Lecture 8b

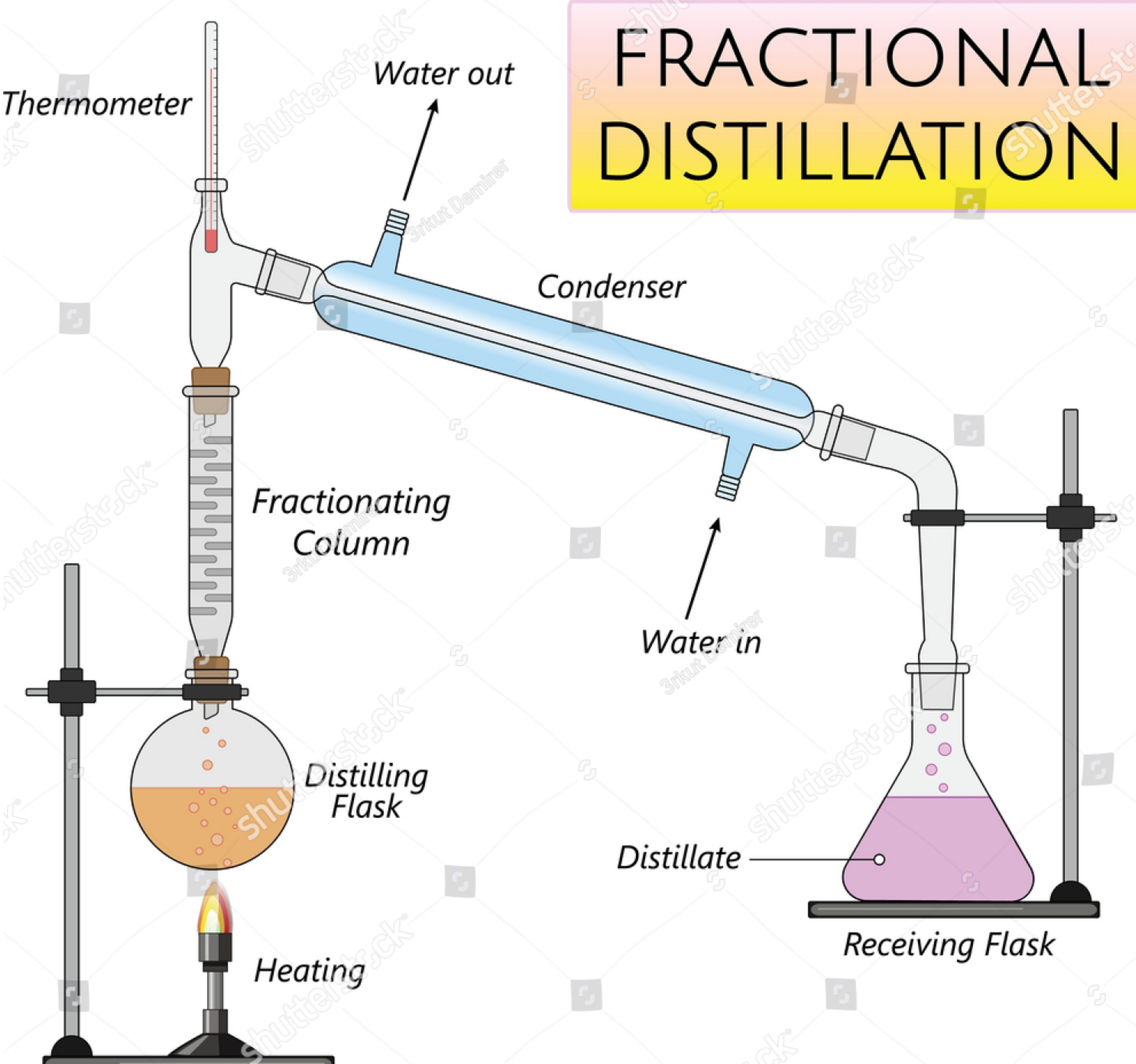
Spring 2022

General Chemistry II

Chem 102

Fractional distillation, FD

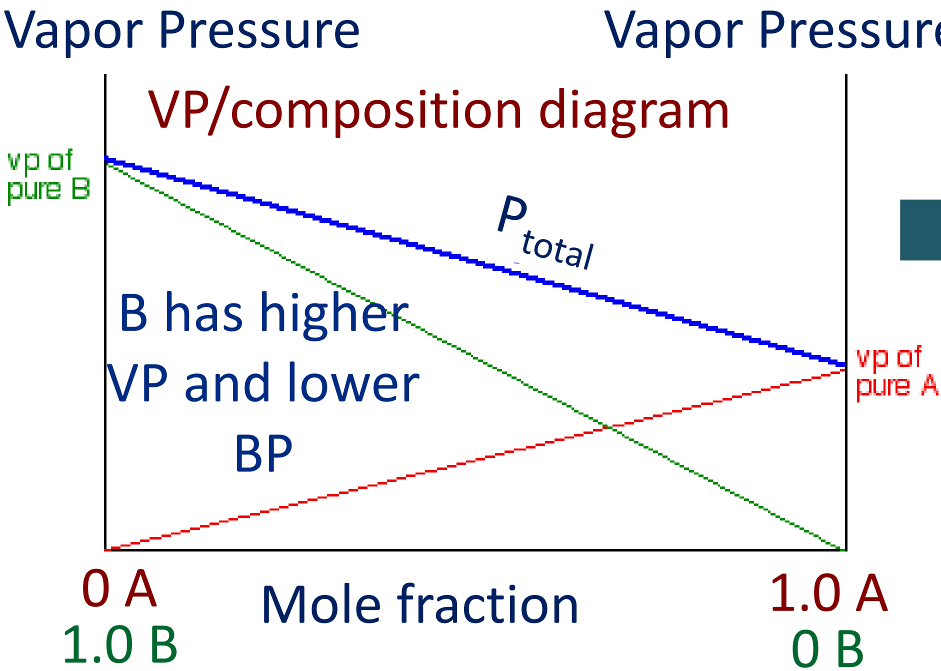
Ahmad Alakraa

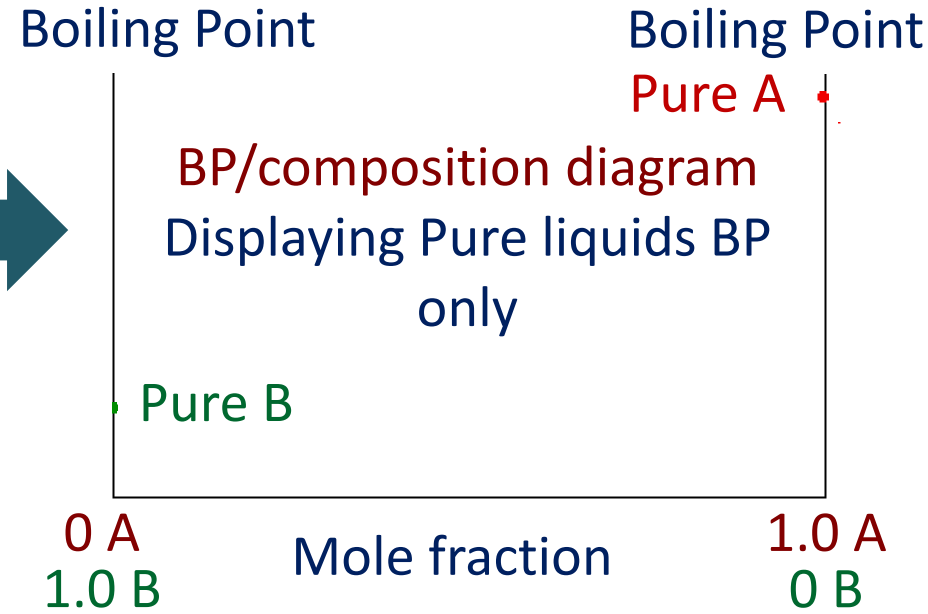

FRACTIONAL DISTILLATION
Thermometer
Water out
Condenser
Fractionating Column
Water in
Distilling Flask
Distillate
Receiving Flask
Heating

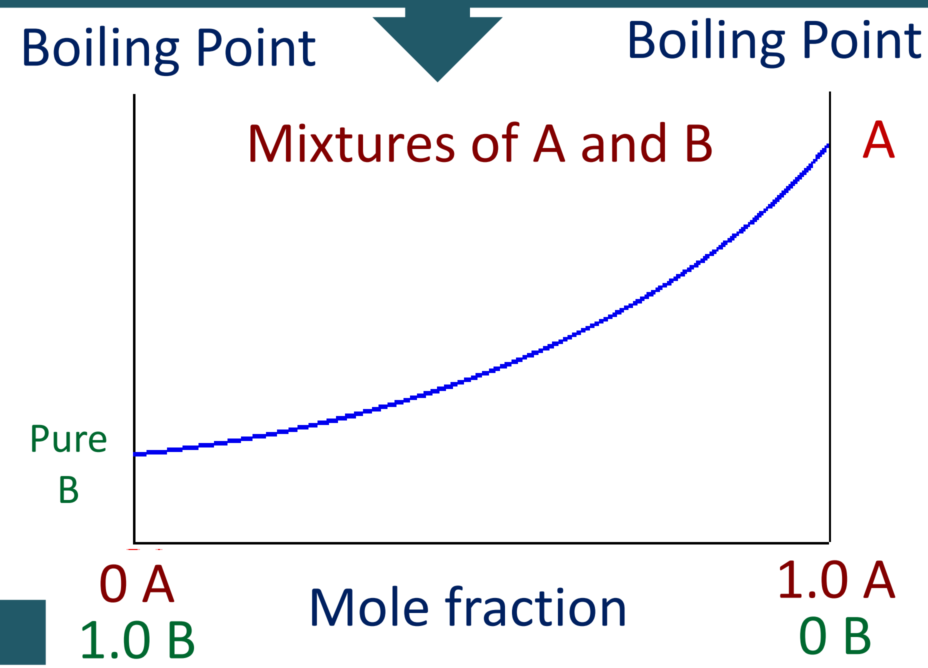
FD (Water + Ethanol)

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 !!!!!!!!.







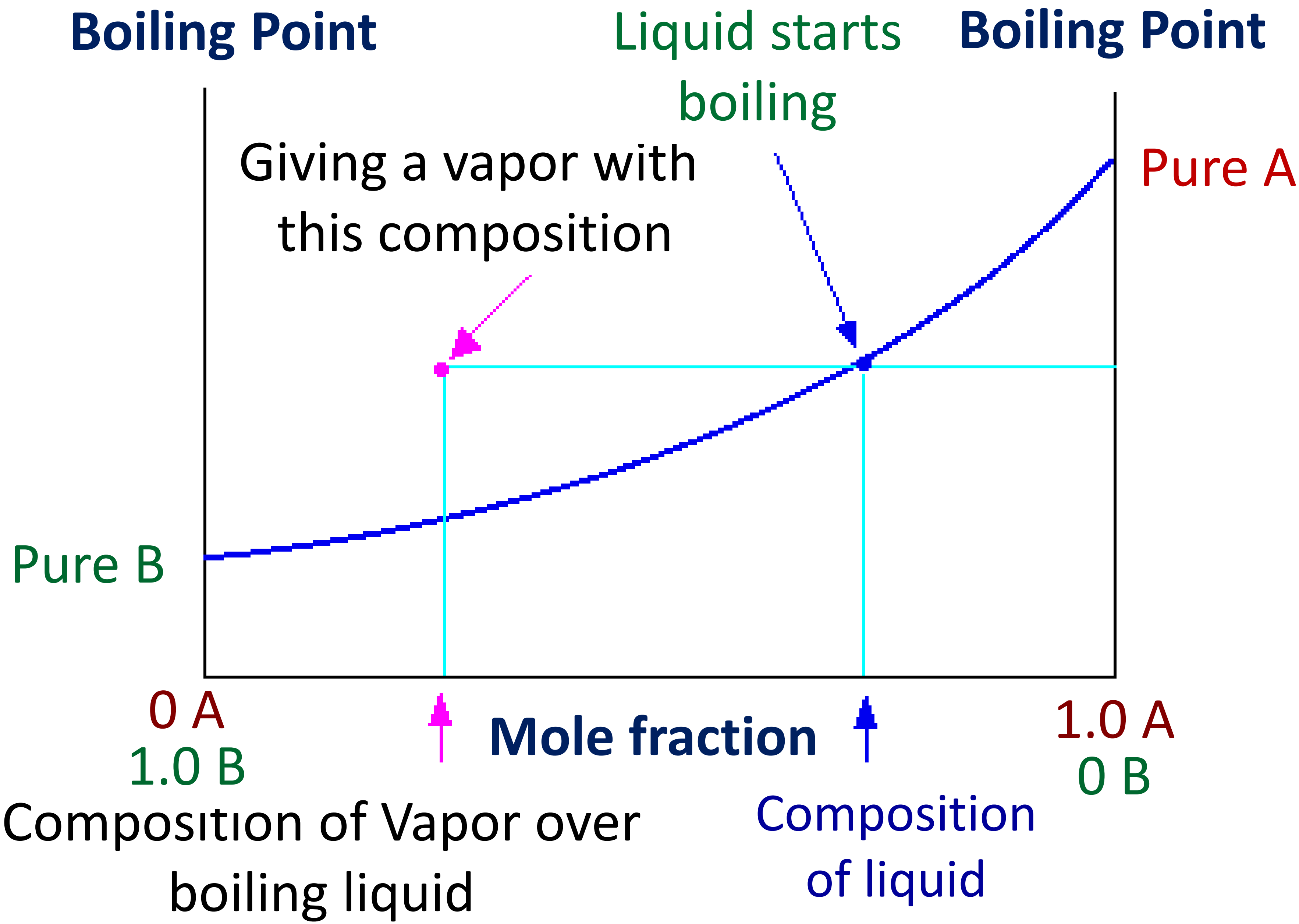
- To make this diagram useful, another line representing the composition of the vapor over the top of any particular boiling liquid is added.

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.

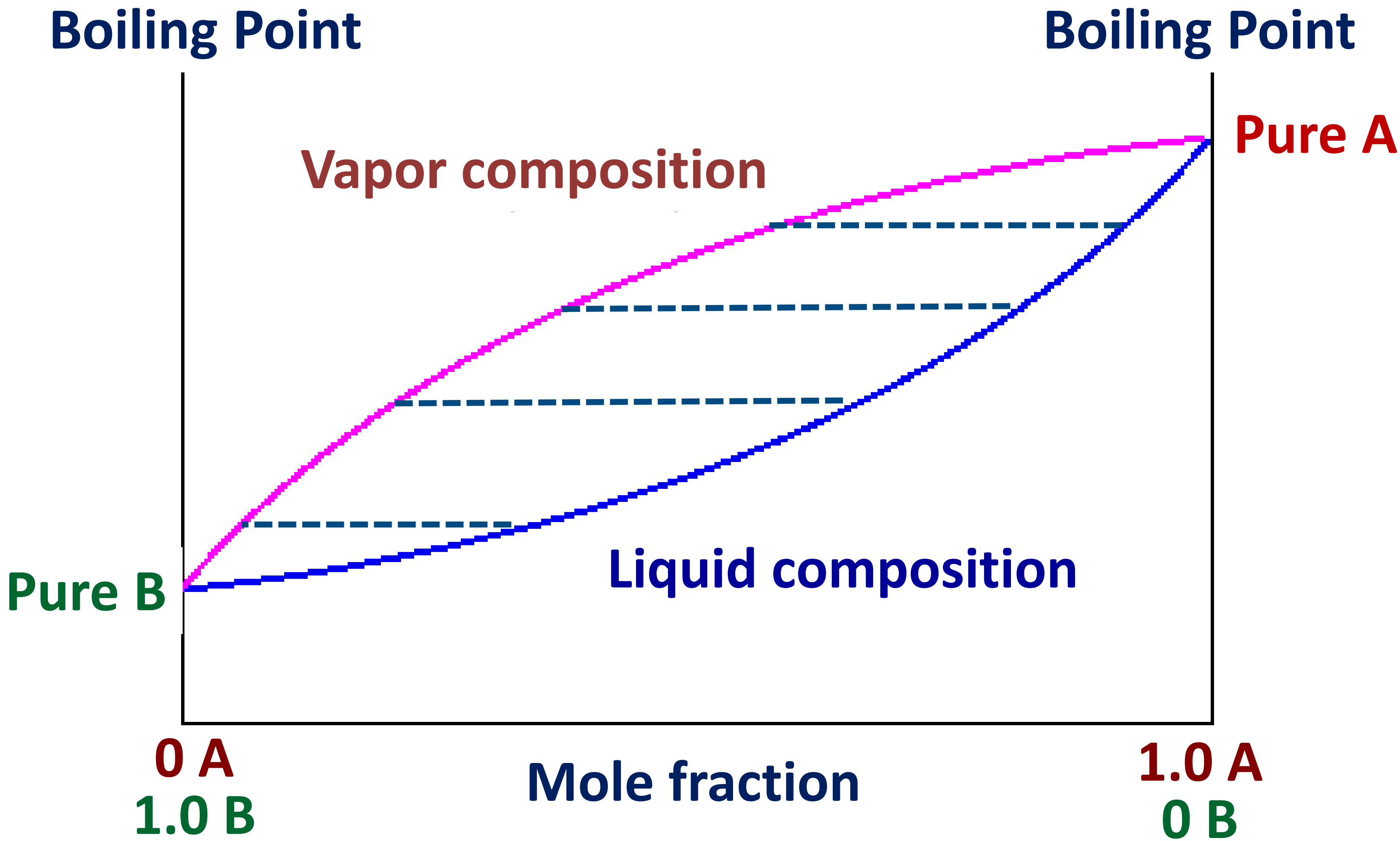
- If you boil this mixture, you would expect that Liquid B escapes to form a vapor more easily than Liquid A.

- 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).



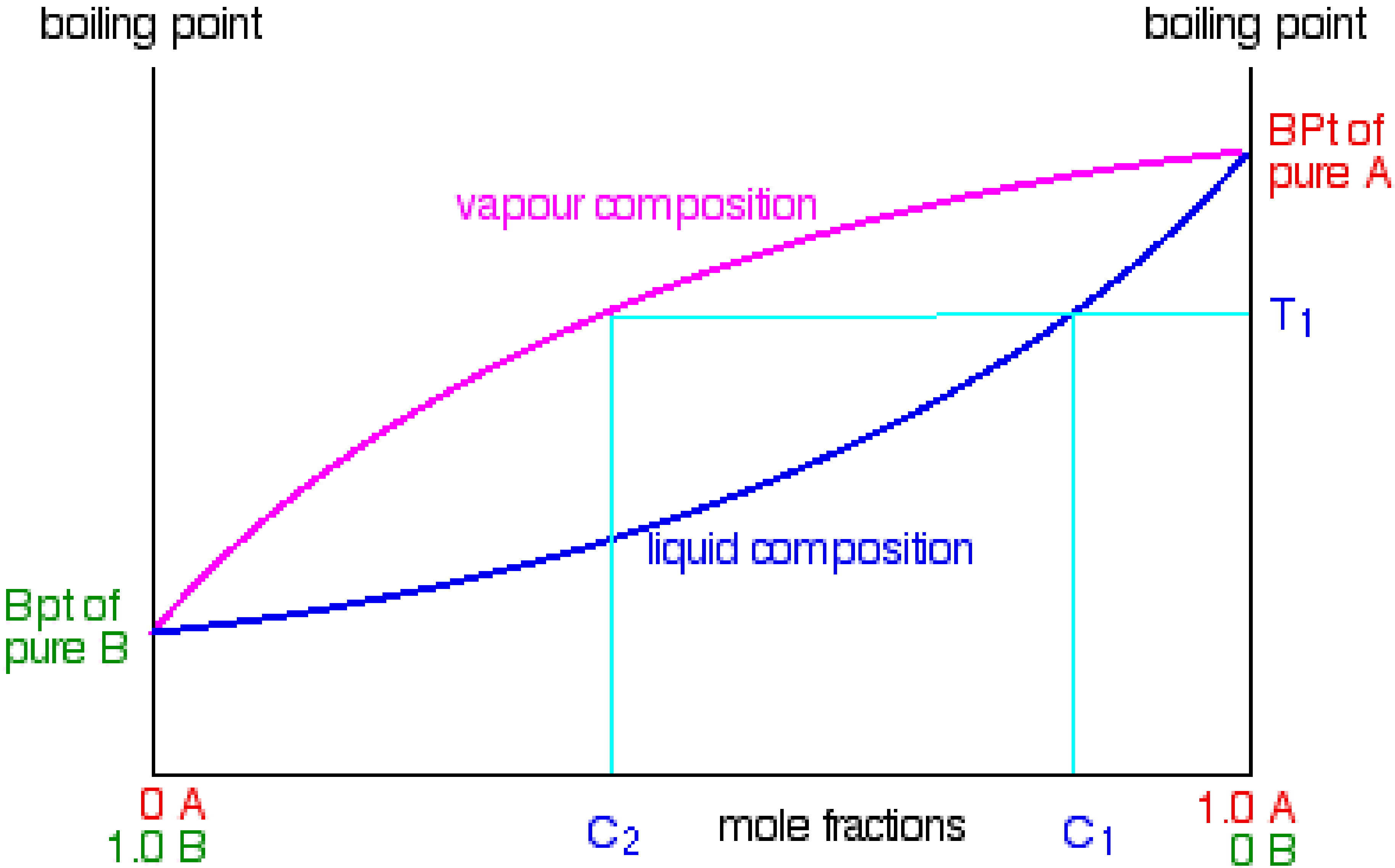
Boiling Point
Liquid starts boiling
Boiling Point
Giving a vapor with this composition
Pure A
Pure B
0 A
1.0 B
Mole fraction
1.0 A
0 B
Composition of Vapor over boiling liquid
Composition of liquid

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

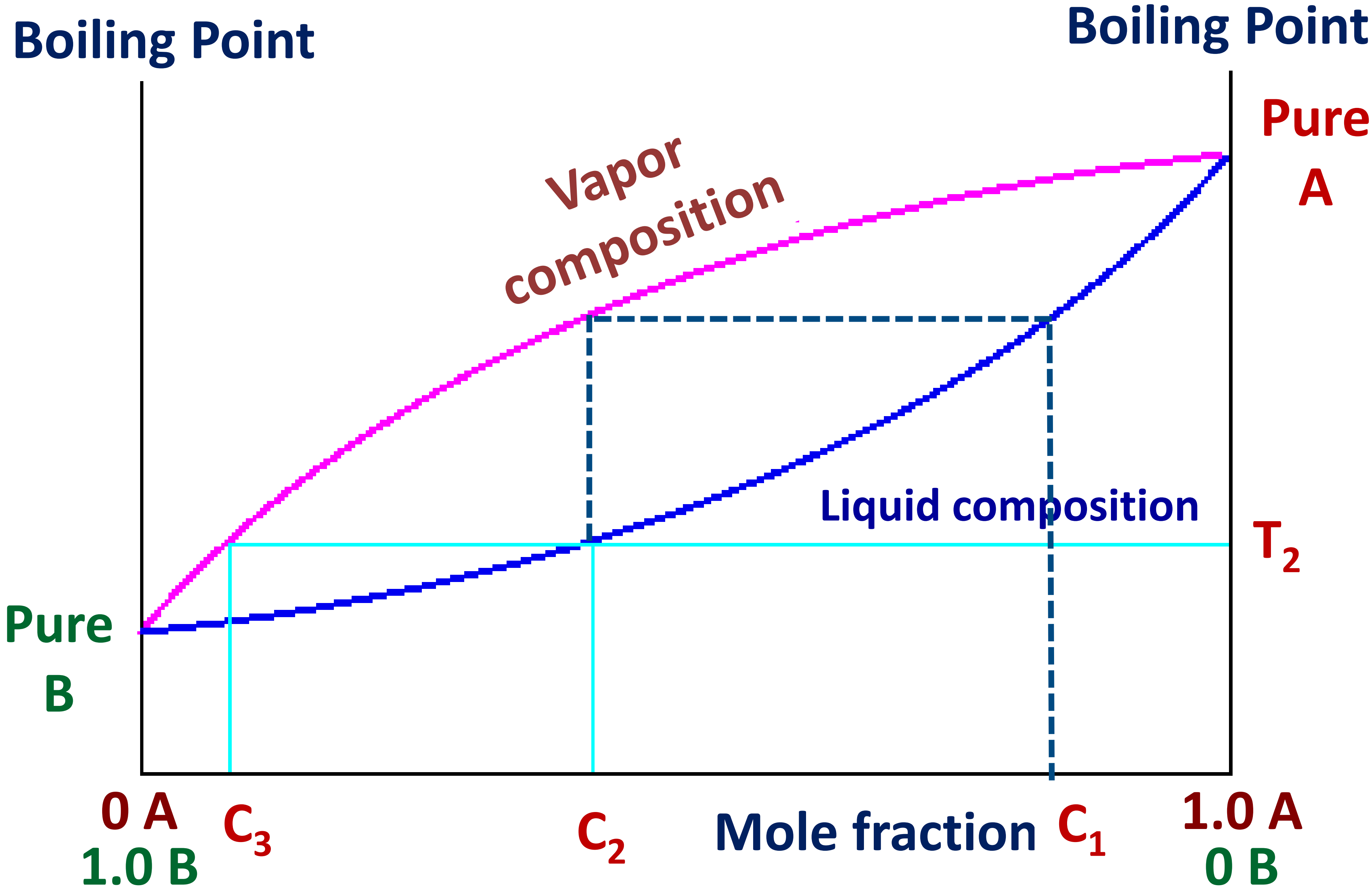
FD

- 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.

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

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

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

Dalton's Law →

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

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

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

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

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

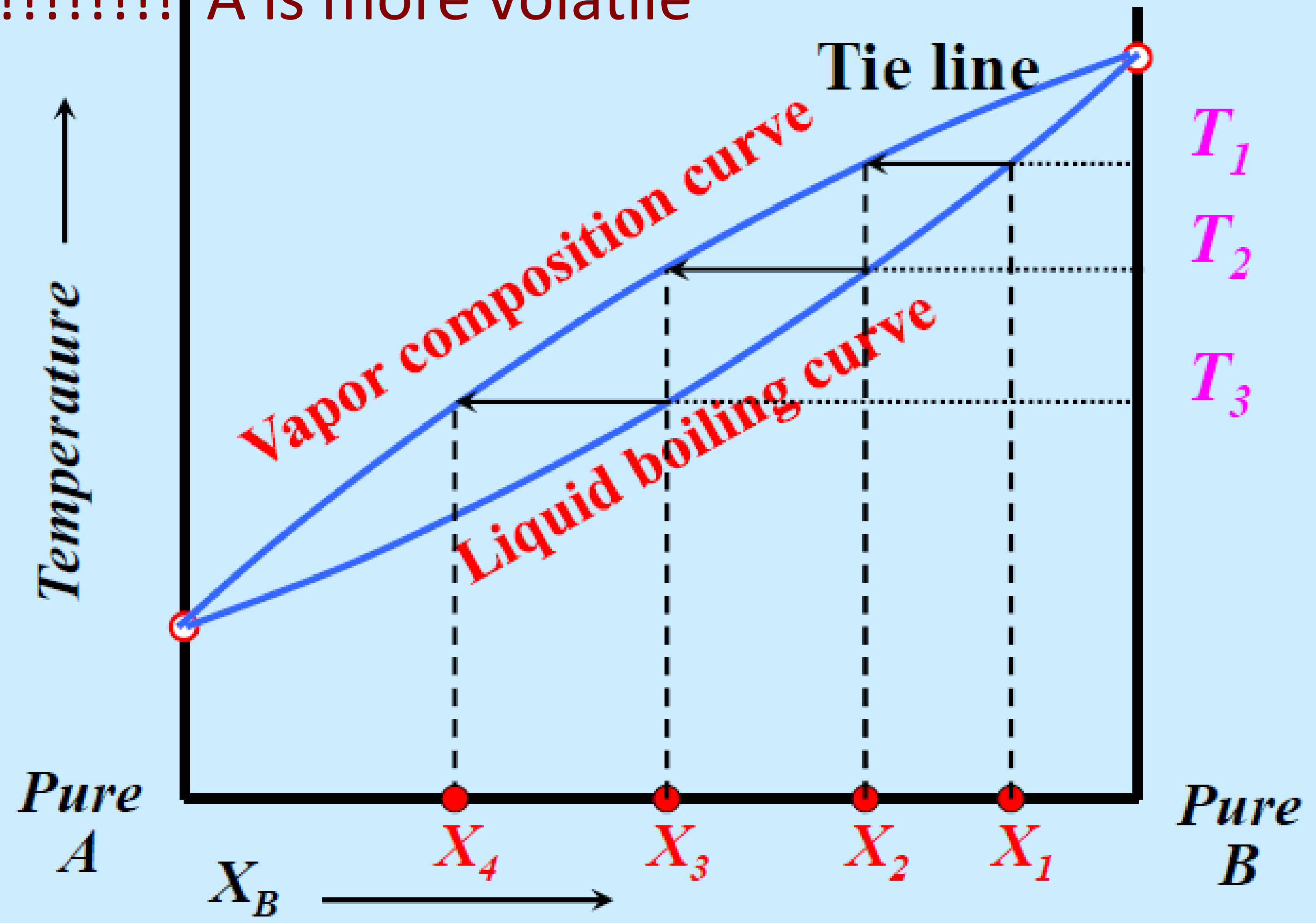
Compare before distillation in the liquid

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

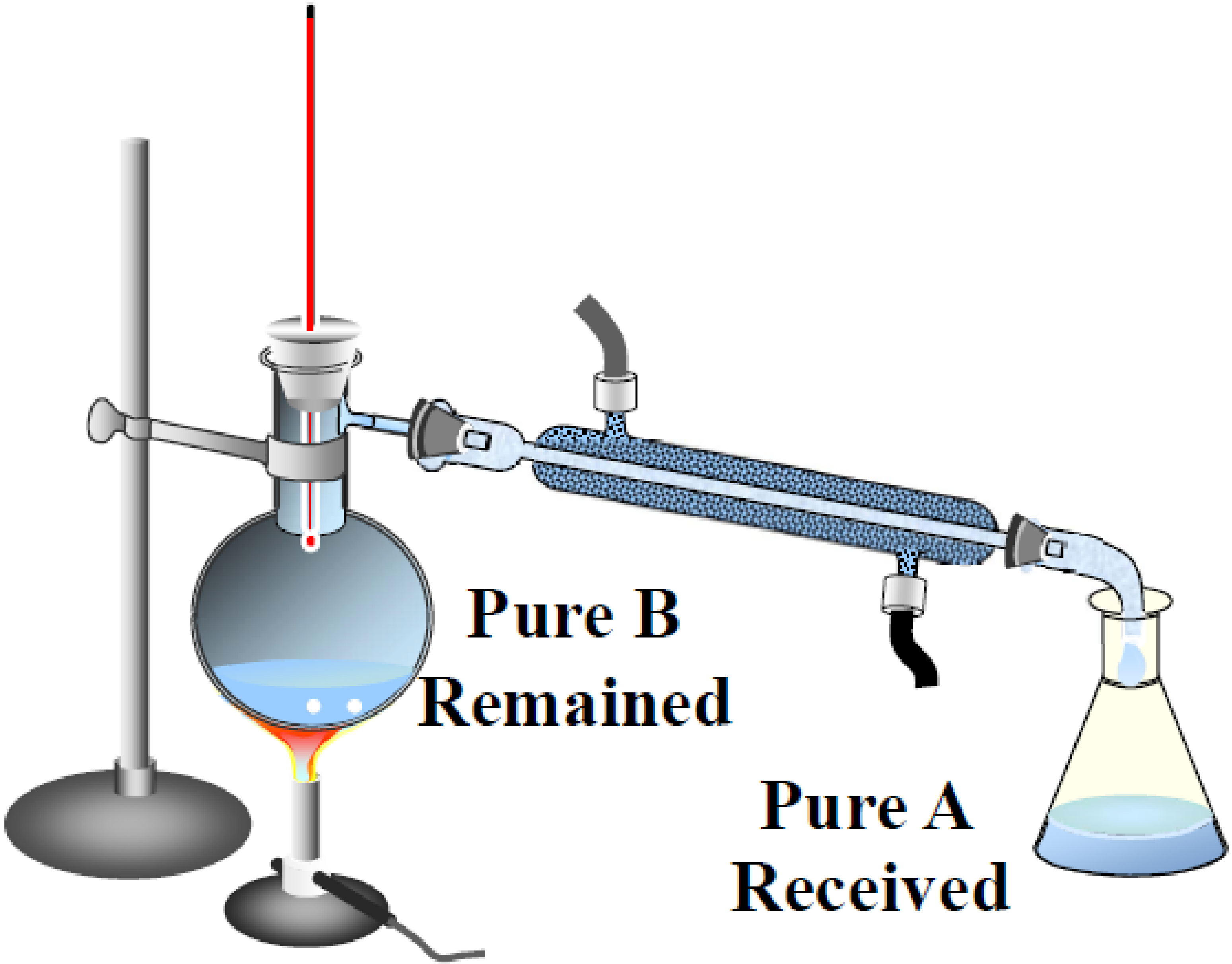
Ideal solutions

BP decreases until finishing separation

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



Ideal solutions

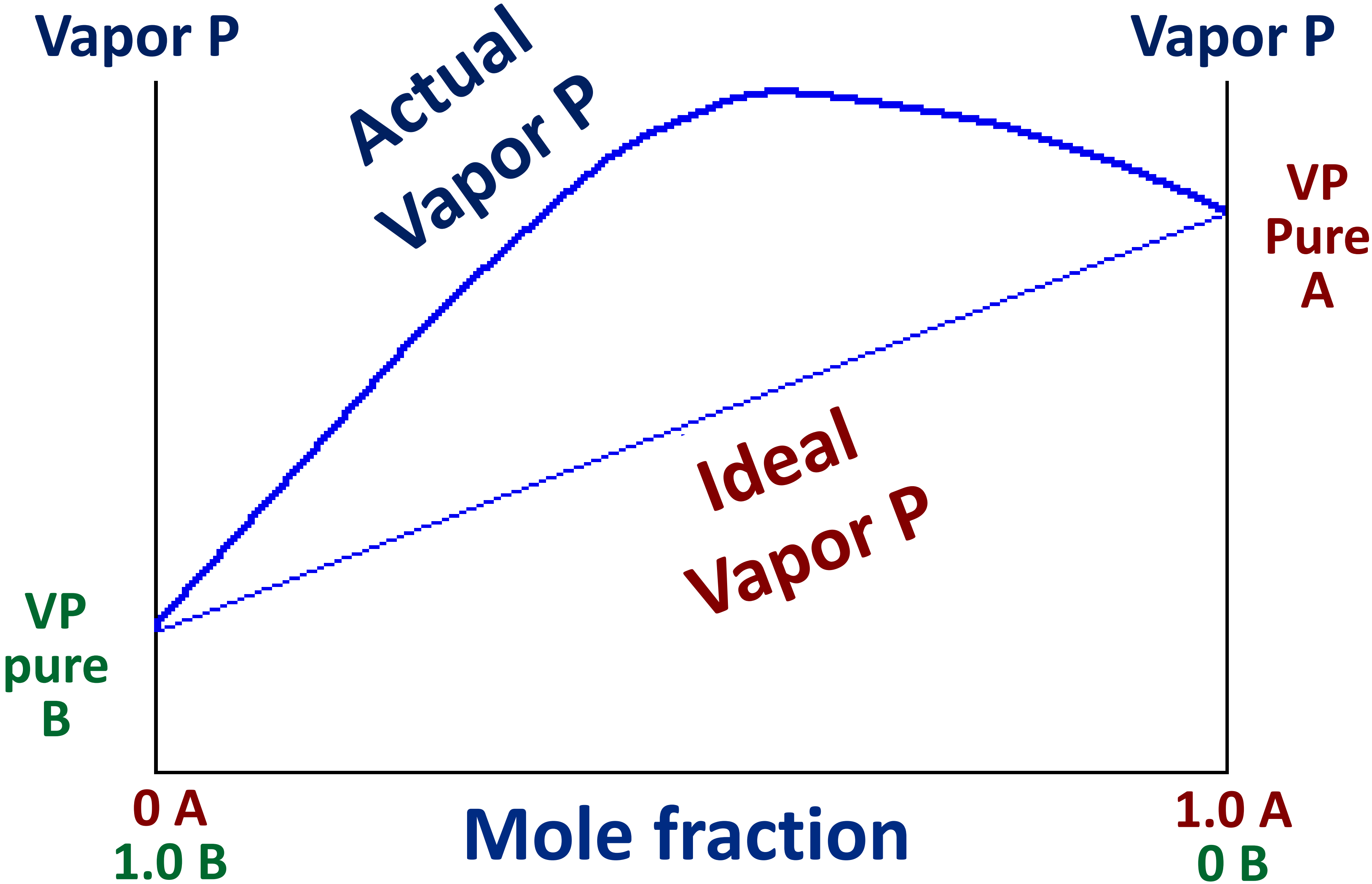


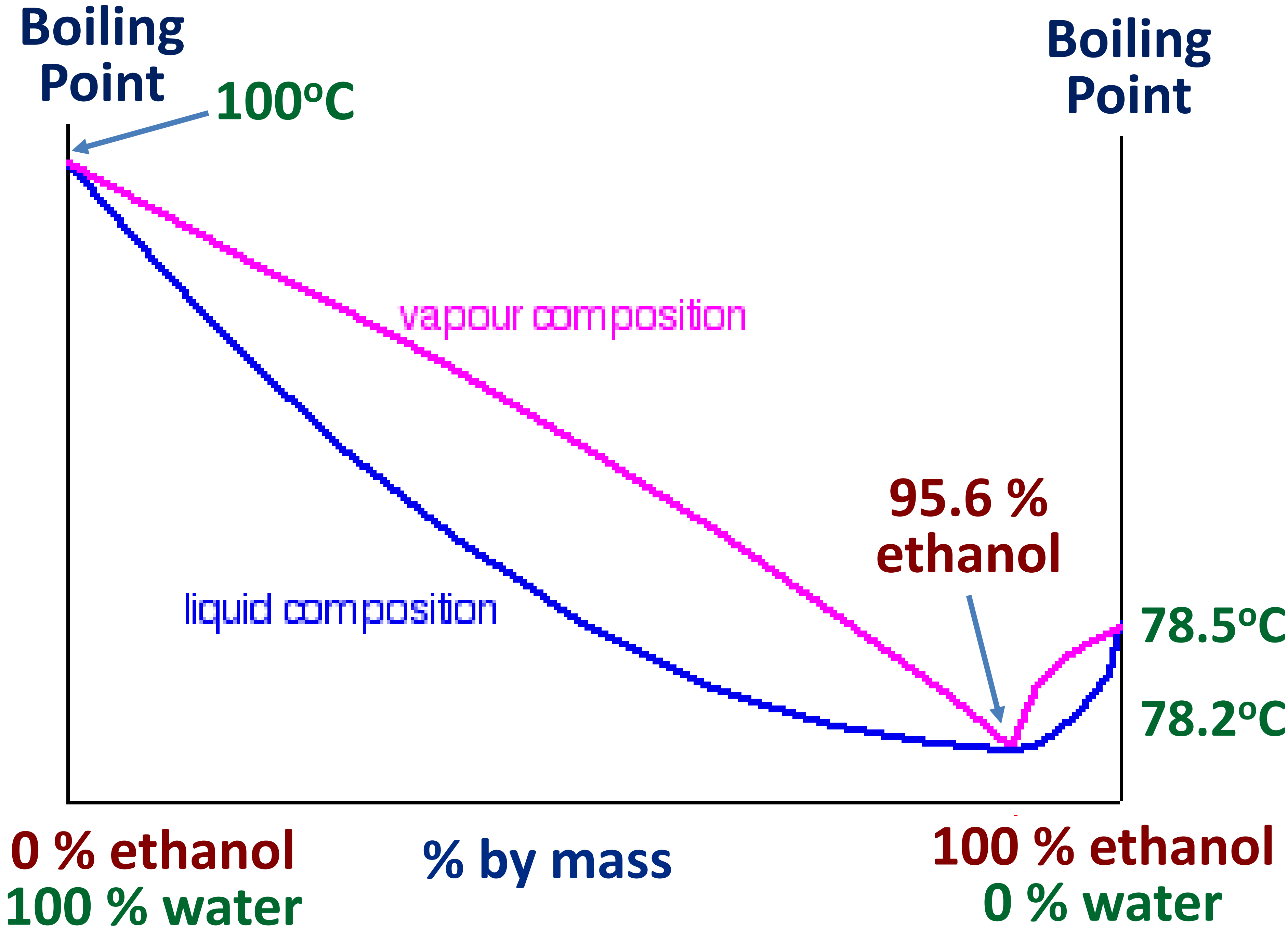
Non-ideal solutions

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

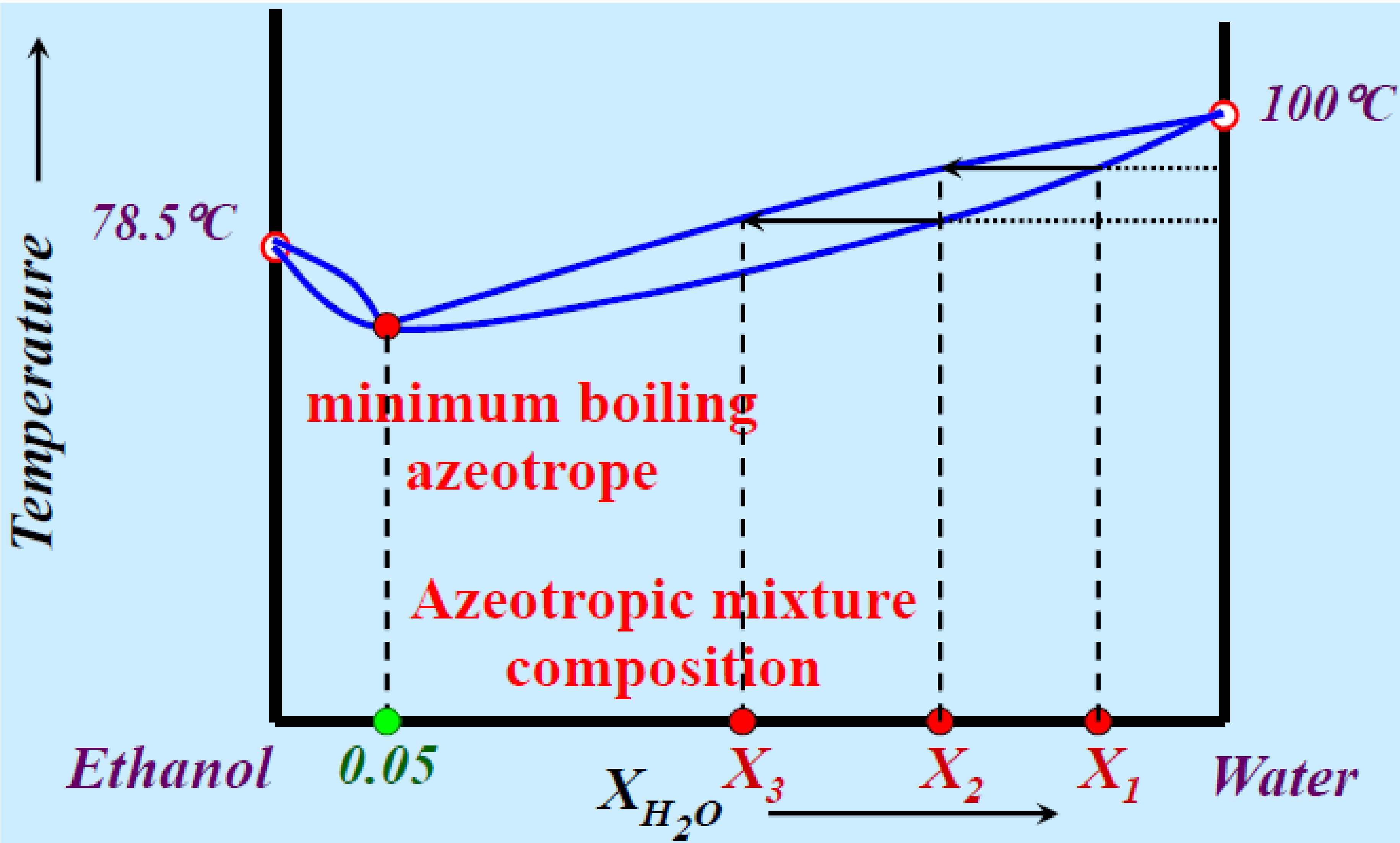
or → Negative deviation


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

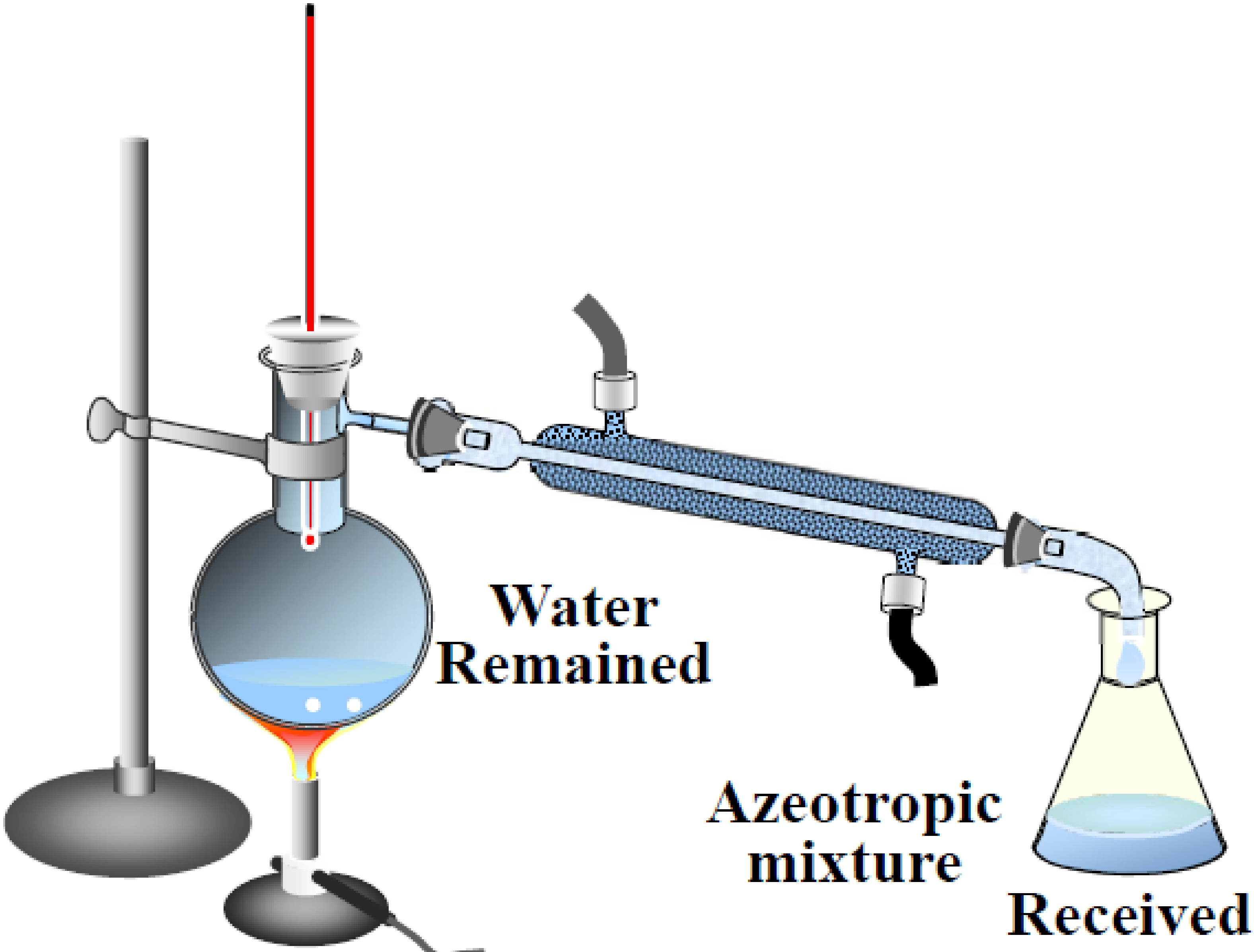


Boiling Point
100°C
Boiling Point
vapour composition
liquid composition
95.6 % ethanol
78.5°C
78.2°C
0 % ethanol
100 % water
% by mass
100 % ethanol
0 % water

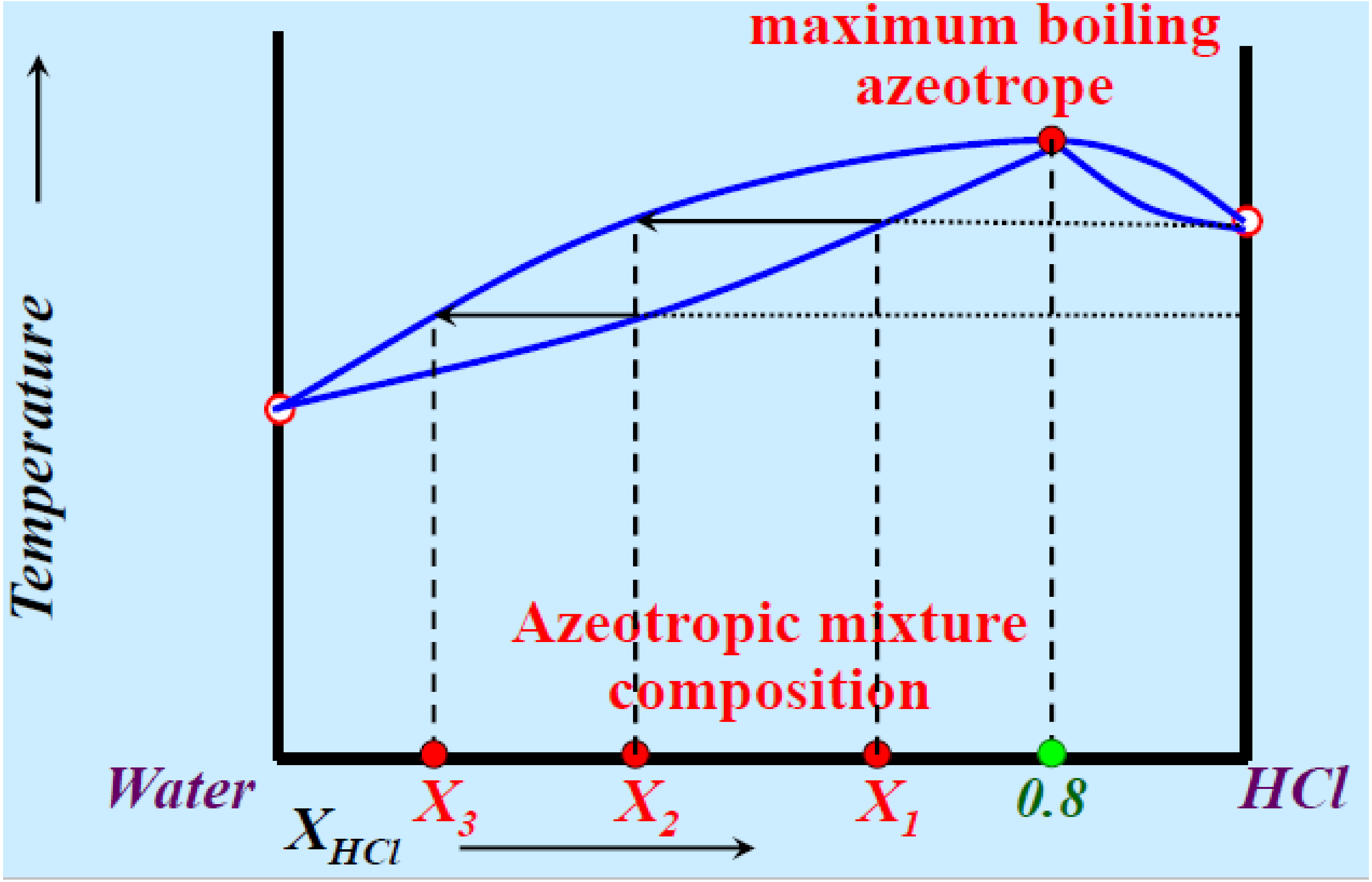
+ve deviation



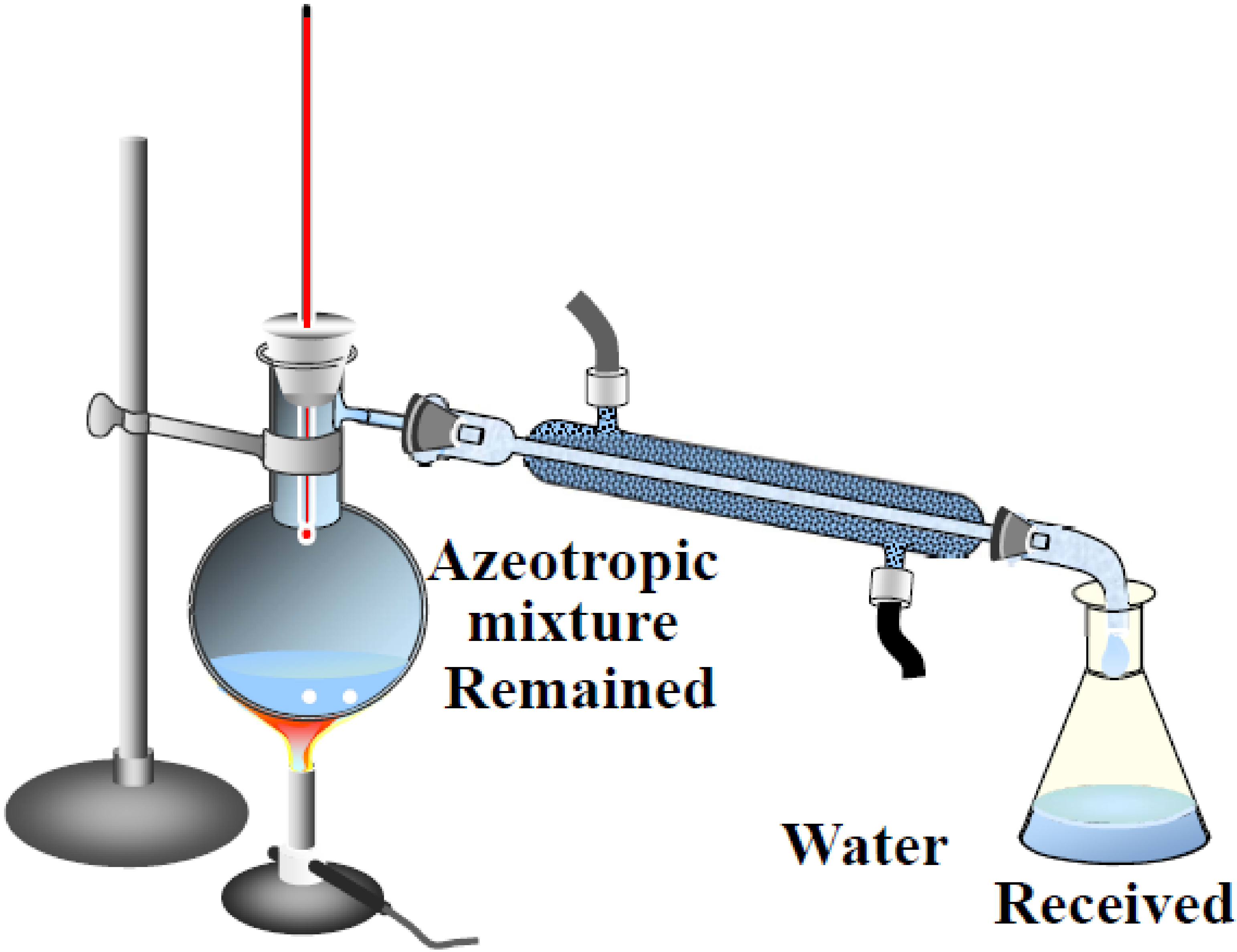
+ve deviation



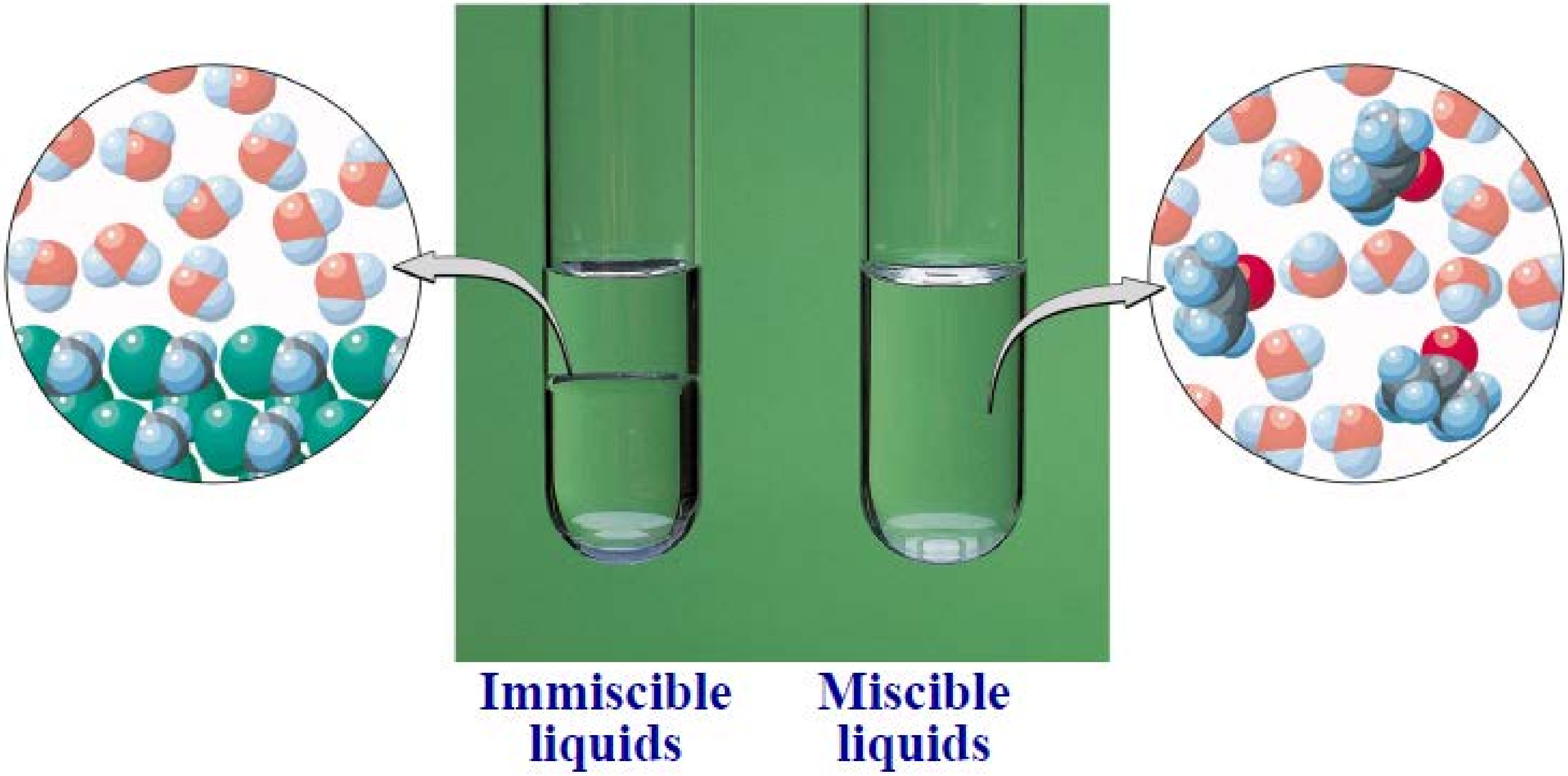
–ve deviation



—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.,

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

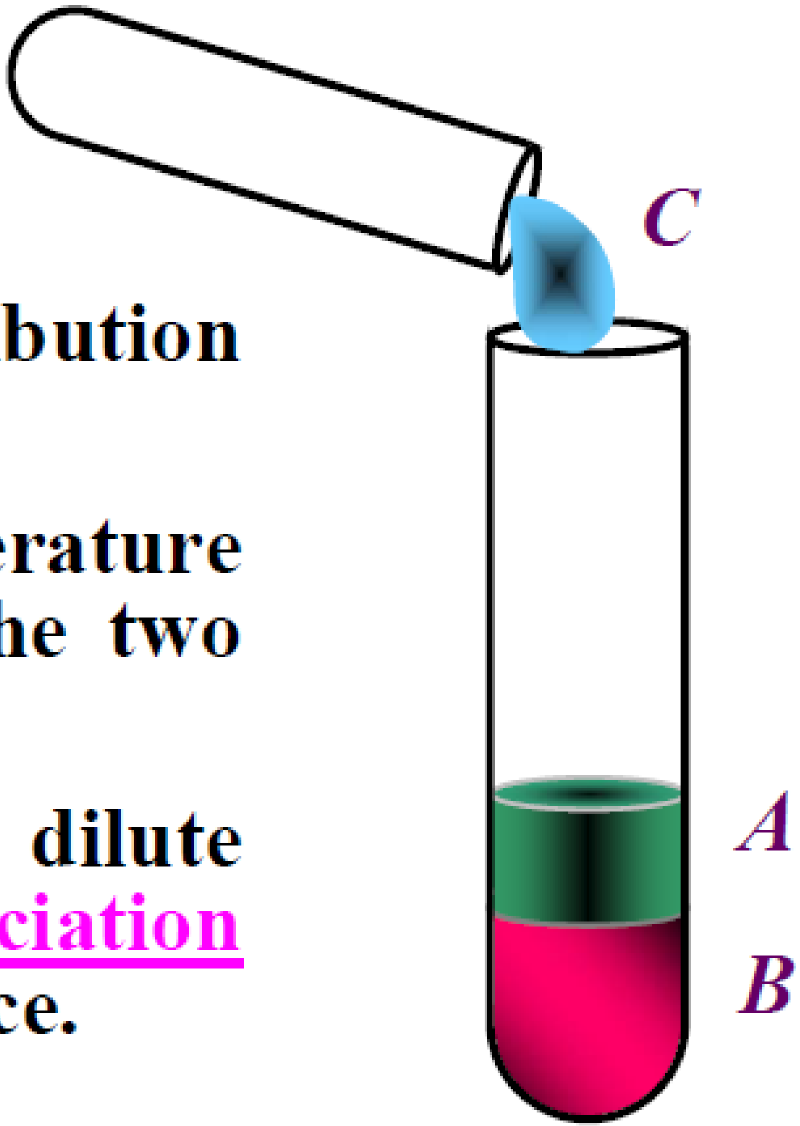
Distribution law

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

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