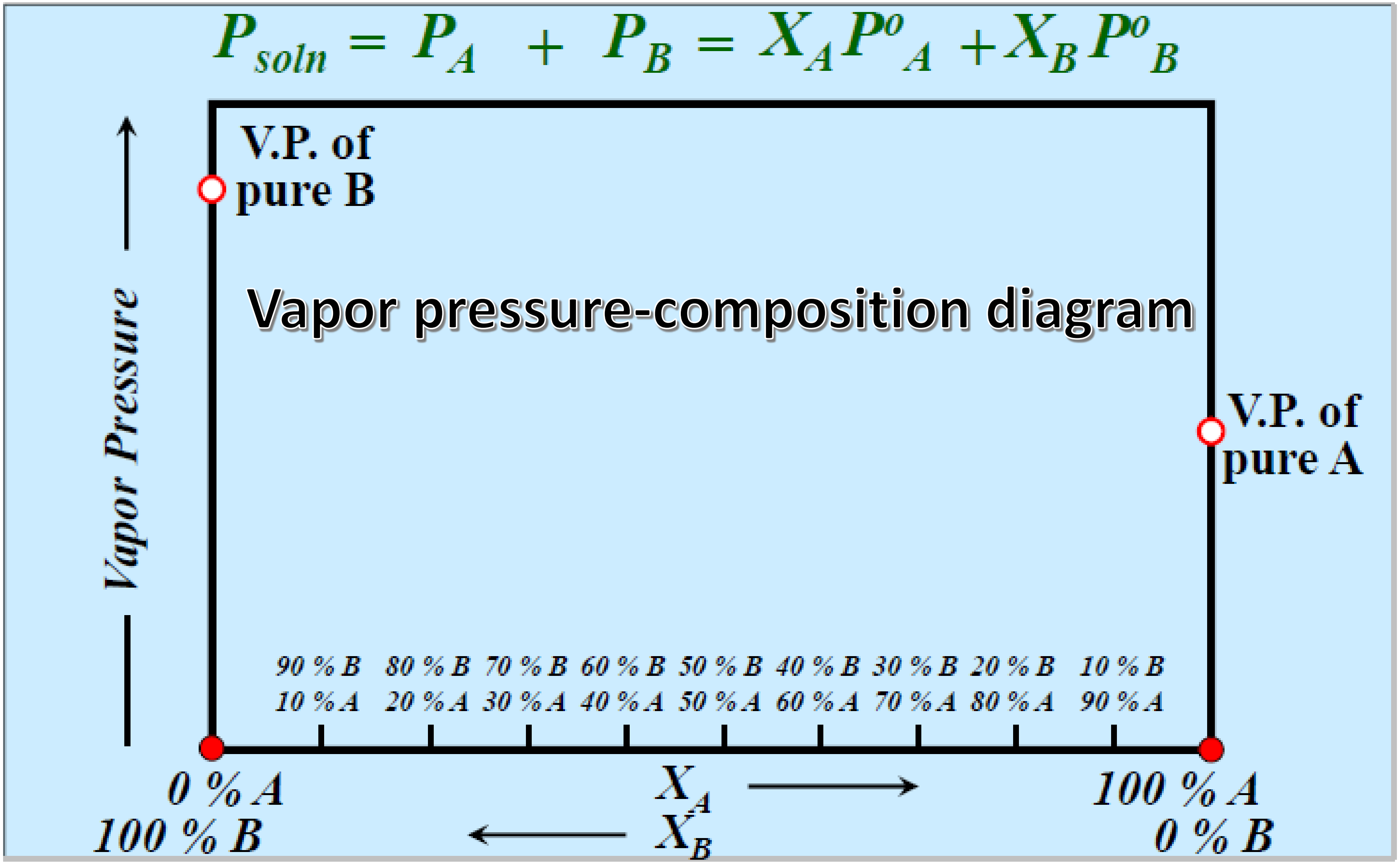
Ideal (liquid-liquid) solutions

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



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

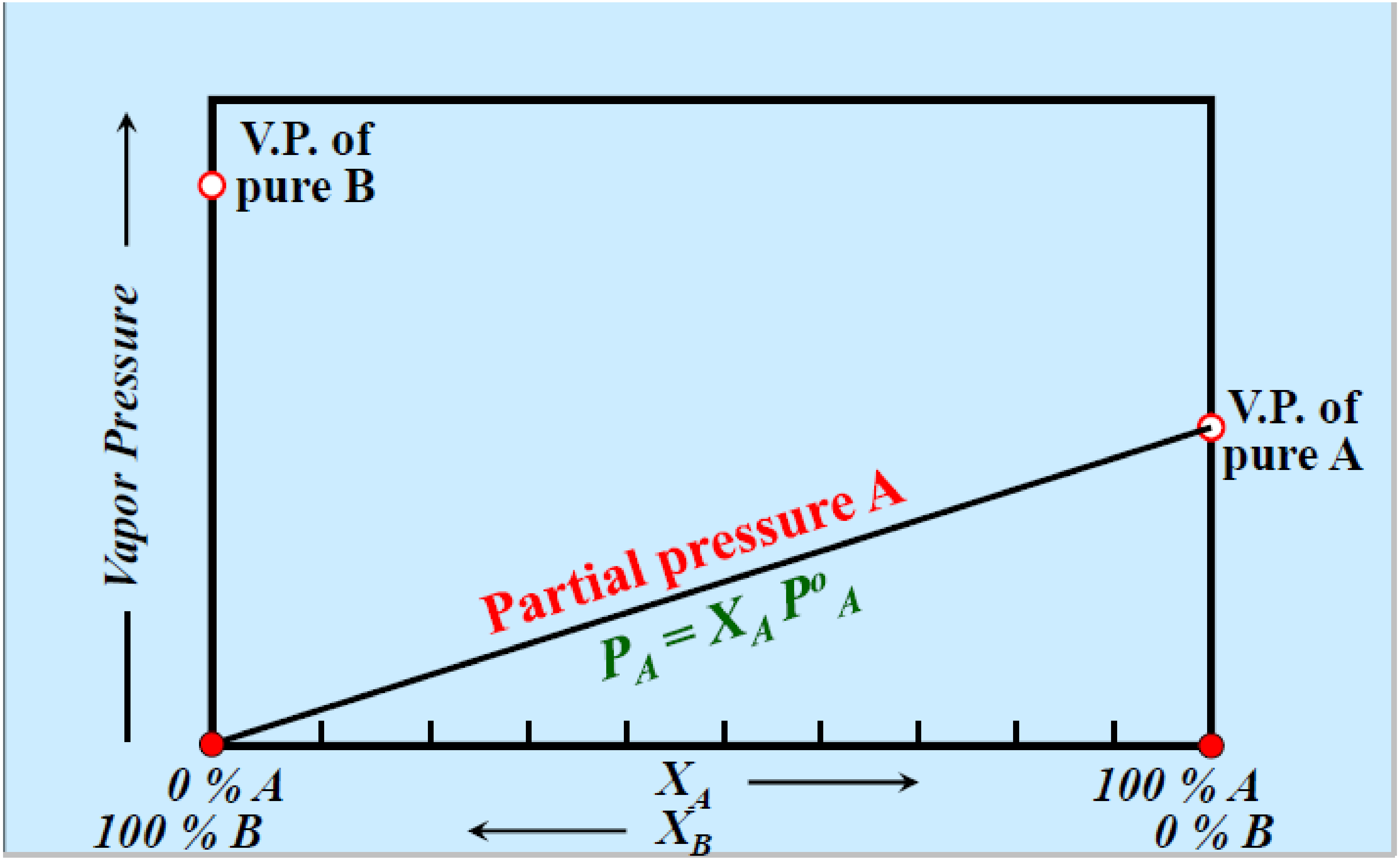
Ideal (liquid-liquid) solutions



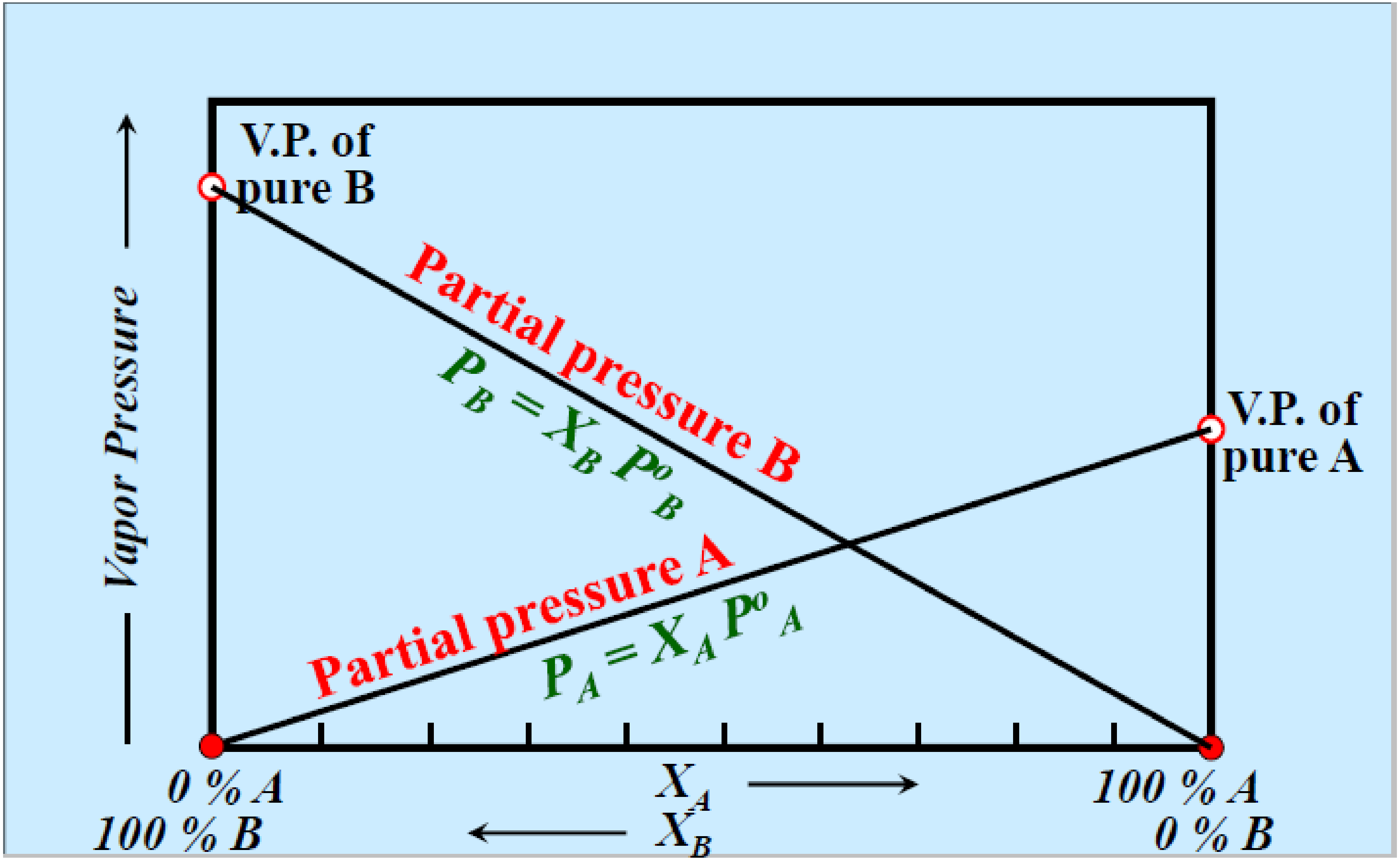
$$P_{soln} = P_A + P_B = X_A P^o{}_A + X_B P^o{}_B$$

Vapor pressure-composition diagram

Ideal (liquid-liquid) solutions

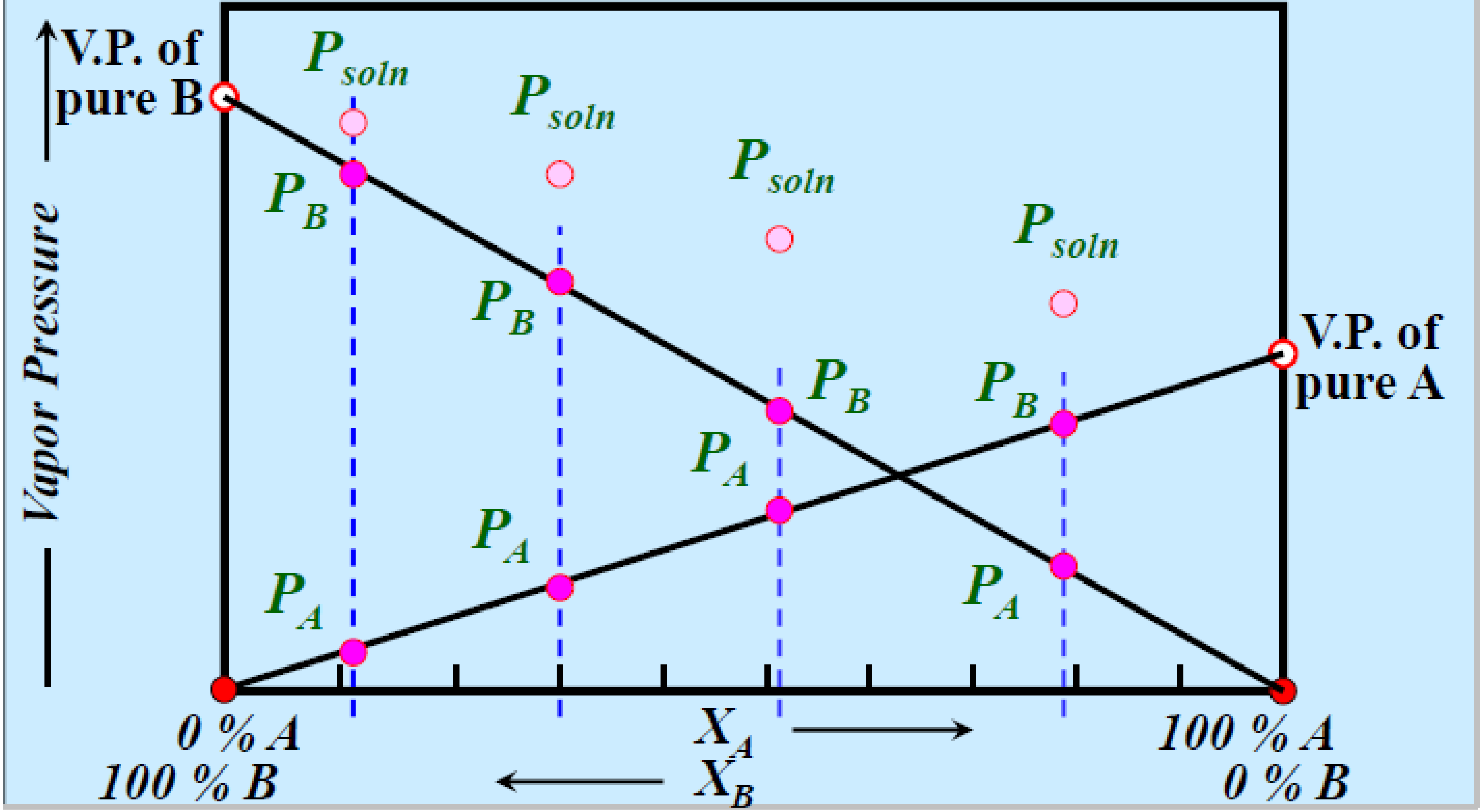


Ideal (liquid-liquid) solutions



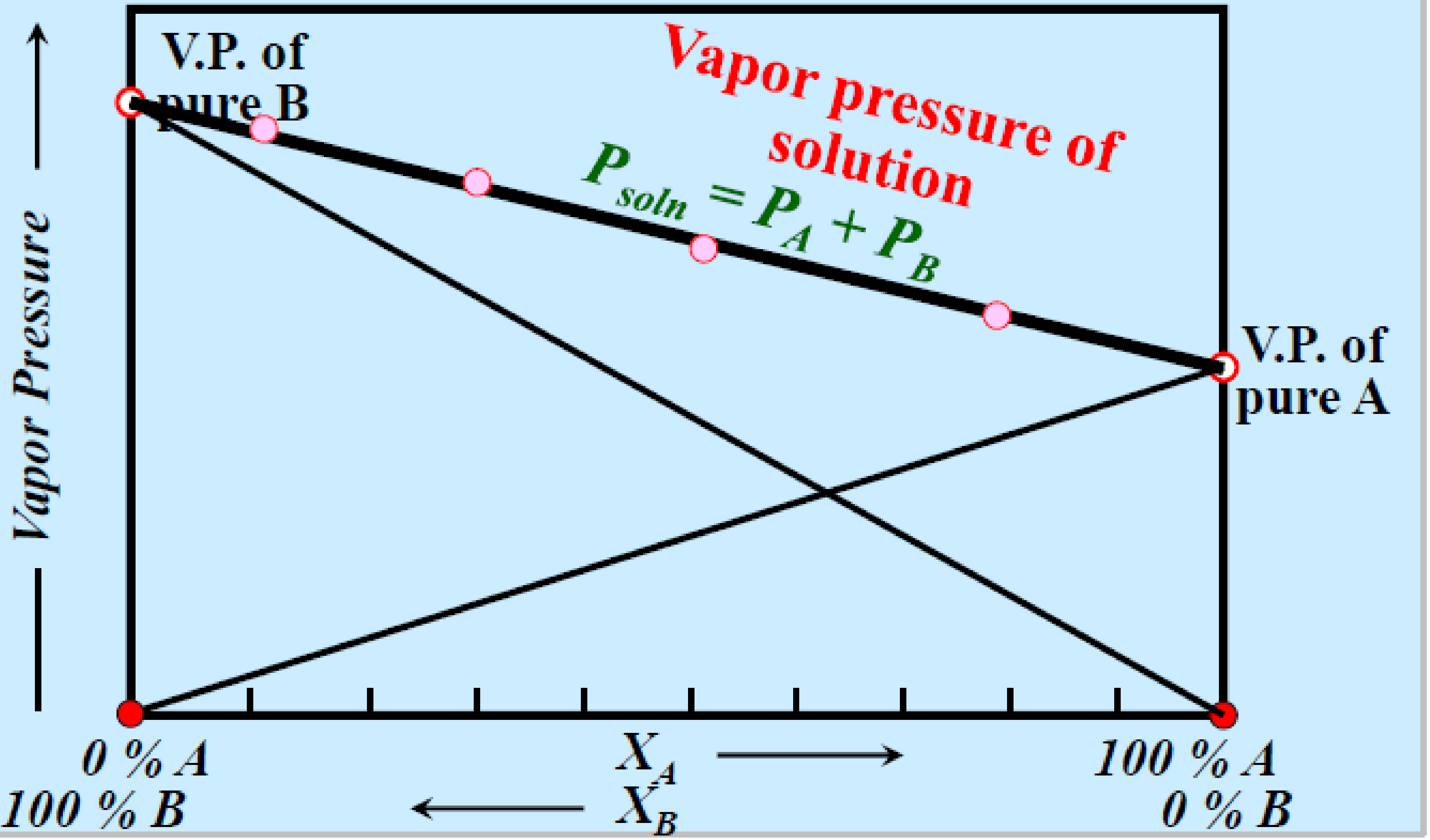
Ideal (liquid-liquid) solutions

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



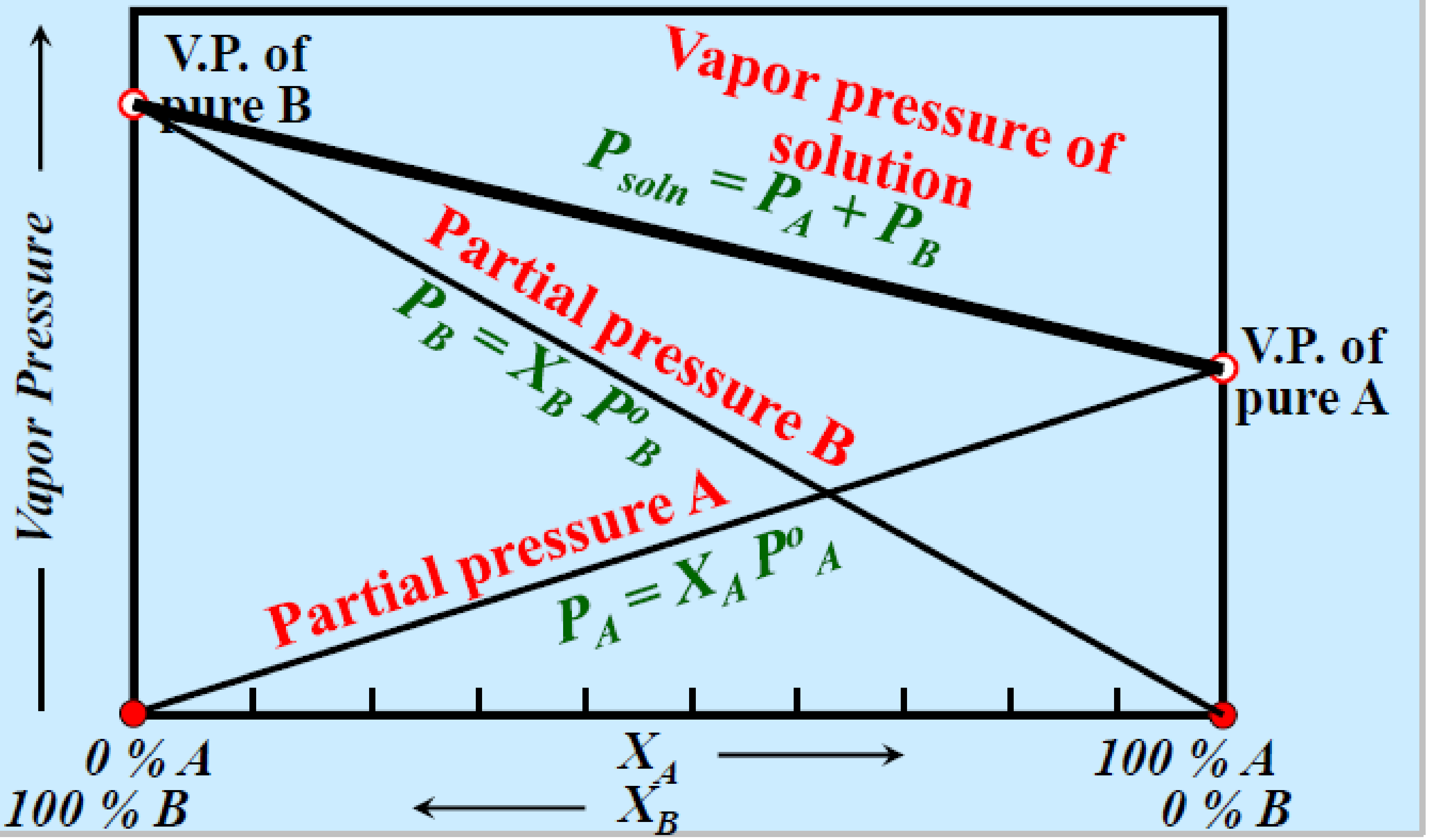
Ideal (liquid-liquid) solutions

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



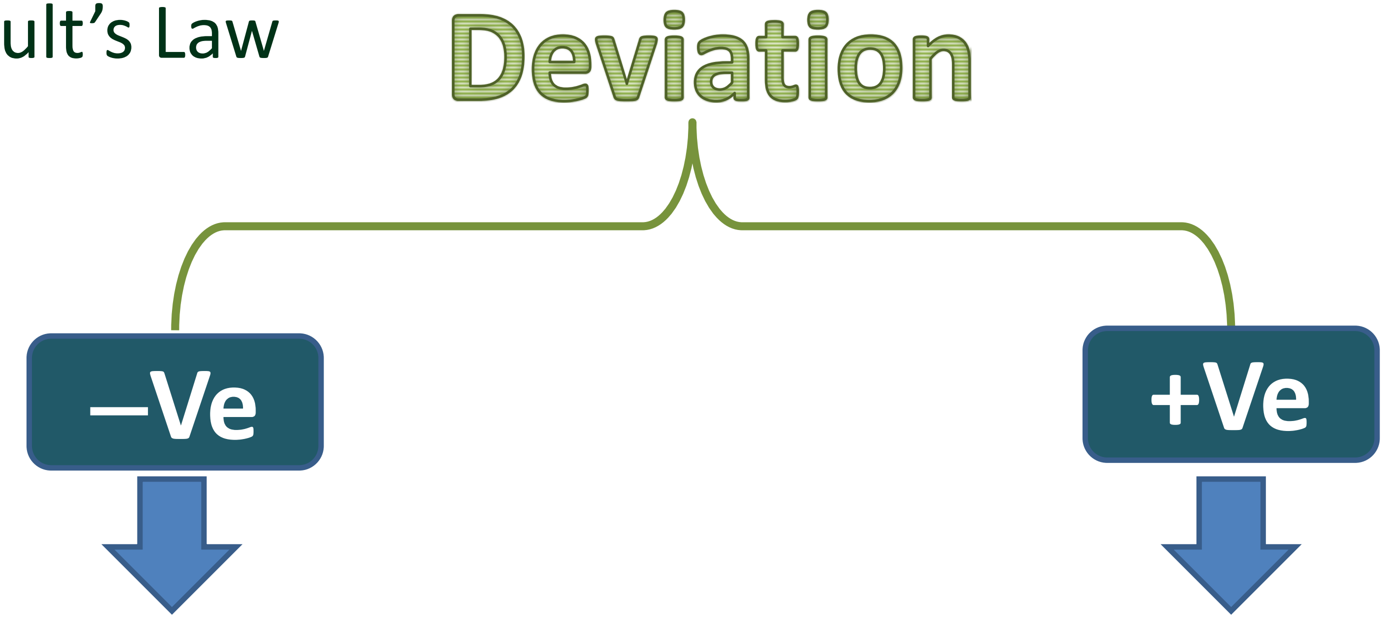
Ideal (liquid-liquid) solutions

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



Non-ideal solutions

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

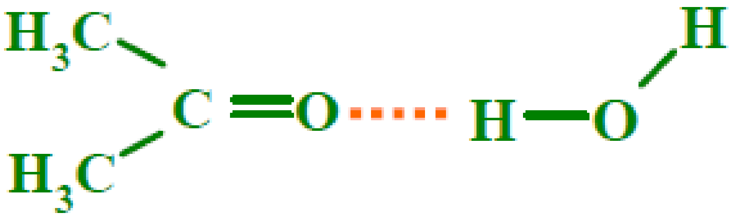


Deviation

–Ve

+Ve

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



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

Deviation

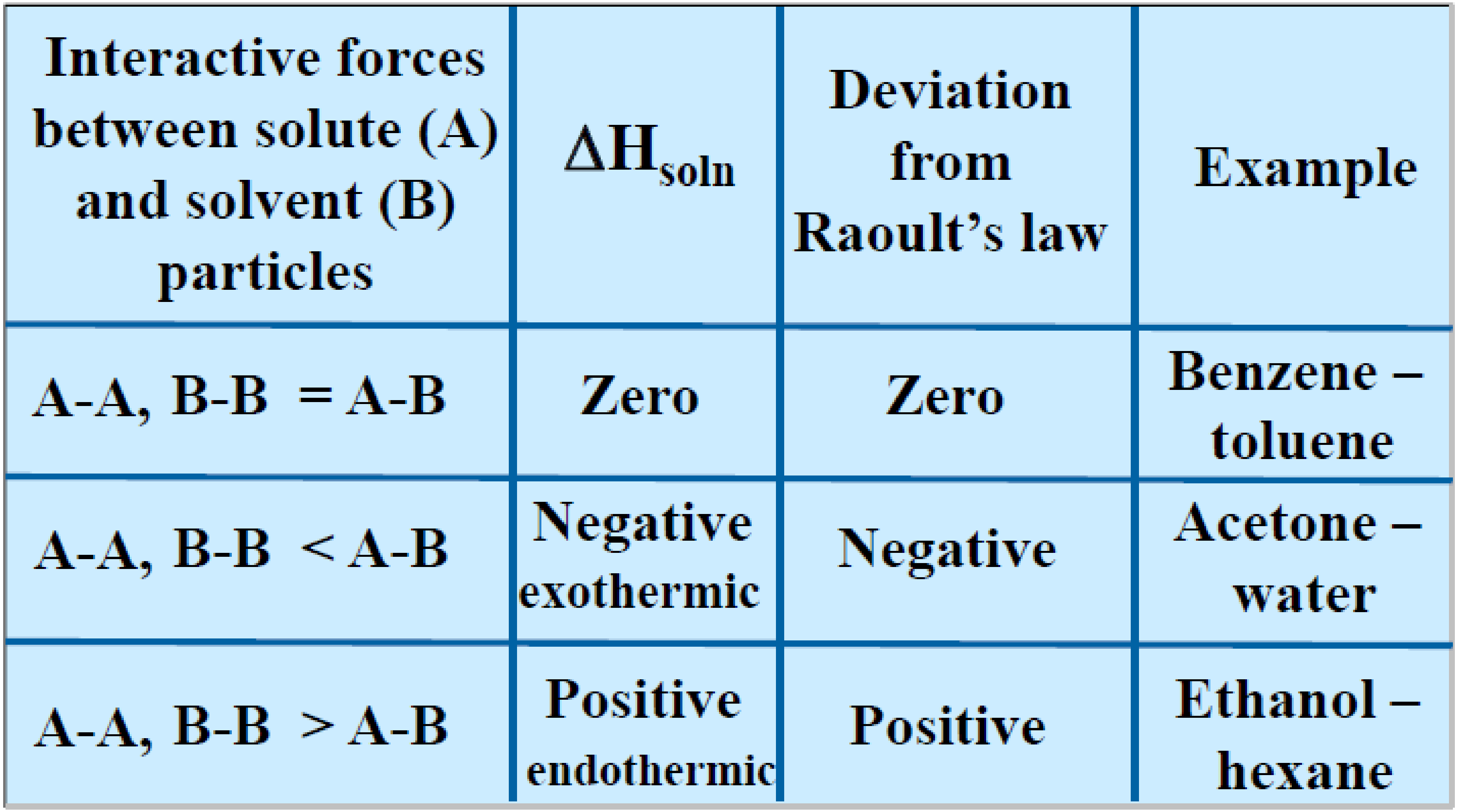
−Ve

- Observed VP < Predicted VP by Raoult’s Law
- ΔH_{sol} is −Ve
- **Exothermic**

+Ve

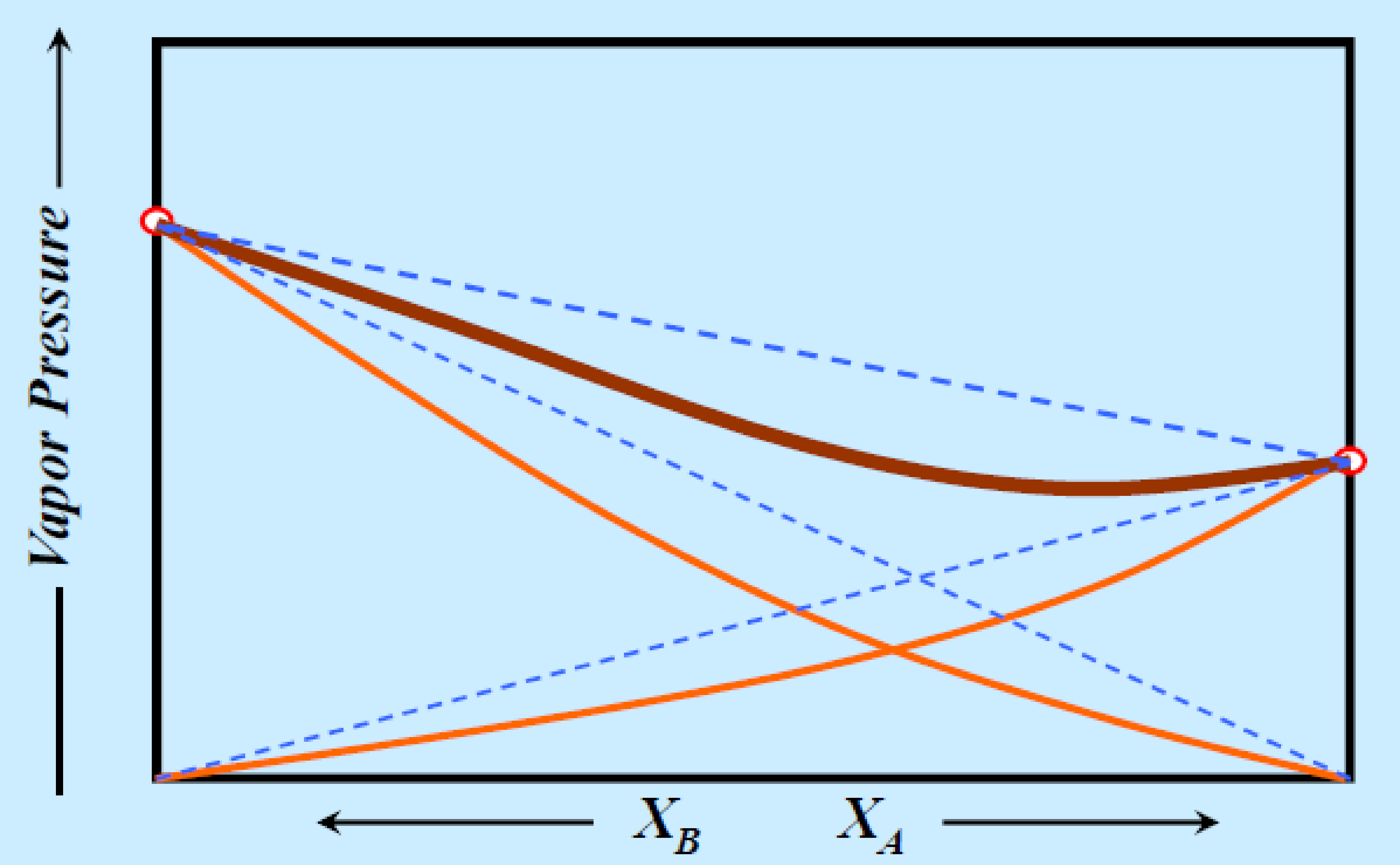
- Observed VP > Predicted VP by Raoult’s Law
- ΔH_{sol} is +Ve
- **Endothermic**

Non-ideal solutions

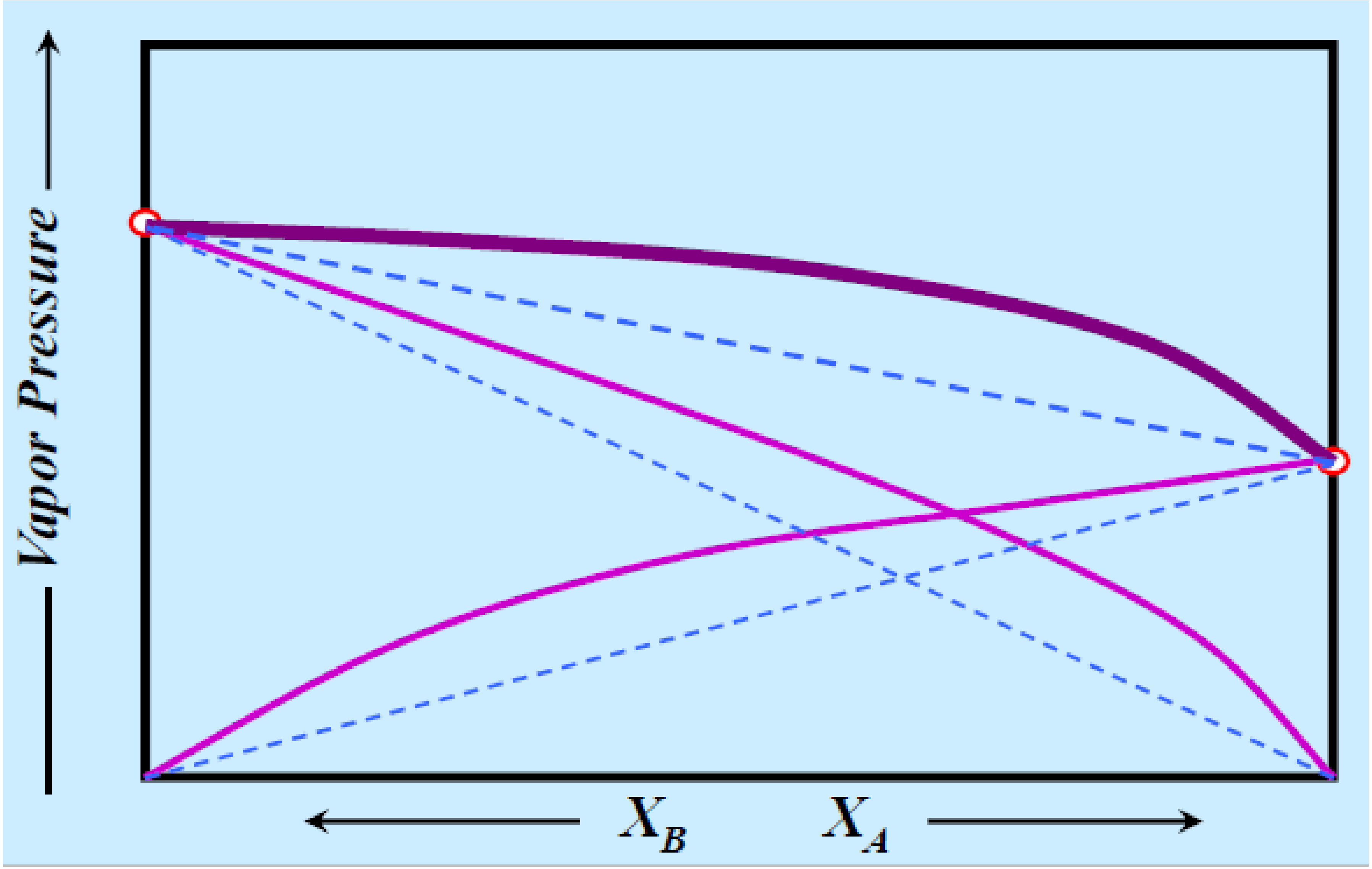


Interactive forces between solute (A) and solvent (B) particles	ΔH_{soln}	Deviation from Raoult's law	Example
A-A, B-B = A-B	Zero	Zero	Benzene – toluene
A-A, B-B < A-B	Negative exothermic	Negative	Acetone – water
A-A, B-B > A-B	Positive endothermic	Positive	Ethanol – hexane

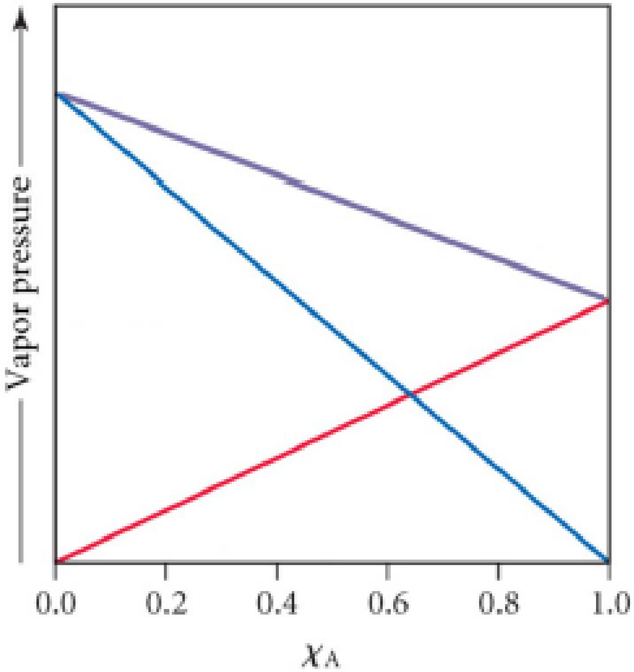
–Ve Deviation



+Ve Deviation

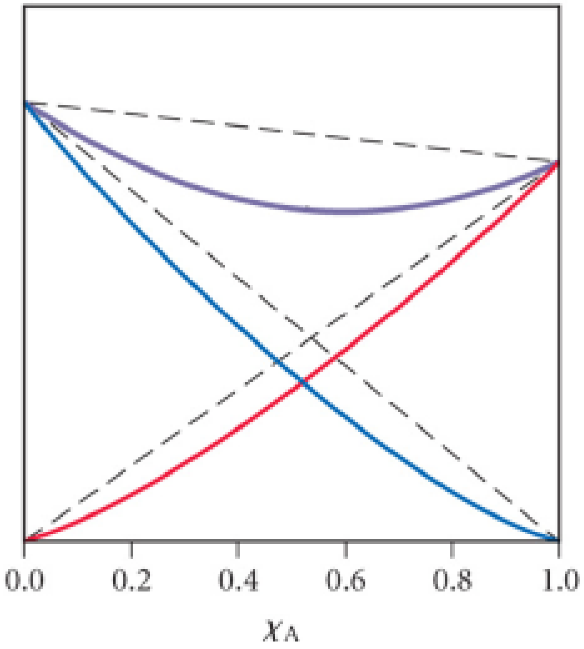


Ideal/Non-ideal



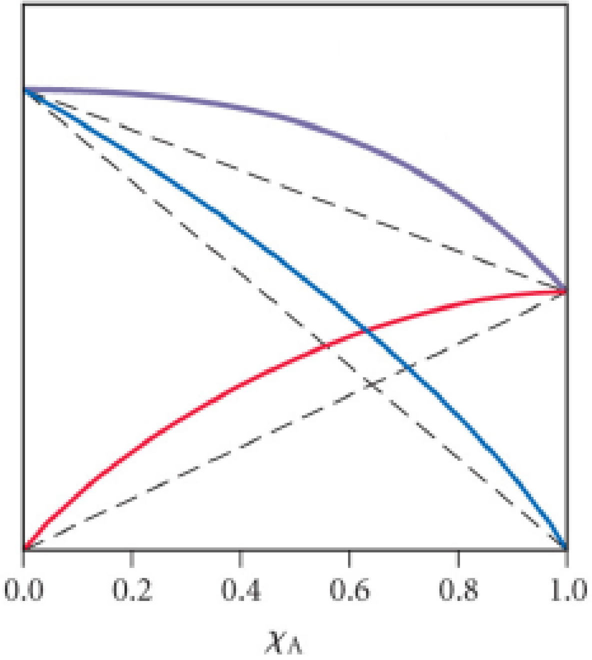
no deviation

Ideal solution



–ve deviation

Strong solute-solvent Interactions



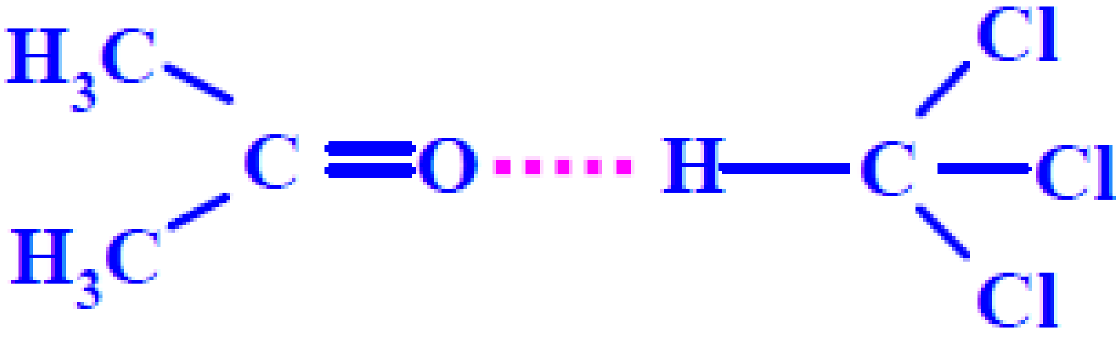
+ve deviation

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

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

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

$$\boxed{\mathbf{X_{acetone}} = \frac{n_{acetone}}{n_{acetone} + n_{chloroform}} = \frac{0.1}{0.1 + 0.1} = 0.5}$$

$$\mathbf{X_{chloroform}} = 1 - 0.5 = 0.5$$

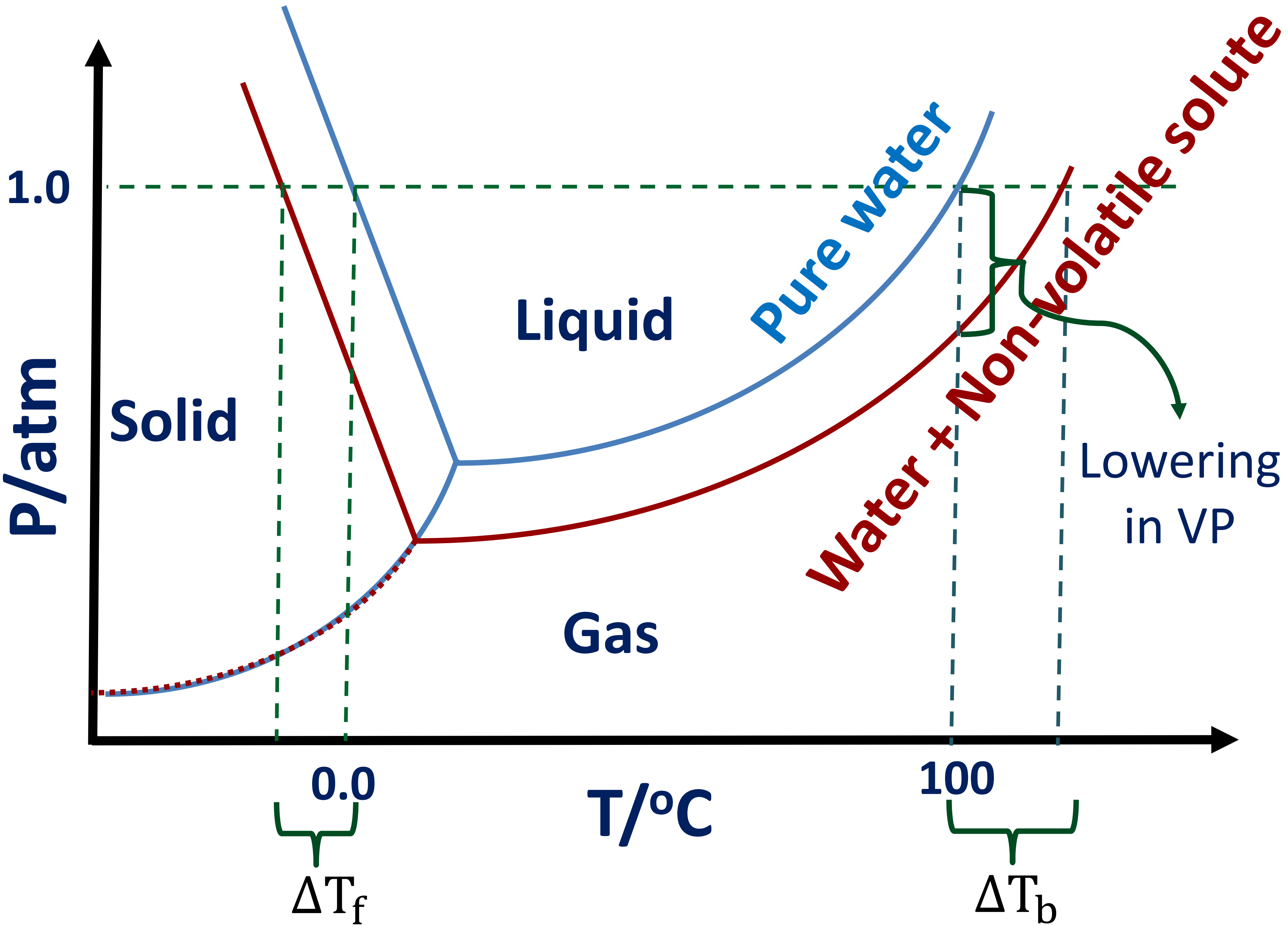
$$P_T = P_A + P_B = X_A\ P_A^o + X_B\ P_B^o$$

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

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

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

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

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

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

for Glucose $i = 1$ $\qquad$ 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

$$\Delta T_f = i\, K_f\, m_{solute}$$
$$= 1 \times 1.86\, ^oC/m \times 2\, m = 3.7\, ^oC$$

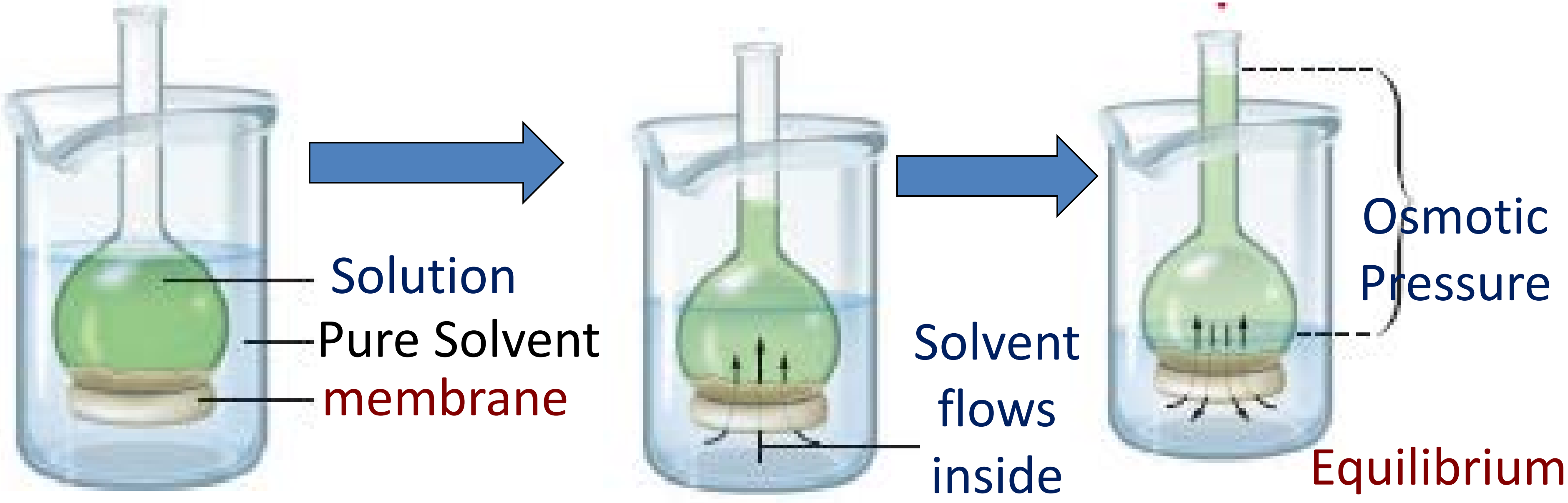
- FP of 2 m glucose

$$= 0 - 3.7 = -3.7°C$$

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.



- **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.**

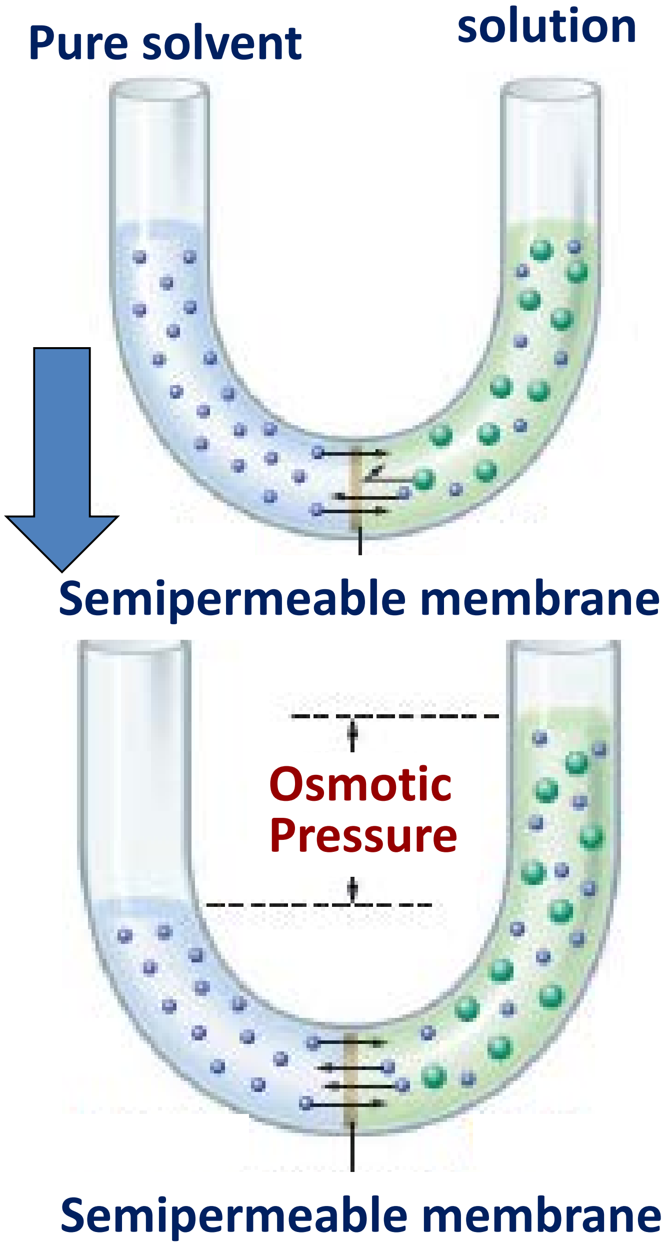
Osmotic Pressure, π

- 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

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

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

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

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

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

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

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

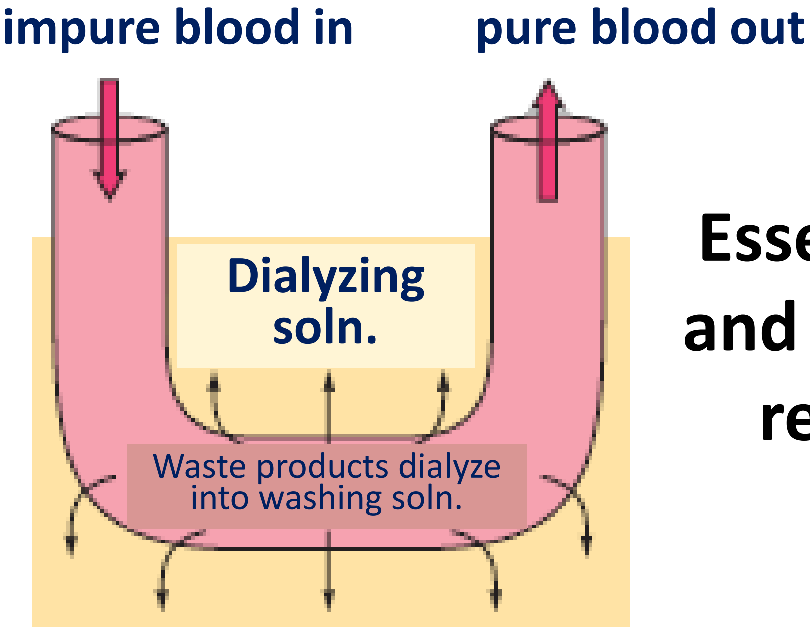
$$\mathbf{i}_{obs} = 4.42$$

$$\mathbf{i}_{obs} < \mathbf{i}_{exp}$$

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



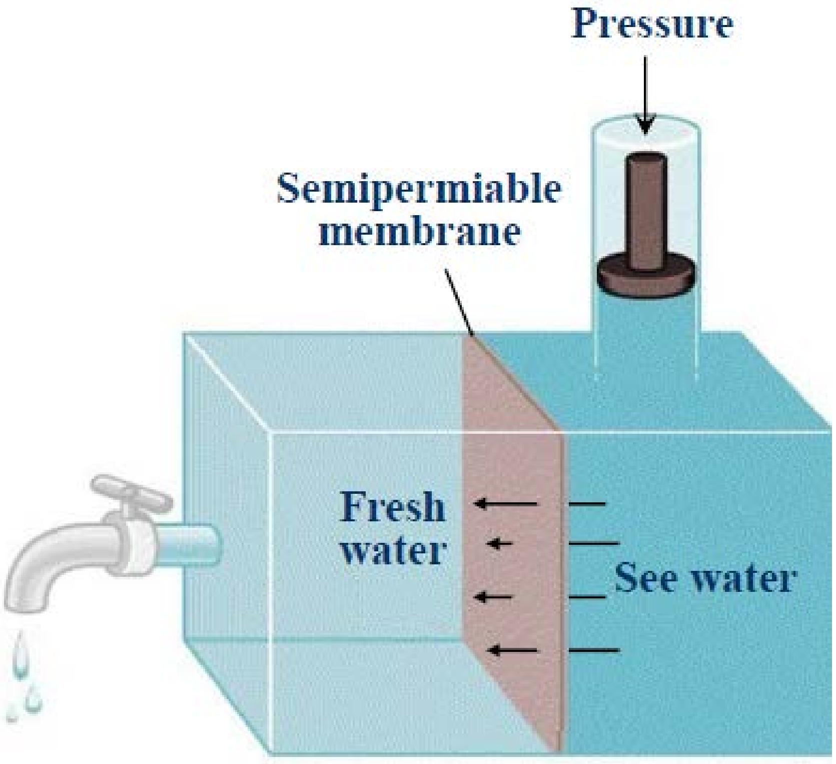
Essential ions and molecules remain in blood

Reverse osmosis/Desalination

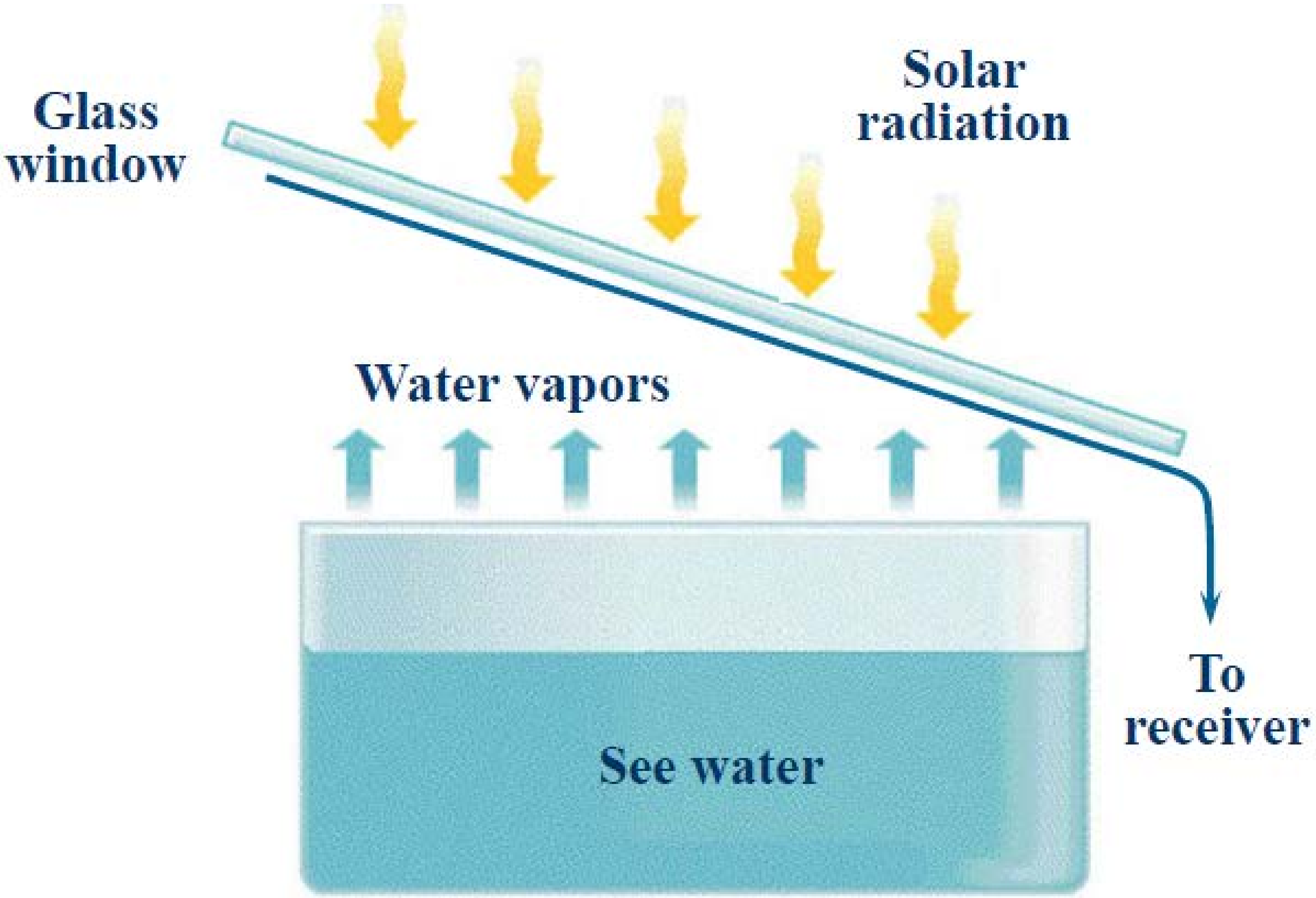
- If a solution in contact with pure solvent across a **semipermeable** membrane is subjected to an **external pressure** larger than its osmotic pressure, **reverse osmosis** occurs.

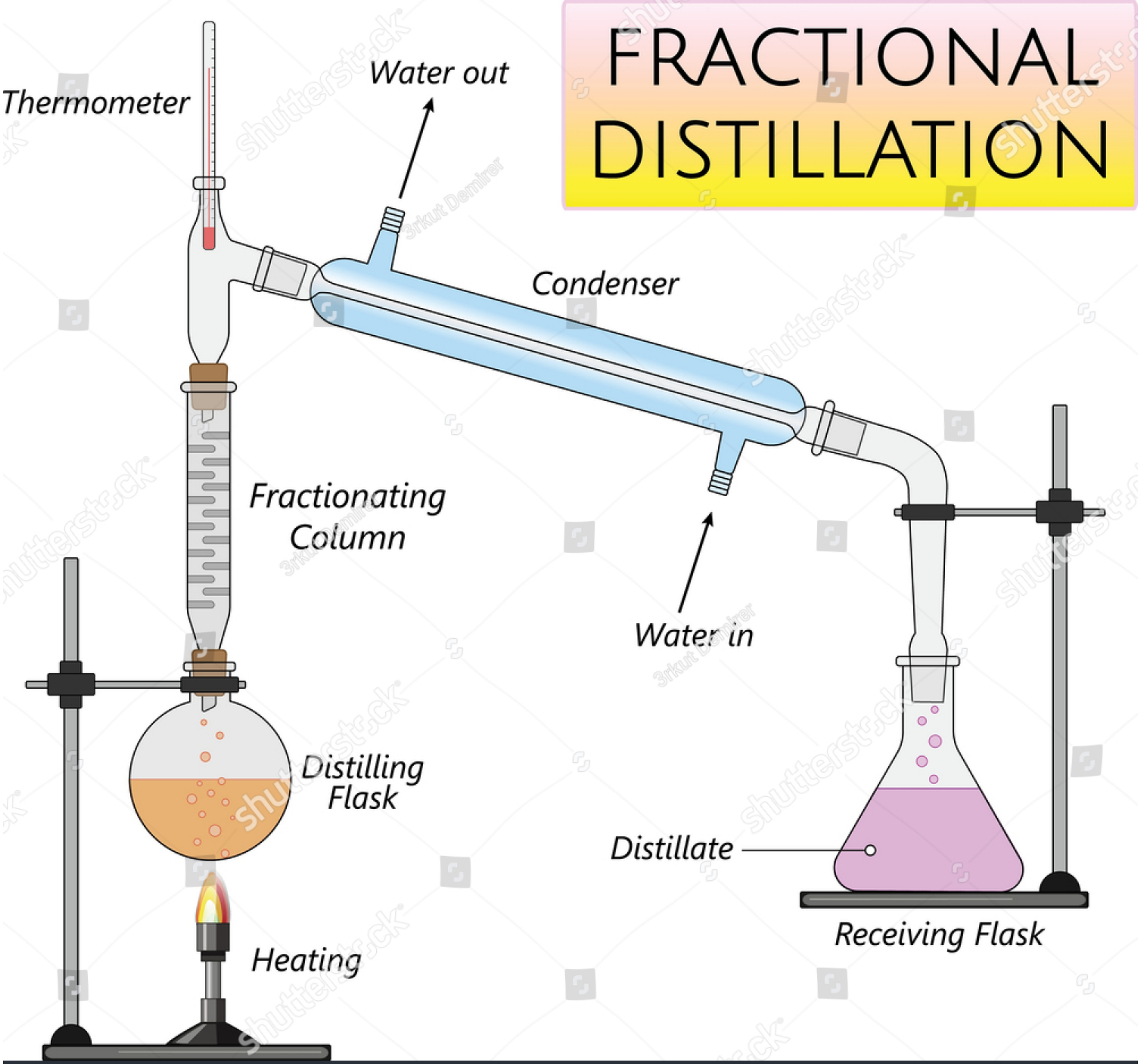
- The pressure will cause a net flow of **solvent** from the solution to the solvent.
- The semipermeable membrane acts as a “**molecular filter**” to remove solute particles.

The process of removing dissolved salts from seawater



Solar Desalination

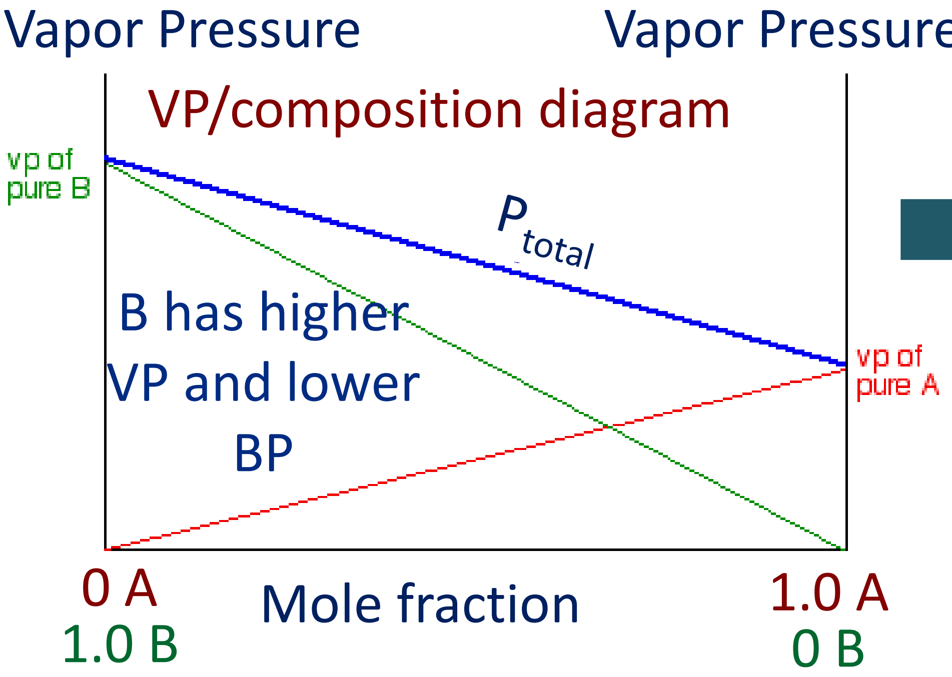


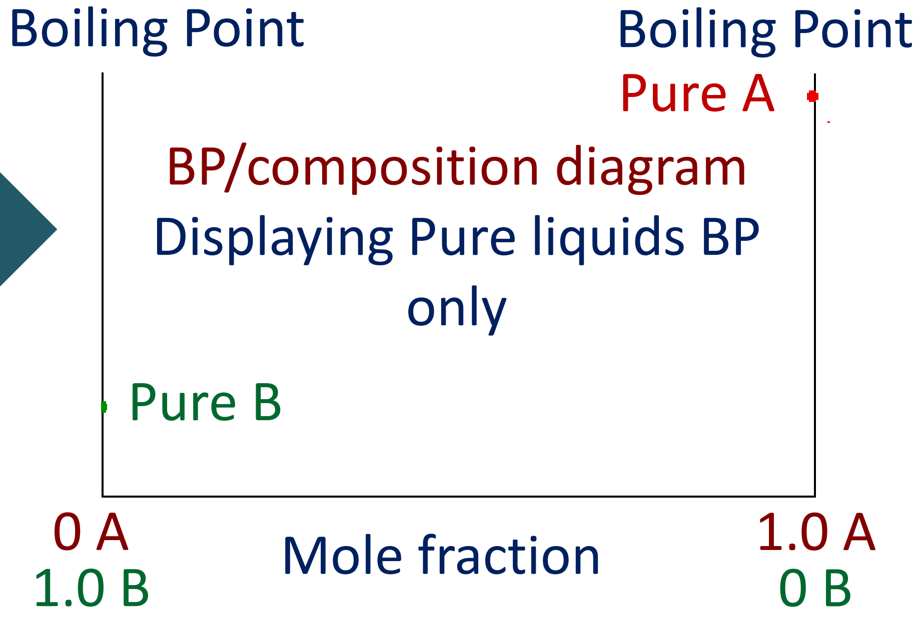

FRACTIONAL
DISTILLATION
Thermometer
Water out
Condenser
Fractionating Column
Water in
Distilling Flask
Distillate
Heating
Receiving Flask

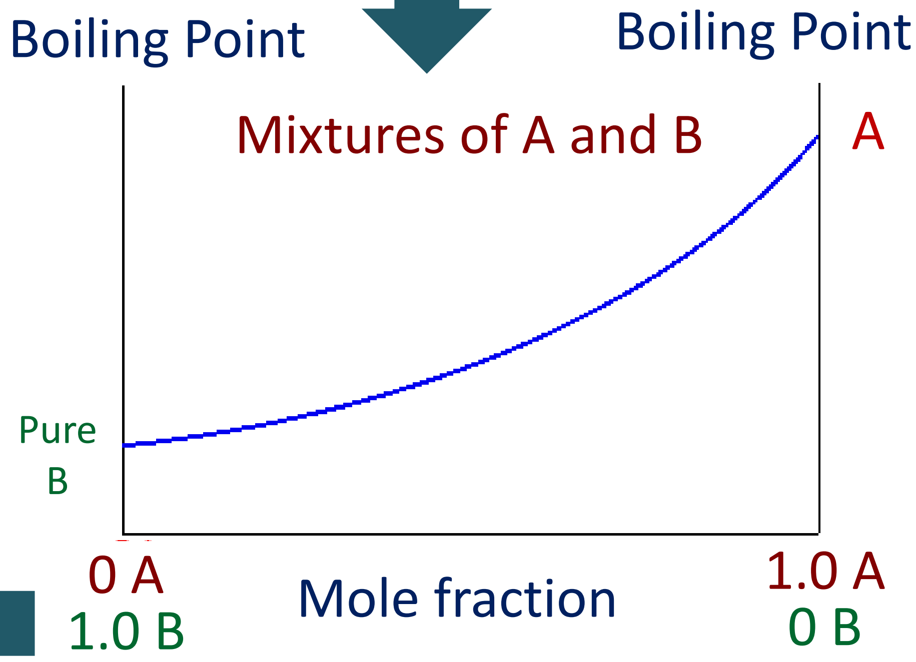
FD (Water + Ethanol)

Both are volatile

- Ethanol boils at 78.4 °C while water boils at 100 °C.
- By heating the mixture, the most volatile component (ethanol) will concentrate (**Hint:** remember that vaporization is different from boiling, i.e., water may vaporize even at RT but with a lower extent than at 50 °C) to a greater degree in the vapor leaving the liquid.
- Some mixtures form **azeotropes**, where the mixture boils at a lower temperature than either component.
- A mixture of 96% ethanol and 4% water boils at 78.2 °C; the mixture is more volatile than pure ethanol.
- For this reason, ethanol cannot be completely purified by direct fractional distillation of ethanol-water mixtures !!!!!!!!.







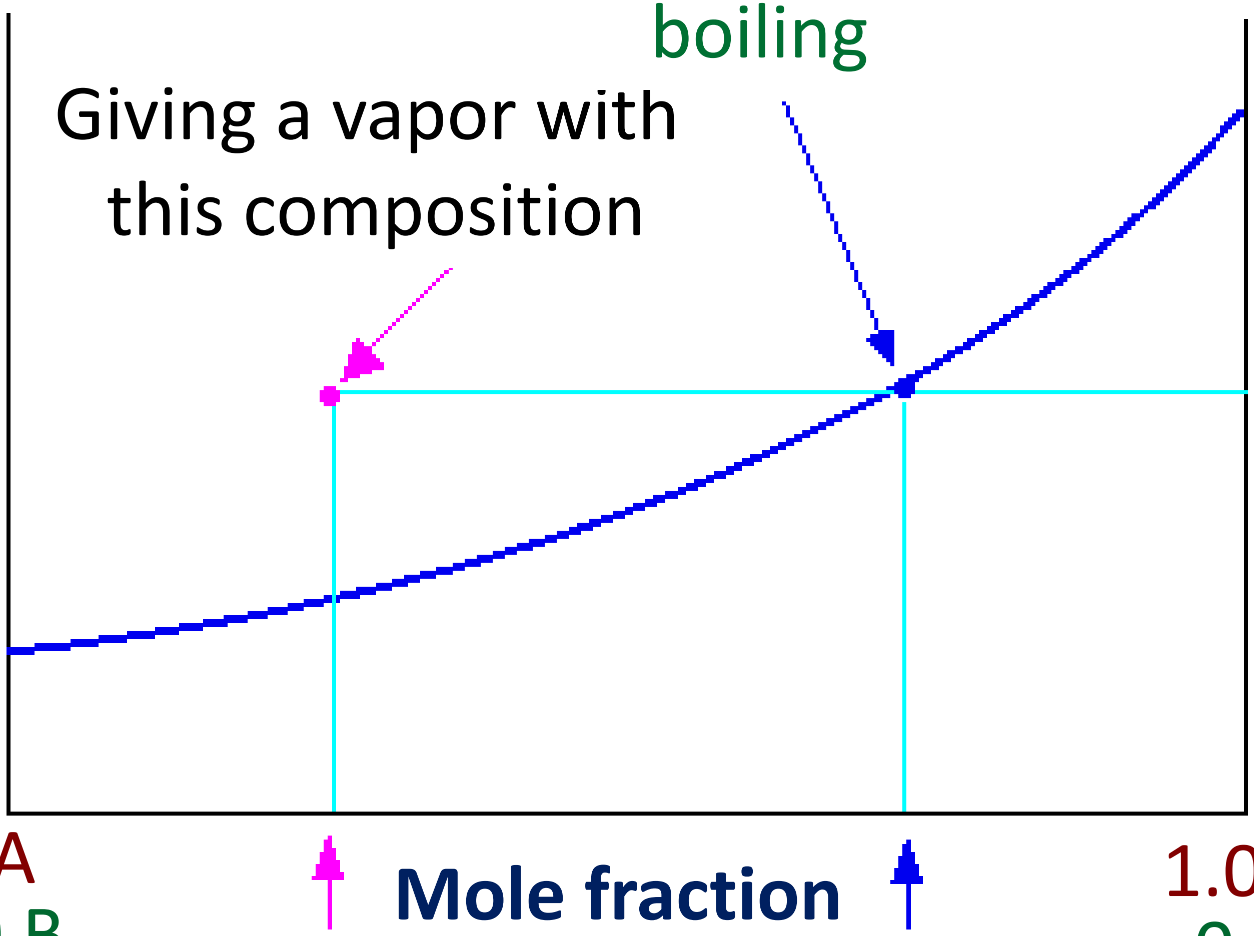
- To make this diagram useful, another line representing the composition of the vapor over the top of any particular boiling liquid is added.

BP-composition diagram

- For a mixture of two volatile liquids (A and B) where B is more volatile having a higher VP, weaker intermolecular forces and lower BP), Liquid B will vaporize more easily at a particular T.

- If you boil this mixture, you would expect that Liquid B escapes to form a vapor more easily than Liquid A.

- If a fractional distillation for this mixture with X_A and X_B (mole fraction) is done, the vapor will be rich in B ($> X_B$) while the remaining liquid will be rich in A ($> X_A$). Condensing the vapor and analyzing it would inform about this vapor composition (a point on the diagram).



Boiling Point

Liquid starts boiling

Boiling Point

Pure A

Giving a vapor with this composition

Pure B

0 A
1.0 B

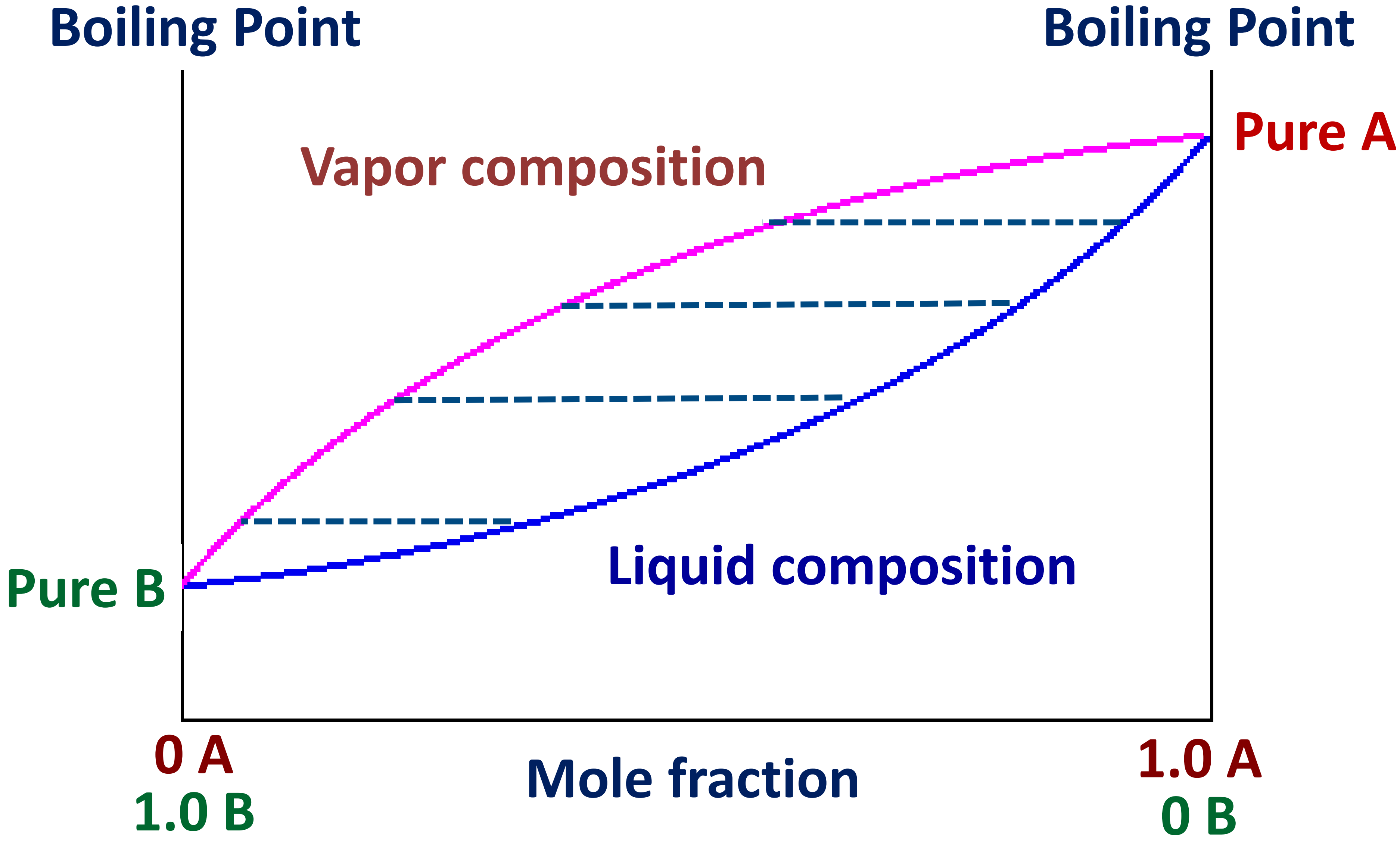
Mole fraction

1.0 A
0 B

Composition of Vapor over boiling liquid

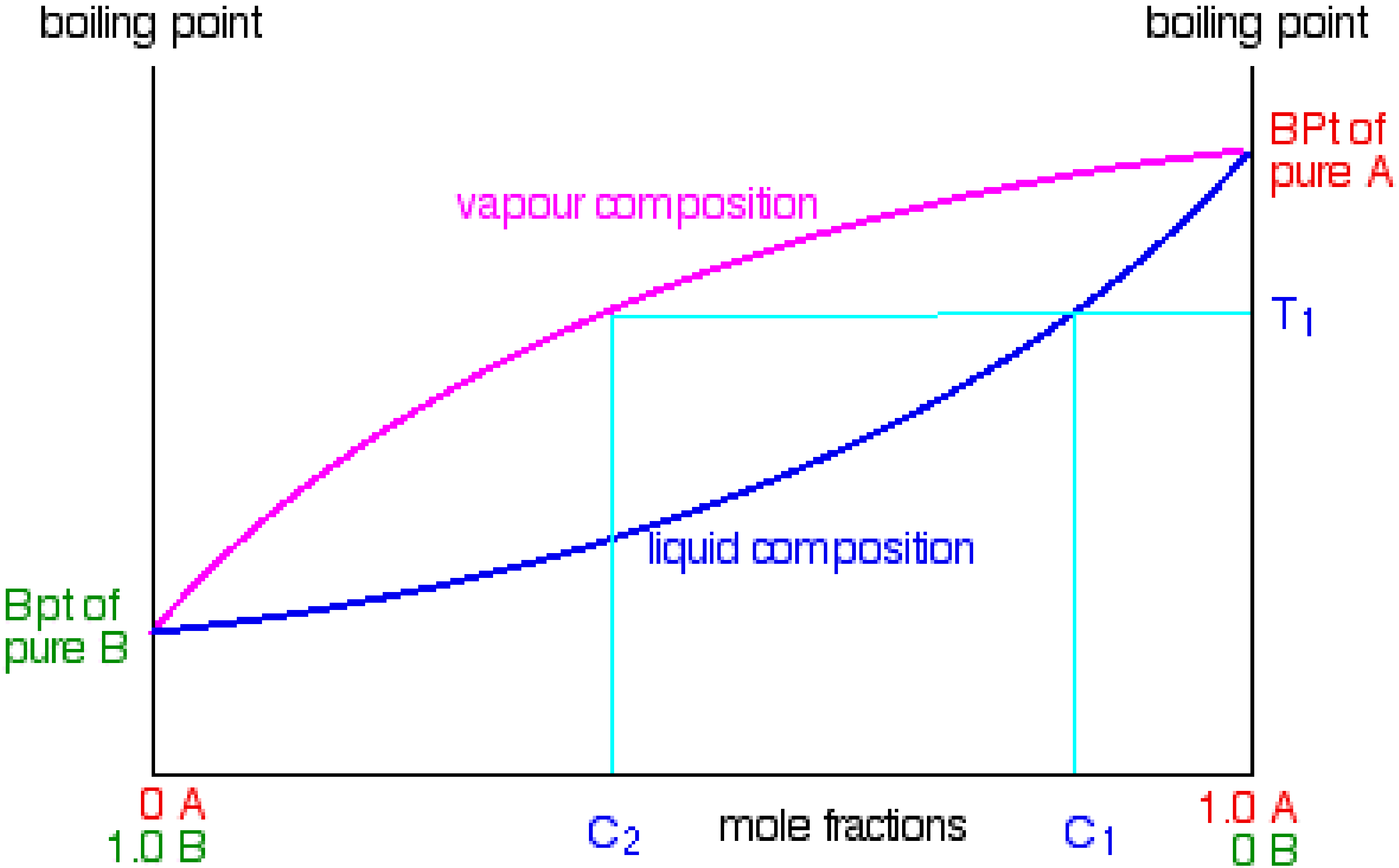
Composition of liquid

Liquids of different compositions



- If you boil a liquid mixture, you can find out the temperature it boils at, and the composition of the vapor over the boiling liquid.

- For example, in the next diagram, if you boil a liquid mixture C_1, it will boil at a temperature T_1 and the vapor over the top of the boiling liquid will have the composition C_2.


boiling point
boiling point
BPt of pure A
vapour composition
T1
liquid composition
Bpt of pure B
0 A
1.0 B
C2
mole fractions
C1
1.0 A
0 B

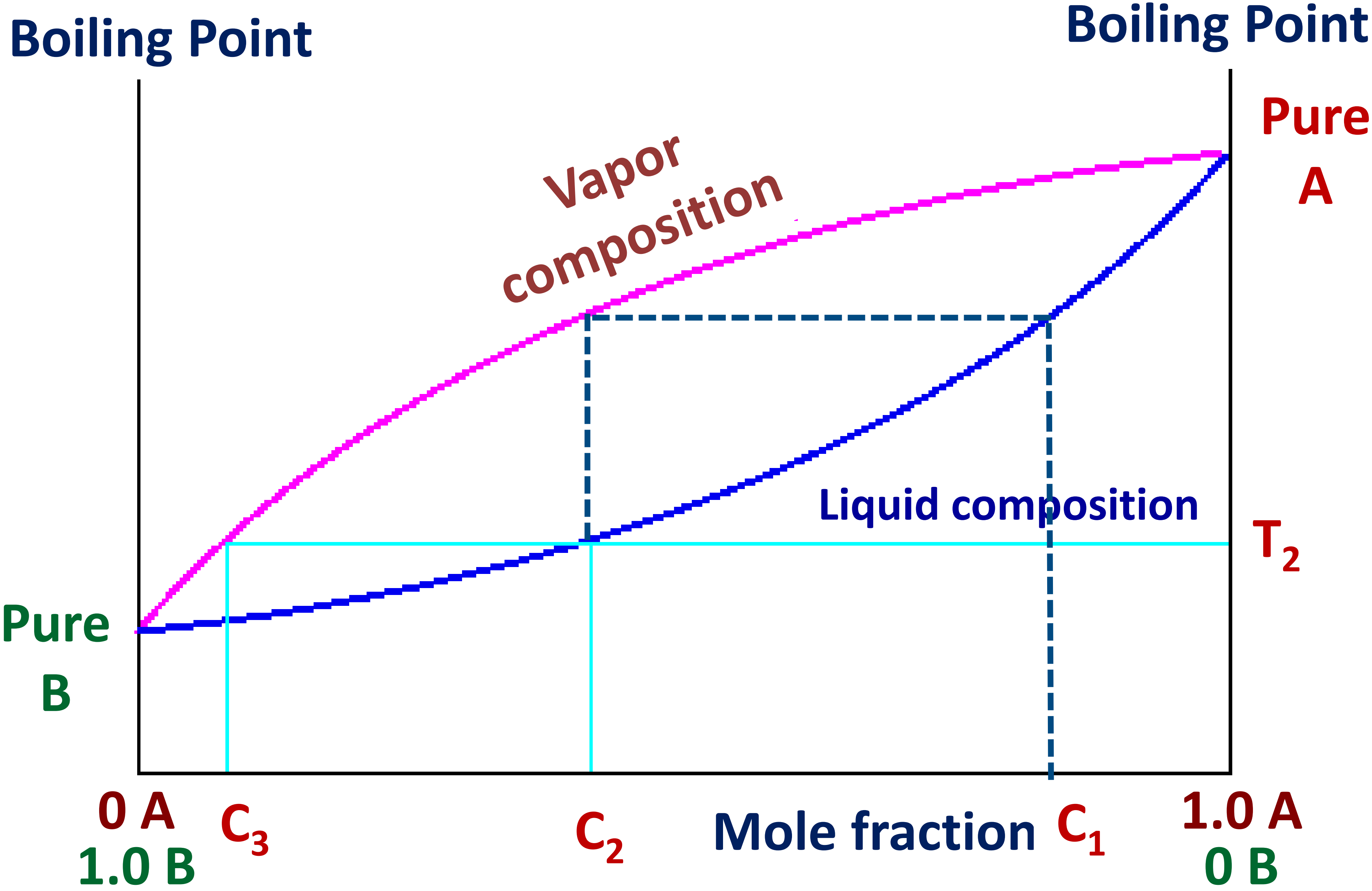
FD

- Suppose that you collected and condensed the vapor over the top of the boiling liquid and re-boiled it.

- You would now be boiling a new liquid which had a composition C_2.

- That would boil at a new temperature T_2, and the vapor over the top of it would have a composition C_3.

- You can see that we now have a vapor which is getting quite close to being pure B. If you keep on doing this (condensing the vapor, and then re-boiling the liquid produced - FD) you will eventually get pure B.


Boiling Point
Boiling Point
Pure A
Vapor composition
Liquid composition
T_2
Pure B
0 A
1.0 B
C_3
C_2
Mole fraction
C_1
1.0 A
0 B

Exercise

- If 1.0 mol of A is mixed with 2.0 mol of B, the resulting mixture boils (at 1.0 atm) at a temperature at which the VP of pure A is 1140 torr and that of pure B is 570 torr. Calculate the composition of the vapor?

Solution

- Mixture boiled at 1 atm $\Rightarrow$ P_T (at boiling)=1 atm.
- Ideally at any given temperature, $P_T = P_A + P_B$
- Raoult's law, $P_A = X_A P_A^0$ and $P_B = X_B P_B^0$, where X_A & X_B are the mole fractions of A & B in solution.

- Note the importance of giving the vapor pressures of pure A (P_A^0) & B (P_B^0) at the **same temperature** of boiling their mixture. It is not necessary that they individually boil at this temperature.

$$P_A = X_A P_A^0 = \frac{1.0}{1.0 + 2.0} \times 1140 = 380 \text{ torr}$$

$$P_B = X_B P_B^0 = \frac{2.0}{1.0 + 2.0} \times 570 = 380 \text{ torr}$$

$$\boxed{P_{Total} = P_A + P_B = 760 \text{ torr} = 1 \text{ atm}}$$

Dalton’s Law ⇨

$$P_A = X_{A(vapor)} P_{T(vapor)}$$

$$P_B = X_{B(vapor)} P_{T(vapor)}$$

- These partial pressures of gases inform about the composition of gases in the vapor

$$X_{A(vapor)} = \frac{P_A}{P_{T(vapor)}} = \frac{380}{760} = 0.5$$

$$X_{B(vapor)} = \frac{P_B}{P_{T(vapor)}} = \frac{380}{760} = 0.5$$

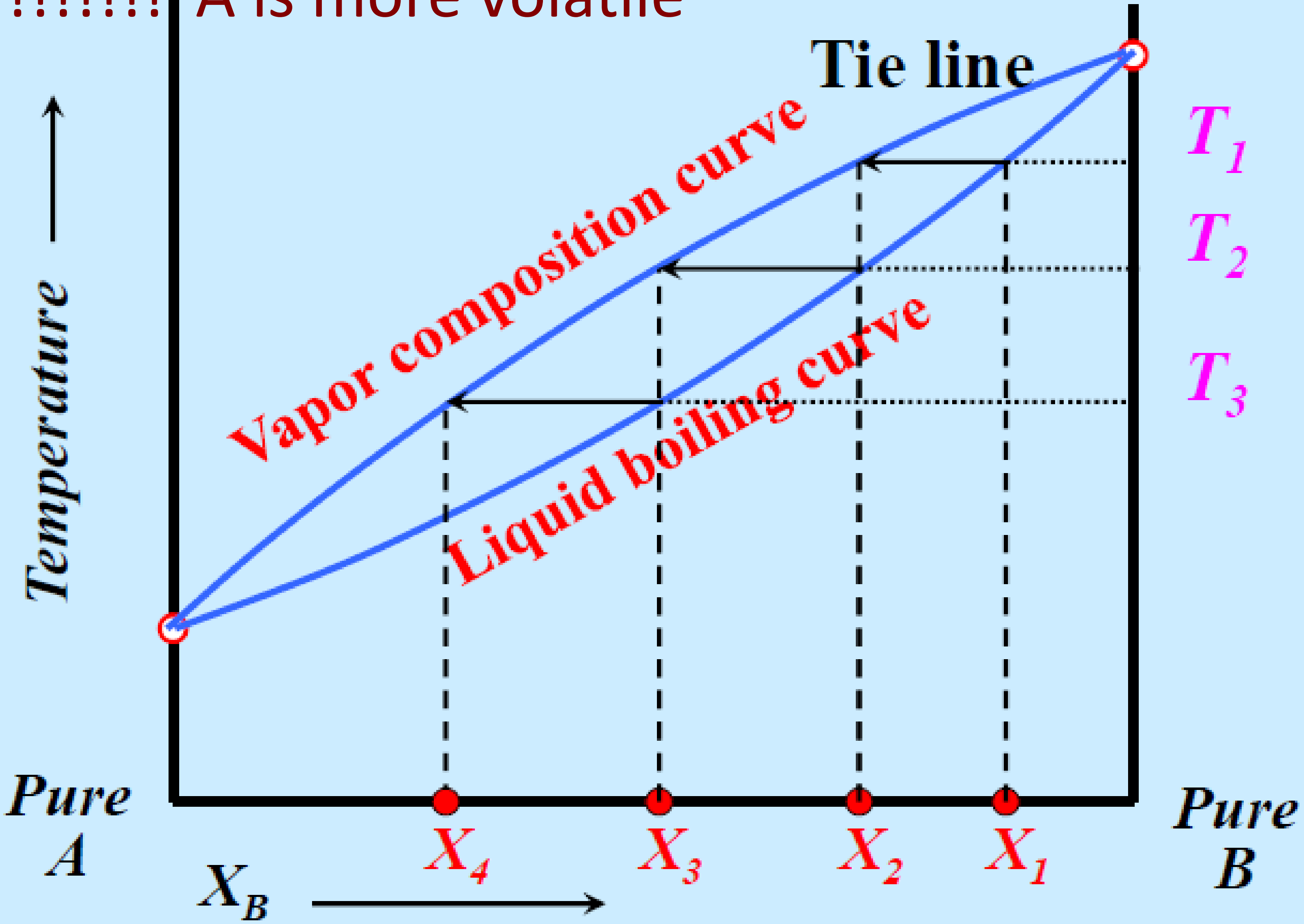
Compare before distillation in the liquid

$$X_A = 0.33 \quad X_B = 0.67$$

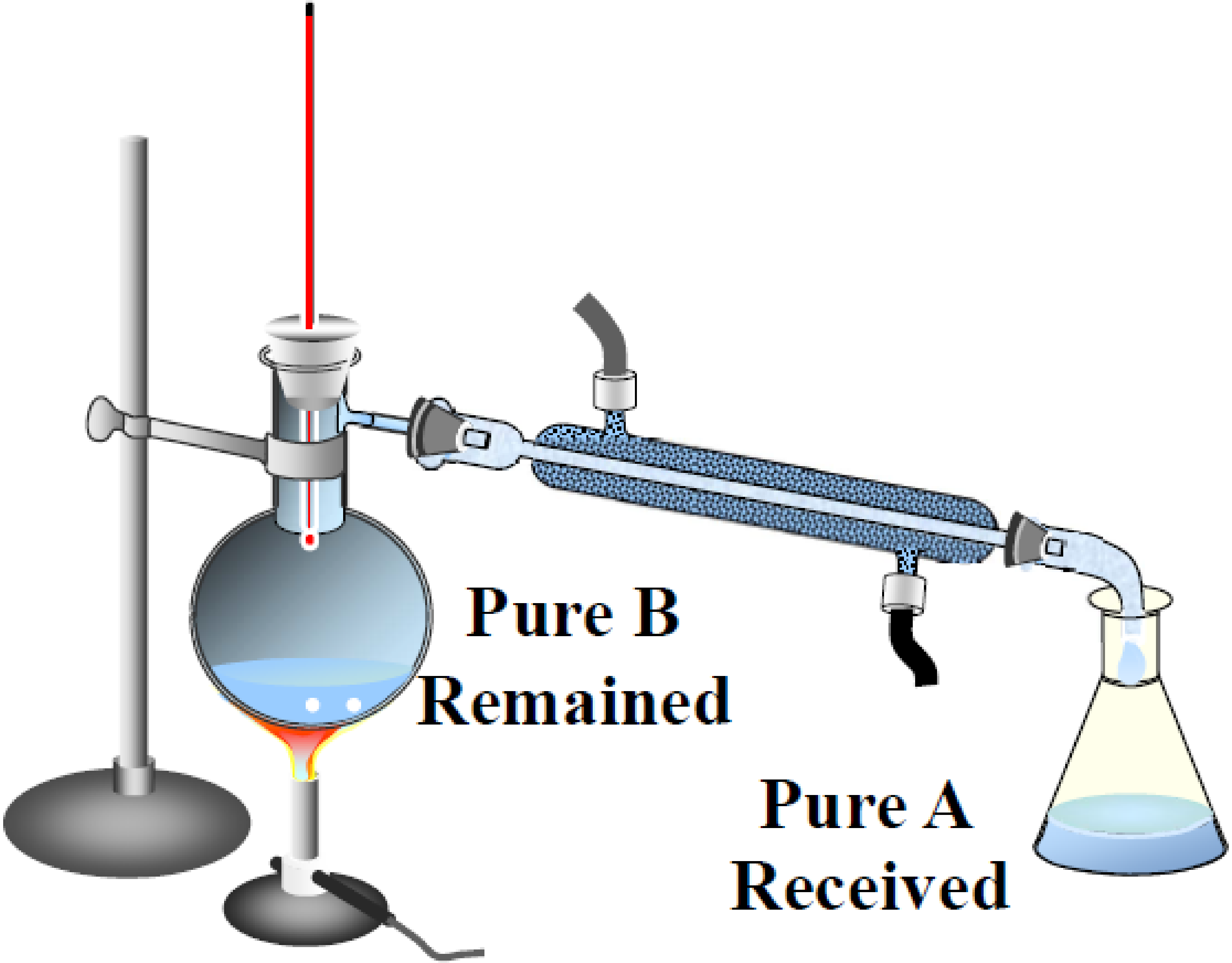
Ideal solutions

BP decreases until finishing separation

!!!!!!!! A is more volatile



Ideal solutions



Pure B
Remained

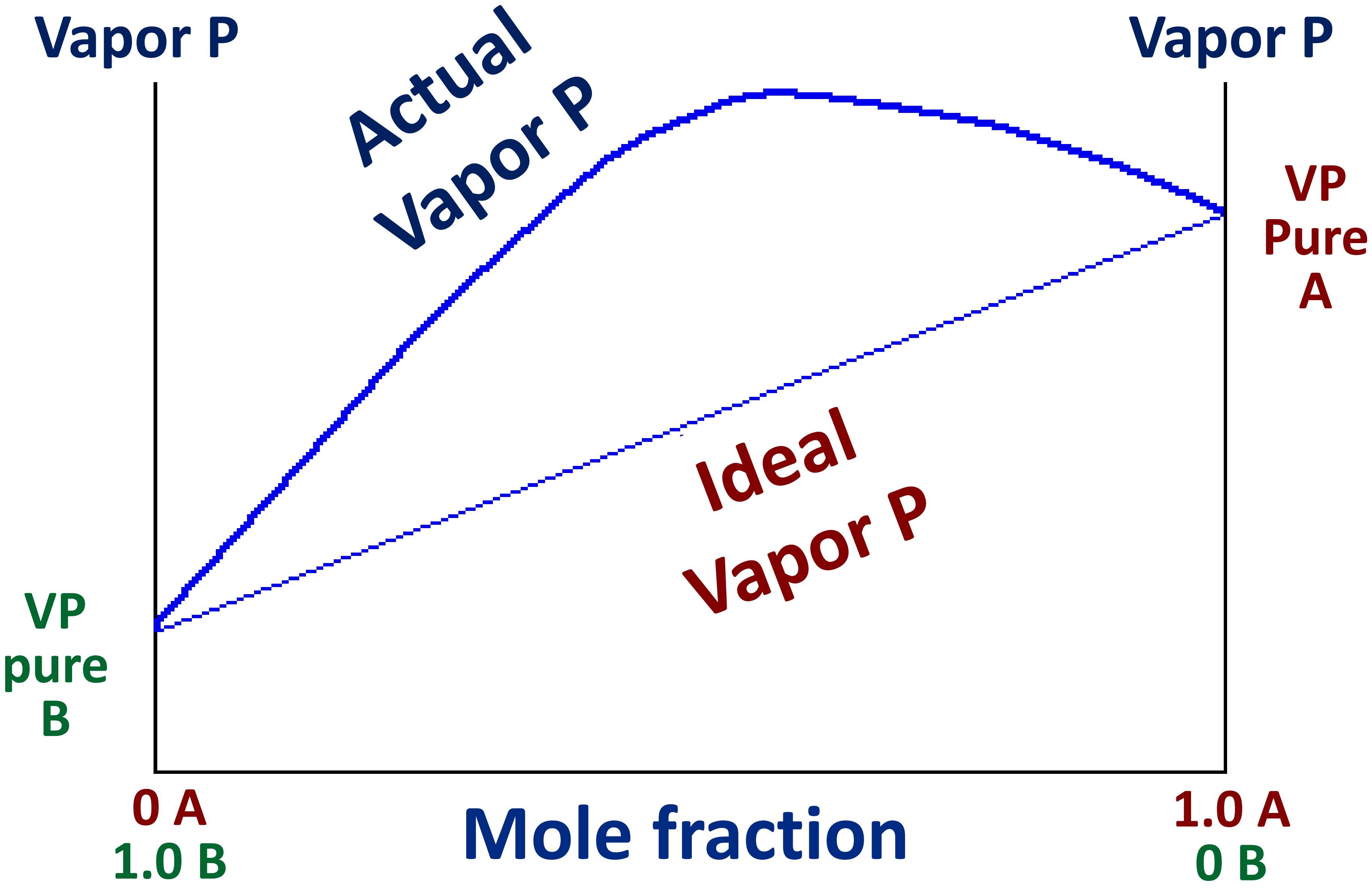
Pure A
Received

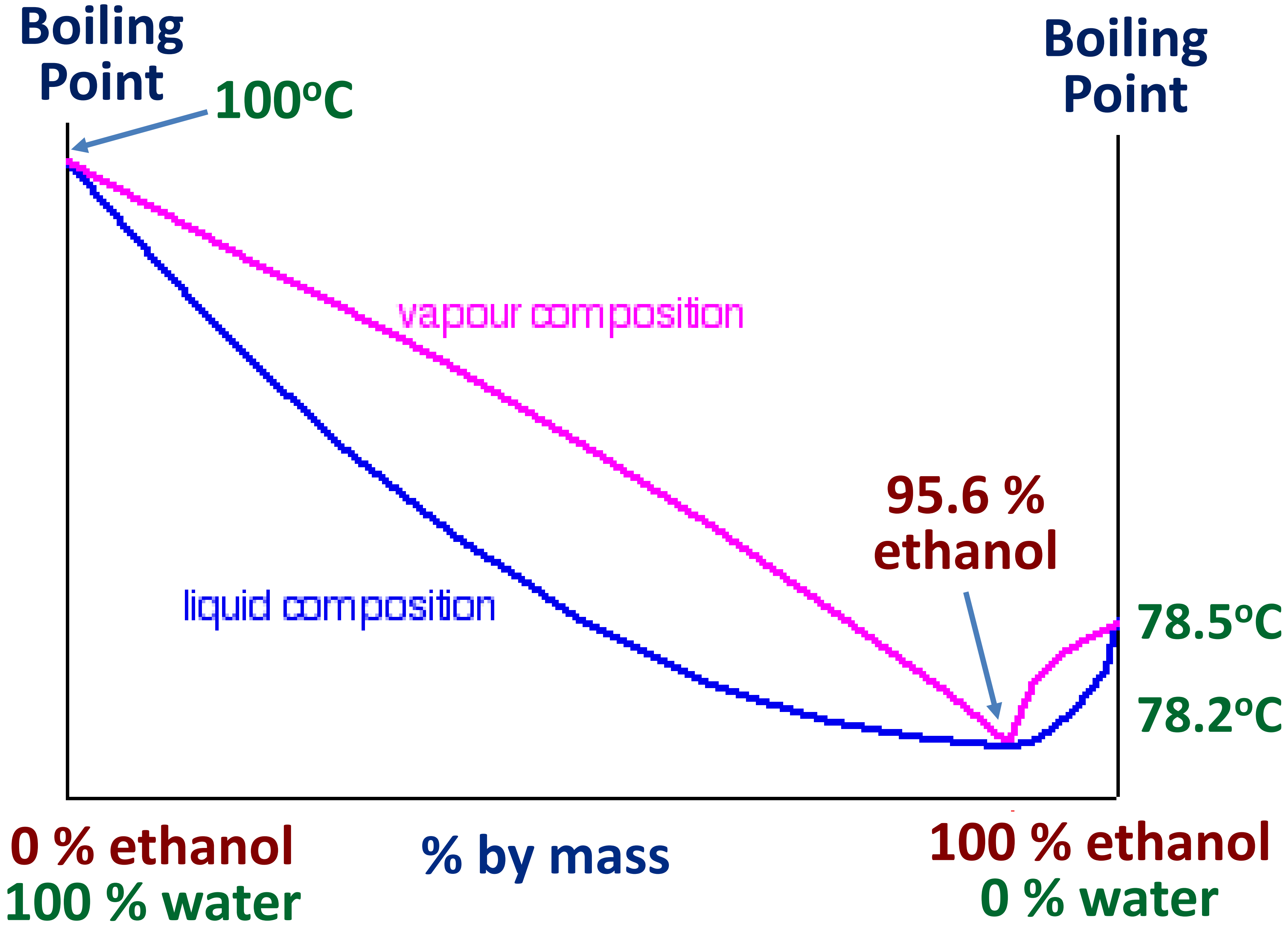
Non-ideal solutions

An azeotrope, constant boiling mixture or an azeotropic mixture: is a mixture of two volatile liquids with a specific composition which on boiling the vapor composition is exactly the same as the liquid. It has a constant boiling point.

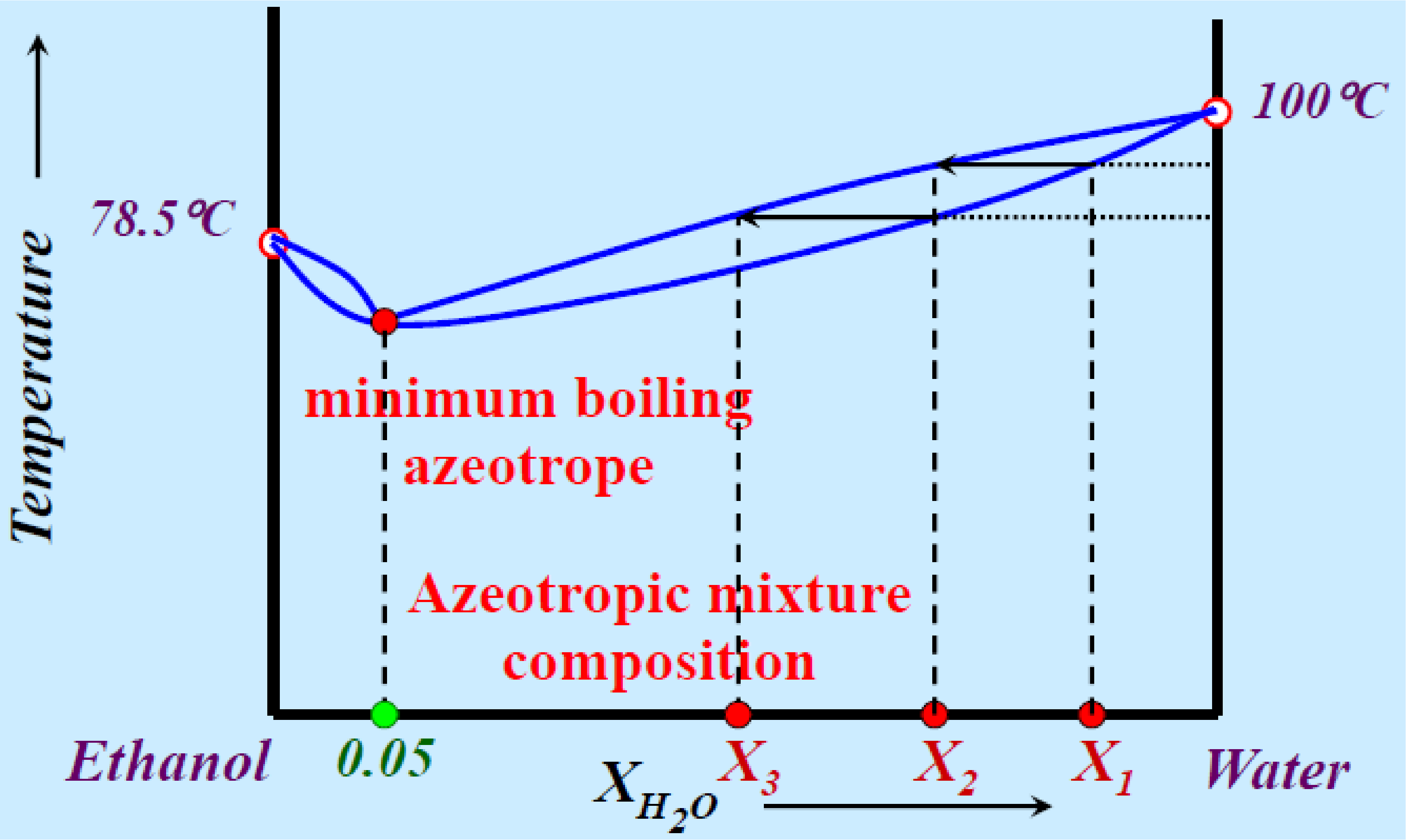
either → Positive deviation

or → Negative deviation

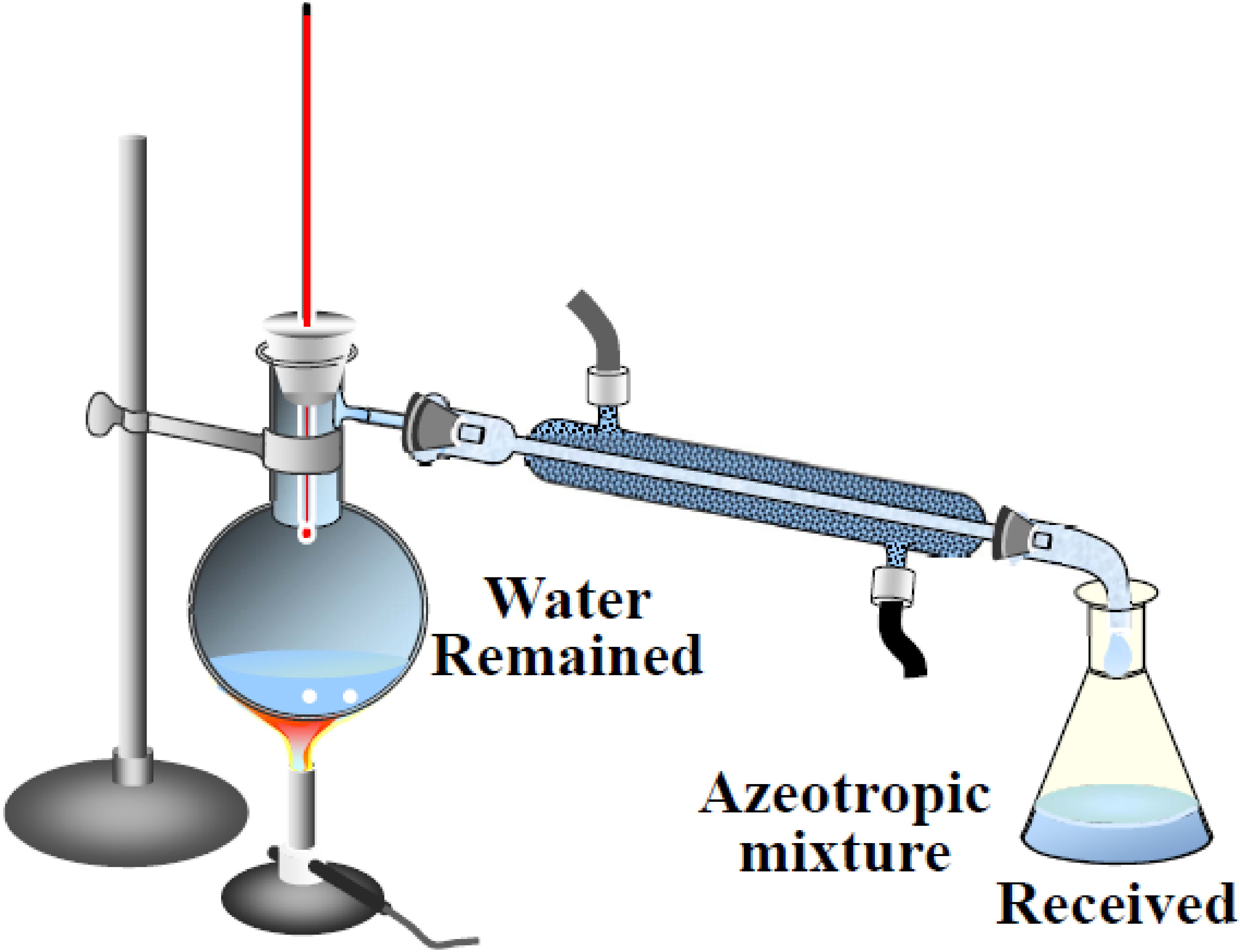

Vapor P
Vapor P
Actual Vapor P
Ideal Vapor P
VP Pure A
VP pure B
0 A
1.0 B
1.0 A
0 B
Mole fraction


Boiling Point
100°C
Boiling Point
vapour composition
liquid composition
95.6 % ethanol
78.5°C
78.2°C
0 % ethanol
100 % water
% by mass
100 % ethanol
0 % water

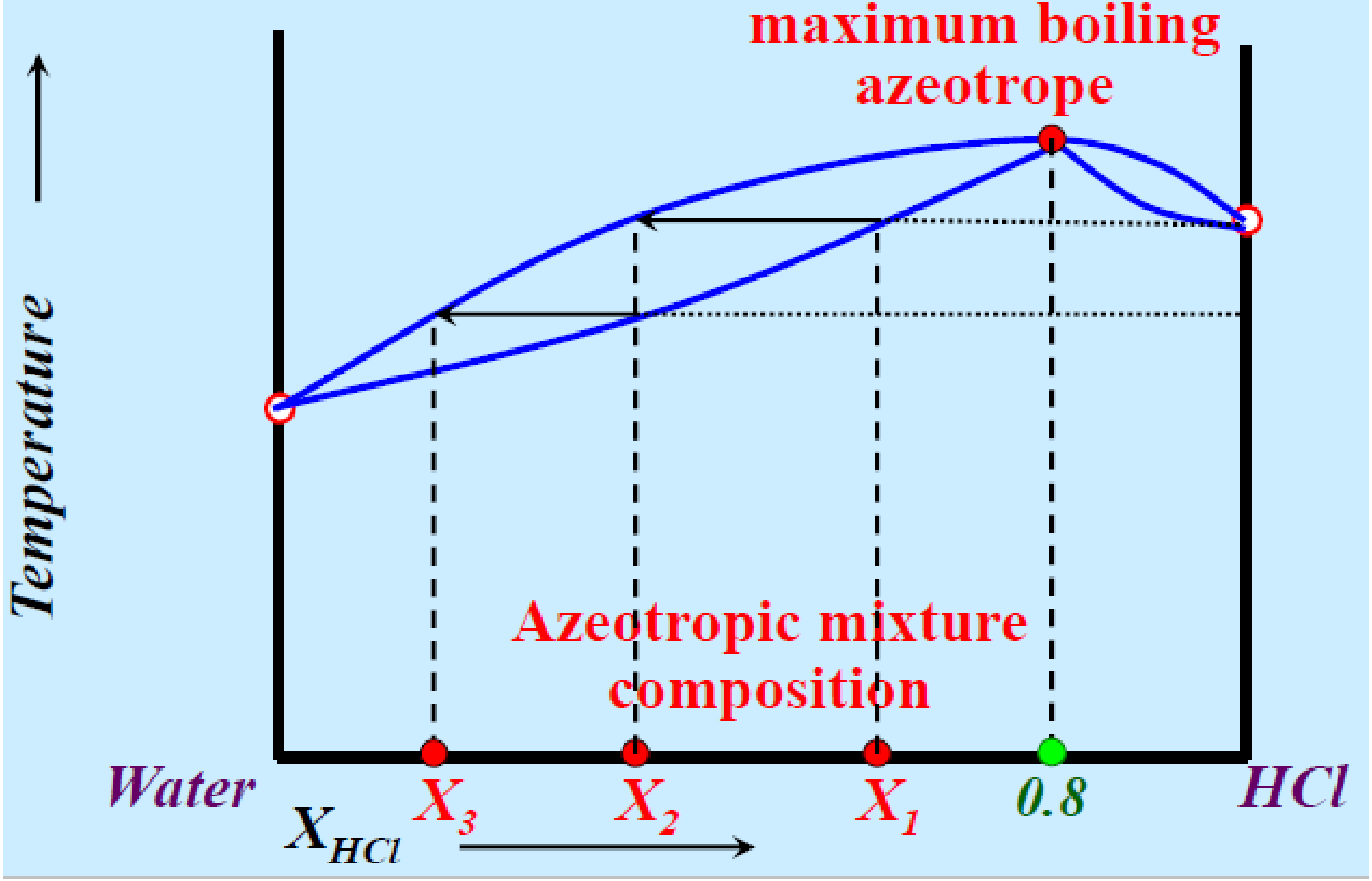
+ve deviation



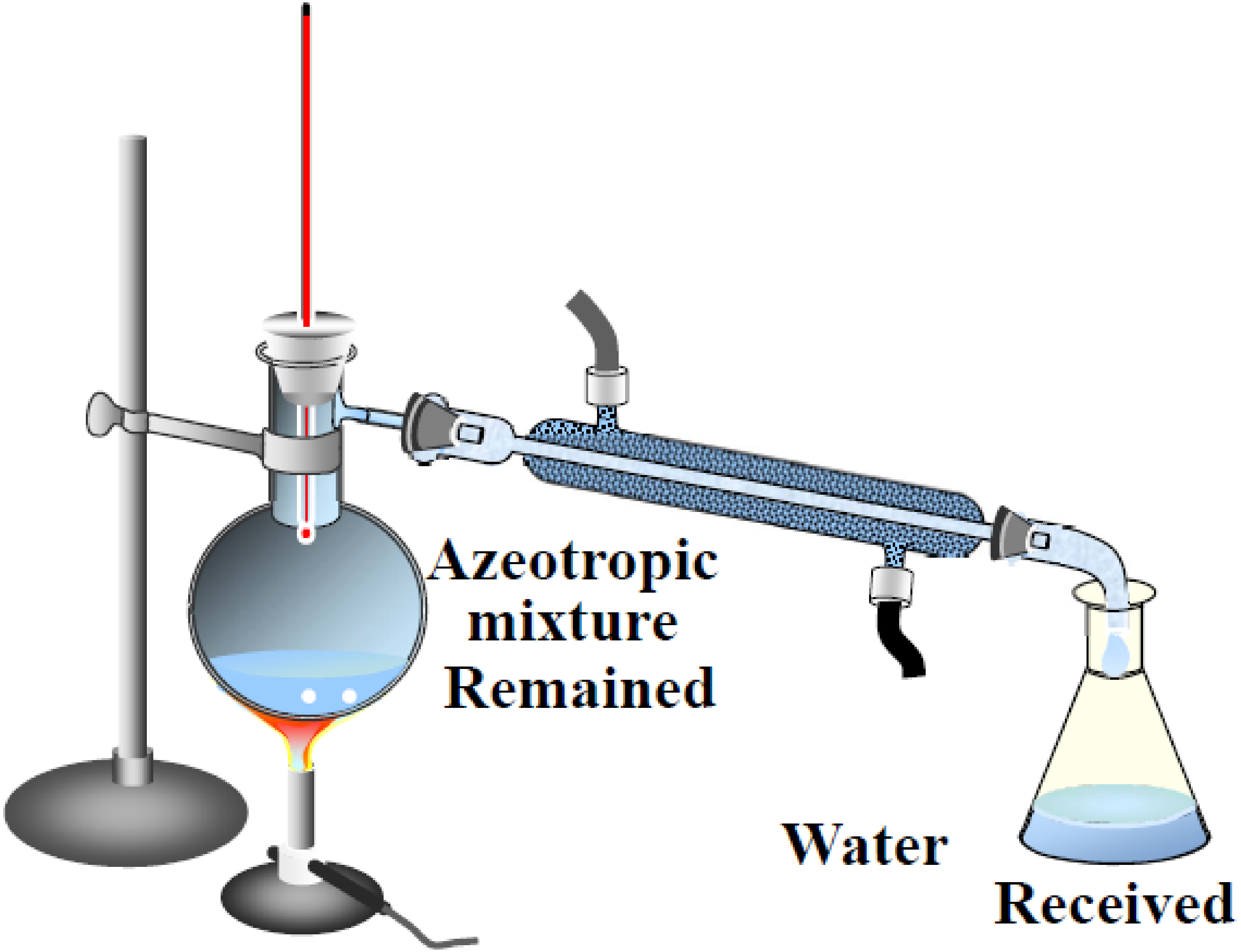
+ve deviation



–ve deviation



–ve deviation



Distribution Law

The distribution of a solute between two non-miscible solvents.

Nernst’s “Partition” Distribution law

- “When a solute is taken up with two immiscible liquids, in both of which the solute is soluble, the solute distributes itself between the two liquids in such a way that the ratio of its concentration in the two liquid phases is constant at a given temperature provided the molecular state of the distributed solute is same in both the phases”. i.e.,

$$\boxed{\frac{C_A}{C_B} = k}$$

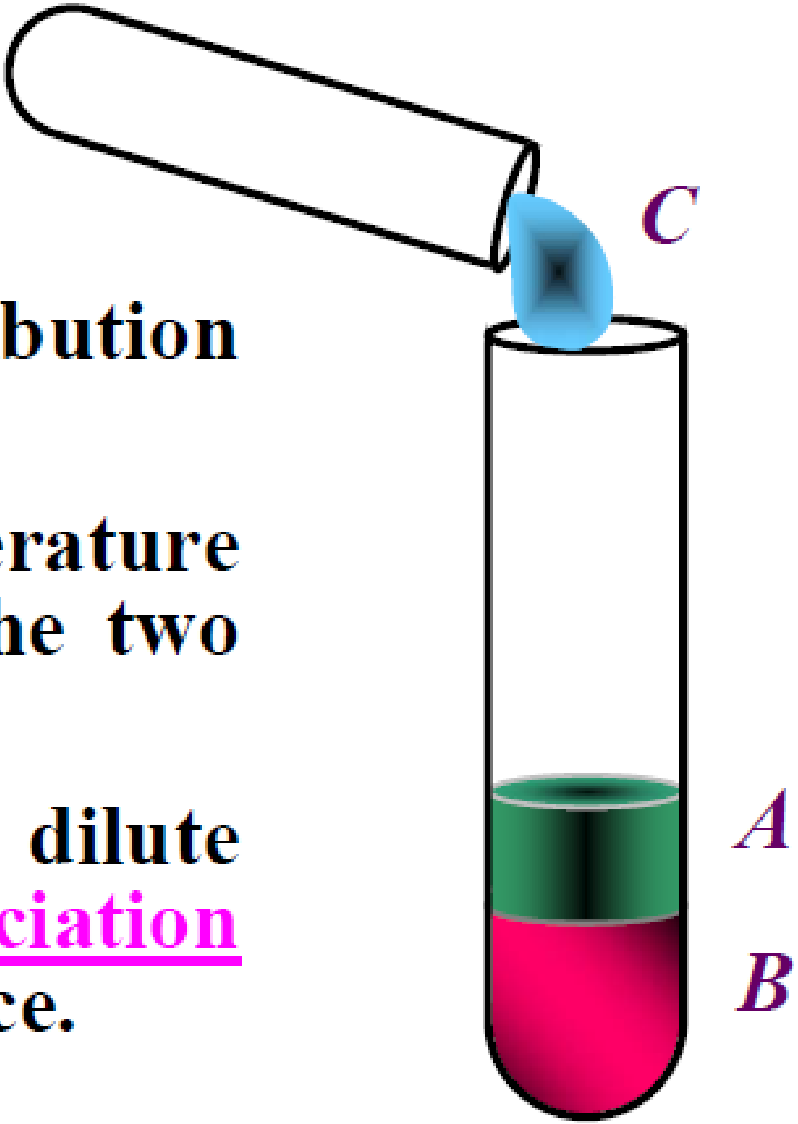
Distribution law

$$\frac{C_A}{C_B} = k$$

where k is the distribution coefficient.

It depends on the temperature and on the nature of the two liquids.

This law holds for dilute solutions where no association or dissociation takes place.



Association

When the solute associates to form double molecules in solvent A only:

$$\frac{\sqrt{C_A}}{C_B} = k$$

Dissociation

If the solute dissociates into two parts in solvent A only:

$$\frac{C^2{}_A}{C_B} = k$$

The phenomenon of distribution is used in extracting organic substances from their aqueous solutions by shacking with an immiscible organic solvent.

- **Ether**
- **benzene**
- **Chloroform**
- **Carbon tetrachloride**