



*Dr. Bbosa Science*

This document is sponsored by  
**The Science Foundation College** Kiwanga- Namanve  
Uganda East Africa  
Senior one to senior six  
+256 778 633 682, 753 802709  
**Based on, best for sciences**



## Vapour pressure, Raoult's law and fractional distillation

### Vapor Pressure

All liquids exhibit tendency for evaporation at their surface. For evaporation to occur molecules at the surface acquire kinetic energy of liquid molecules overcomes the intermolecular force of attraction in the liquid state.

When evaporation is in a closed container system, the vapors molecules of liquid remain in contact with surface of liquid. Like gas molecules, vapor molecules also execute continuous random motion. During this motions, molecules collide with each other and also with the walls of the container, losses their energy and returns back to liquid state. This process is called as 'condensation'.

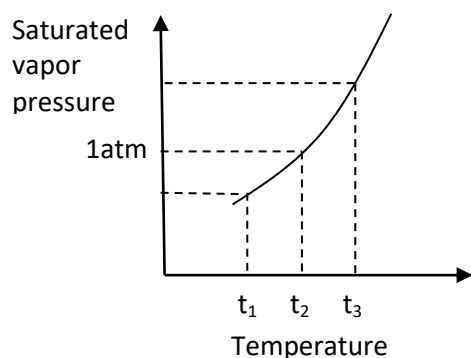
Evaporation and condensation are continuous processes. Hence, after some time equilibrium is established, at constant temperature between the rate of evaporation and rate condensation. At equilibrium number of molecules in vapor state remains constant at constant temperature.

"The pressure exerted by vapors of liquid on the surface of liquid when equilibrium is established between liquid and its vapor is called VAPOUR PRESSURE or SATURATED VAPOR pressure of liquid.

The vapor pressure increases with temperature. **When the saturated vapor pressure equals the external pressure the liquid boils**, thus lowering pressure lowers the boiling point of a liquid whereas increasing external pressure increases the boiling the boiling points of liquids.

The former principle is employed during distillation of at reduced pressure (distillation in a vacuum) to purify substances which would decompose at their normal boiling points.

A plot of the saturated vapor pressure against temperature is shown below

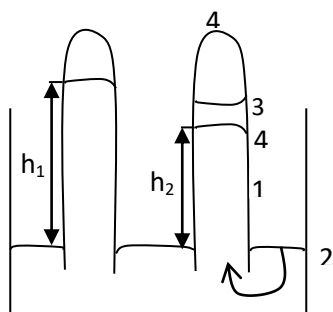


$t_1$  = boiling point at reduced pressure

$t_2$  = boiling point at 1 atmosphere

$t_3$  = boiling point at external pressure above 1 atmosphere

Measuring the saturated vapor pressure of a liquid



1. mercury barometer is set up
2. Some liquid is introduced into the barometer
3. Liquid float to the top of mercury
4. Vapor is formed. The vapor exerts a pressure on the column of mercury
5. The level of mercury drops. The difference ( $h_1 - h_2$ ) mm is the saturated vapor pressure of the liquid at this temperature.

The saturated vapor pressure of a liquid can be used to calculate the mass of the liquid that is present in vapor at a stated temperature

### Example 1

A  $1.00\text{dm}^3$  contains air at  $1.01 \times 10^5 \text{Nm}^{-2}$  at  $0^\circ\text{C}$ . After  $1.000\text{g}$  of water is introduced into the vessel, the temperature is raised to  $90^\circ\text{C}$ . Calculate the mass of water that will vaporize. The saturated vapor pressure of water at  $90^\circ\text{C}$  is  $6.99 \times 10^4 \text{Nm}^{-2}$ .

Method

Use the ideal gas equation

$$PV = nRT$$

Substitute

$$P = 6.99 \times 10^4 \text{Nm}^{-2}$$

$$R = 8.314 \text{JK}^{-1}\text{mol}^{-1}$$

$$T = 363 \text{K}$$

$$V = 1.000 \text{dm}^3 = 1.000 \times 10^{-3} \text{m}^3$$

$$1.99 \times 10^4 \times 1.000 \times 10^{-3} = n \times 8.314 \times 363$$

Moles of water vapor,  $n = 2.32 \times 10^{-2}$  moles

Mass of water vapor =  $2.32 \times 10^{-2} \times 18 = 0.417 \text{g}$

### Trial 1

Explain the following

- (a) Why distillation under reduced pressure often employed in purification of chemical
- (b) Heat must be supplied to the boiling liquid to evaporate. What happens to this heat?

### Trial 2

Use  $R = 8.314 \text{JK}^{-1}\text{mol}^{-1}$ ,  $1 \text{atm} = 1.01 \times 10^5 \text{Nm}^{-2}$

- (a) A liquid of empirical formula  $\text{CH}_2$  was vaporized. From 0.108g of the liquid, the volume of the vapor was  $50.8 \text{cm}^3$  measured at  $22^\circ\text{C}$  and  $9.8 \text{kNm}^{-2}$ . Calculate the molar mass of the liquid.
- (b) By vaporizing 0.100g of a liquid at  $100^\circ\text{C}$  and  $1.01 \times 10^5 \text{Nm}^{-2}$ ,  $20 \text{cm}^3$  of the vapor were obtained. Find the molar mass of the liquid

## Effect of a solute on the vapor pressure of solvent

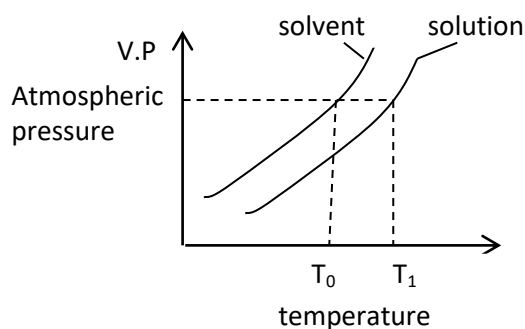
### (a) Nonvolatile solute

This lowers the vapor pressure of a solvent

### Reason

The presence of the particles of *the* nonvolatile solute reduces the escaping tendency of the solvent molecules from the surface of the liquid. That is, in the presence of the solute molecules, the probability of the solvent molecules to escape into vapour decreases. Therefore, the vapor above the solution and the vapor pressure of the solution is reduced

The vapor pressure versus temperature diagram for solvent and solution



$T_0$  = boiling point of solvent

$T_1$  = boiling point of solution

The diagram indicates that nonvolatile solute raises the boiling point of solvent.

### Explanation

The presence of nonvolatile solute reduces the vapor pressure of the solvent and therefore, the solution must be heated to higher temperature than that of the boiling point of the solvent to make its vapor pressure equal to that of the atmosphere.

Raoult's law of relative lowering of vapor pressure

**Raoult's law** states that the relative lowering of vapour pressure of a solution containing a **nonvolatile solute** is equal to the mole fraction of the **solute** in the solution.

If the vapor pressure of the pure solvent at a given temperature,  $t = P$

Then vapor pressure of solution =  $\frac{n_1}{n_1 - n_2} P$

where  $n_1$  = moles of solvent;  $n_2$  = moles of solute and  $\frac{n_1}{n_1 - n_2}$  is the mole fraction of solvent.

### Trial 3

- Explain the term mole fraction
- Calculate the mole fraction of sodium chloride in aqueous solution containing 10g of sodium chloride per 100g of water. (Na = 23, Cl = 35.5)
- Calculate the boiling point of solution in d(ii) ( $K_b = 0.52^\circ\text{C}$  for 1000g of water)

### (b) Volatile solute

Both the solute and solvent are volatile and therefore each vaporizes and contributes to the vapor pressure above the solution. However, the more volatile component will contribute more to the vapor pressure than the other. Each component lowers the vapor pressure of the other.

### Raoult's Law

The partial pressure of any component at a given temperature in an ideal mixture varies linearly with its concentration.

Or

The partial vapor pressure of any component in a mixture at a given temperature is the product of its mole fraction in solution and the vapor pressure of the pure form at that temperature.

or

$$P_A = X_A P_A^0$$

$P_A$  = Partial pressure of A in solution

$P_A^0$  = vapor pressure of pure A

$$X_A = \text{mole fraction of A} = \frac{\text{moles of A}}{\text{total moles of components.}}$$

Consider a solution containing two components A and B and the number of moles of A and B are **a** and **b** respectively

$$\text{Then the mole fraction of A } (X_A) = \frac{a}{a+b}$$

$$\text{and the mole fraction of B } (X_B) = \frac{b}{a+b}$$

According to Raoult's Law

$$P_t = X_A P_A^0 + X_B P_B^0 \text{ where } P_t \text{ is the vapor pressure of the mixture}$$

The total saturate vapor pressure is the sum of the partial pressure.

An ideal solution is solution that obeys Raoult's law.

#### Definition

Partial pressure is the pressure that would be exerted by a component if it alone occupied by the volume occupied by the mixture.

#### Properties of ideal solution

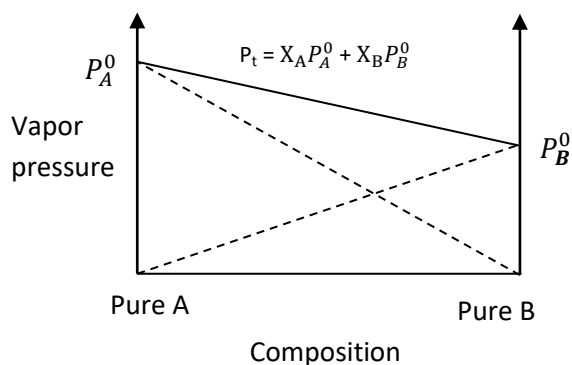
- (i) the interactions between unlike molecules must be of the same magnitude as those between like molecules.
- (ii) Formation of ideal solution does not involve change in volume nor temperature.

Ideal solutions are often obtained by mixing two or more non polar solvents, example Heptane and octane.

A component that has higher vapor pressure at a given temperature is said to be more volatile than a component with low vapor pressure at the same temperature.

A plot of the vapor pressure against composition gives a [vapor pressure composition curve](#).

The vapor pressure composition diagram for an Ideal mixture (A more volatile than B)



### Composition of the vapor

The composition of the mixture above an ideal solution is obtained from Dalton's Law that states that in an ideal mixture of gases which do not react chemically, the total pressure of the mixture is the sum of the partial pressures of the constituent gases.

It follows that the mole fraction of A ( $X'_A$ ) in the vapor  $= \frac{P_A}{P_{total}}$   
 or  $X_A = \frac{P_A}{P_A + P_B}$

### Example 3

- State Raoult's Law
- A mixture of liquids A and B obey Raoult's Law. The vapor pressure of A and B are  $10.00 \text{ kNm}^{-2}$  and  $2.92 \text{ kNm}^{-2}$  respectively at  $20^\circ\text{C}$ 
  - Calculate the composition of the vapor of a mixture containing 0.5 moles of each liquid at  $20^\circ\text{C}$  (3marks)

### Solution

(b)(i) From,  $P_t = X_A P_A^0 + X_B P_B^0$

$$P_{total} = \frac{0.5}{0.5+0.5} \times 10.00 + \frac{0.5}{0.5+0.5} \times 2.92$$

$$= 6.46 \text{ kNm}^{-2}$$

$$X_A \text{ in vapor} = \frac{P_A}{P_{total}} = \frac{5}{6.46} = 0.77$$

- Which of the liquids is more volatile? Give a reason for your answer

A is more volatile because has a higher vapor pressure than B at the same temperature.

### Trial 4.

Heptane and octane form an ideal solution

- State Raoult's law
- Explain what is meant by an ideal solution?
- Calculate the vapor pressure of solution containing 50g heptane and 38g octane at  $20^\circ\text{C}$  (H=1, C = 12)  
 The vapor pressure of heptane at  $20^\circ\text{C} = 473.2 \text{ Pa}$  and the vapor pressure of octane at  $20^\circ\text{C} = 139.8 \text{ Pa}$
- Calculate the percentage octane in vapor.

## Raoult's Law and fractional distillation

When the vapor pressure of a liquid equates atmospheric pressure, the liquid boils. Liquid or mixtures with high vapor pressure have lower boiling points than liquids or mixtures with lower vapor pressure. Actually liquids with low vapor pressure have to be heated to higher temperatures in order to bring their vapor pressures equals to atmospheric pressure to boil.

Consider two components A and B

$$P_A^0 = 500\text{mmHg} \quad P_B^0 = 100\text{mmHg}$$

Suppose A and B are mixed such that, the solution contains 20% A at a fixed temperature and we assume Ideal behavior.

$$P_A = X_A P_A^0 = \frac{20}{100} \times 500 = 100\text{mmHg}$$

$$P_B = X_B P_B^0 = \frac{80}{100} \times 100 = 80\text{mmHg}$$

$$P_{\text{total}} = P_A + P_B = 100 + 80 = 180\text{mmHg}$$

The composition of the vapor above the solution is obtained using Dalton's Law of partial pressures;

$P_A = X_A P_t$ , where  $P_A$  is the partial pressure of component A and  $P_t$  is the total pressure.

$$X_A = \frac{100}{180} = \frac{5}{9} \text{ and } X_B = \frac{80}{180} = \frac{4}{9}$$

It is observed that the vapor contains more of the more volatile component than the less volatile component B compared what was contained in the liquid mixture.

If the vapor is condensed, the distillate will have the same composition as the vapor and its total vapor pressure will be

$$\begin{aligned} P_t &= X_A P_A^0 + X_B P_B^0 \\ &= \frac{5}{9} \times 500 + \frac{4}{9} \times 100 = 322\text{mmHg} \end{aligned}$$

Composition of distillate II will have the same composition as the vapor above

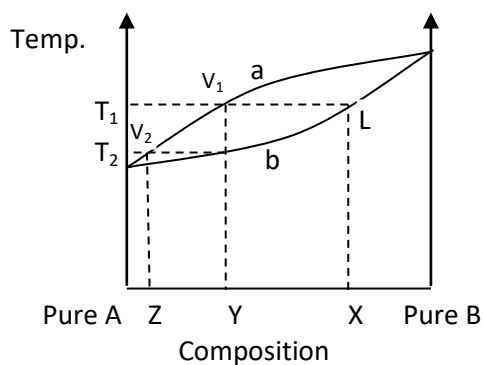
$$X_A'' = 86.3\% \text{ and } X_B'' = 13.7\%$$

Again if this vapor is condensed into distillate III, the composition of the vapor of the distillate will be

$$X_A''' = 97\% \text{ and } X_B''' = 3\%$$

The composition of the more volatile component keeps on increasing on every successive distillation; and if the procedure is repeated a number of times, time comes when the vapor contains only those of A (the more volatile component) hence complete separation of A from B. The residue will contain B

In practice, it is more convenient to perform distillation at constant pressure rather than constant temperature. The various steps in the distillation are better illustrated on the diagram below



Key

a = Vapor composition curve

b = Vapor composition curve

The lower curve shows the variation of boiling point of the liquid as distillation progresses.

Suppose the mixture to be distilled has composition X (20%A, 80%B) this mixture is represented by L on the diagram above. The boiling of this liquid commences at a temperature  $T_1$ . The vapor given off at  $T_1$  has a composition represented by  $V_1$ . When this vapor is condensed, the resultant liquid (composition Y) will be richer in the more volatile component A, and thus boils of at a lower temperature  $T_2$ . The vapor given of at this temperature has composition  $V_2$ . If this vapor is condensed a liquid of composition Z is obtained.

By repeating the process, a sufficient number of times, we can obtain pure A. i.e. we can achieve complete separation of components

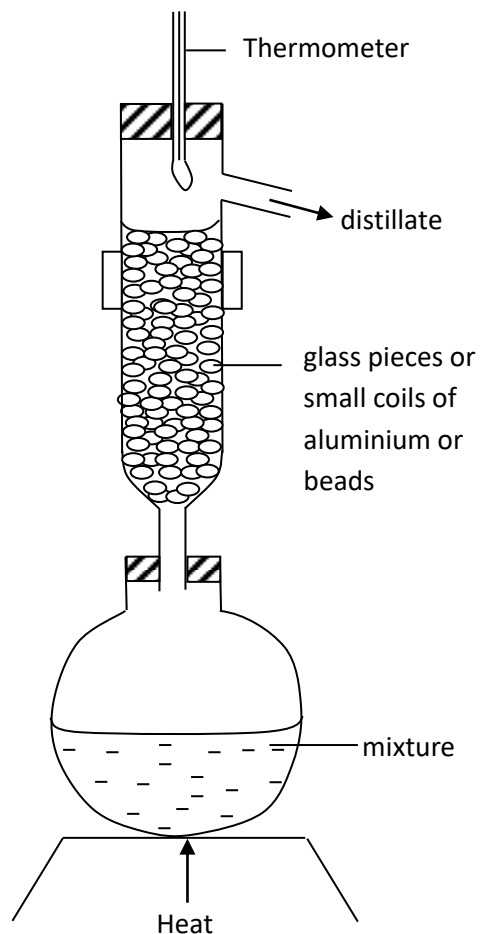
The number of distillation required to obtain the two pure components from equal proportions of the two components depend on the differences in their boiling points. Such a separation of two completely miscible liquids by utilization of differences in their boiling points is known as fraction distillation. However, the method just described above is slow and yield only small amounts of the pure components. In practice fractional distillation is carried out efficiently at constant pressure rather than at constant temperature with the help of a fractionating column (see below). In this case re-distillations are combined in one operation.

During distillation the temperature decreases progressively from bottom to top of the column and the ascending vapor is partially condensed. Condensation of the vapor is effected by the large surface area of the glass pieces or beads and also by the liquid already condensed. The vapor of the less volatile component condenses more readily than those of the more volatile component and return into the flask. Therefore, the higher the vapor ascends in the column the richer it is in the more volatile component in the end, the two components will be able to separate.



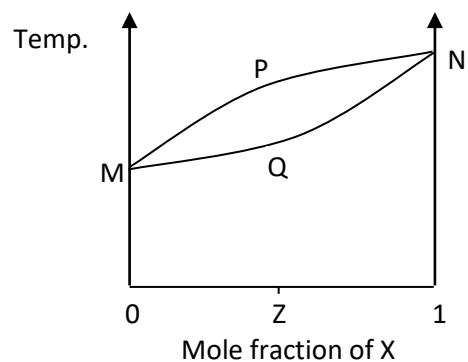
## Fractionating column

These are various forms and one of them is shown below



### Example 4

The diagram below shows the boiling point composition of a mixture of liquid X and Y.



- (i) Identify curves P and Q and points M and N

(4marks)

*P*- Vapor composition curve

*Q*- Liquid composition curve

**M-** Boiling point of Y

**N-** Boiling point of X

- (ii) Which of the liquids is more volatile? Give a reason for your answers  
*Y because it has lower boiling point and hence high vapor pressure.*
- (iii) Describe what happens when the liquid of composition Z is boiled (4MKS)  
*The vapor coming off will contain more Y and the residue will contain a higher proportion of X*
- (iv) Explain how the principle in (iii) can be used to separate liquid mixtures by fractional distillation  
*If the vapor from (iii) is condensed, a liquid that contains more Y than in a liquid of composition Z is obtained.*

*Evaporating the distillate in (iii) gives a second distillate which is even richer in Y, than the distillate in (iii). This process of boiling a liquid of any composition and subsequent condensation of the vapor eventually give a vapor and hence a distillate of pure volatile component Y, the residue in the distillation flask will be the less volatile component X.*

### Trial 5

Compound A (bp 272<sup>o</sup>C) and compound B (bp 399<sup>o</sup>C) form an ideal solution

- (i) sketch a labeled boiling/composition diagram for the mixture  
(ii) Using the diagram describe and explain how pure B can be obtained from a mixture containing 50% of B  
(iii) Sketch a vapor pressure composition curve of a mixture of A and B

### Trial 6

- (a) (i) State Raoult's law and mention its limitation (3marks)  
(ii) Sketch a diagram of boiling point against composition of two liquids that obey Raoult's Law.  
(iii) Discuss with aid of a diagram (ii) above what would happen when a typical mixture in (ii) above is fractional distilled.

### Deviations from Raoult's law:

A solution is said to deviate from Raoult's law when the adhesive and cohesive forces of attraction are not uniform between the two liquids molecule; consequently its vapor pressure (actual) differs from that calculated using Raoult's law (ideal condition).

### Positive deviation from Raoult's law

Positive deviation from ideality is said to occur when the vapor pressure of the mixture is higher than what it would be from calculations of Raoult's law.

$$\text{i.e. } P_{total} > X_A P_A^0 + X_B P_B^0$$

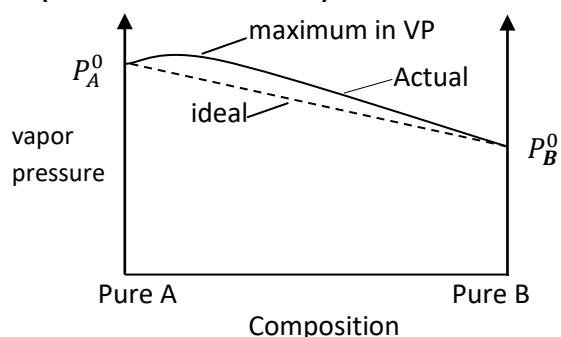
Causes of positive deviation

Unlike molecules interact (attract) with one another *less strongly* than like molecules do.

$$\text{i.e. } A \leftrightarrow B < A \leftrightarrow A \text{ or } B \leftrightarrow B$$

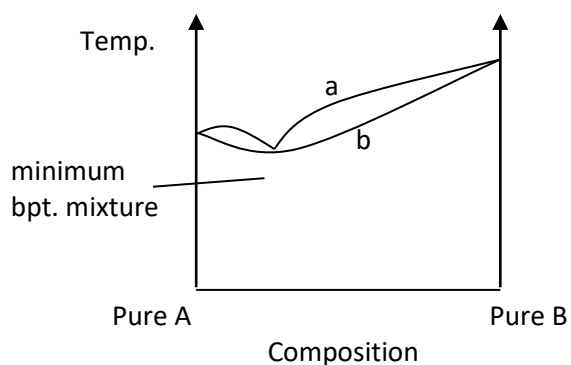
In this case  $P_A > X_A P_A^0$  and  $P_B > X_B P_B^0$   
and therefore  $P_A + P_B > P_{total}(\text{Ideal})$

**Vapor pressure /composition diagram for a solution which deviate positively  
(A more volatile than B)**



NB: maximum in vapor pressure forms towards the more volatile component.

**Boiling point versus composition for a mixture that deviates positively at constant pressure**



Key  
a = Vapor composition curve  
b = Vapor composition curve

A maximum in vapor pressure produces a minimum in boiling point. When such a mixture that shows a positive deviation from ideality is distilled, a minimum in boiling point will be observed at certain composition and at this point the mixture has the same composition as the vapor above it. And further separation of the mixture into either component will be impossible. The mixture corresponding to this minimum boiling point is called **azeotrope** and the corresponding temperature is called **azeotropic temperature**.

**Definition**

An **azeotrope** is a mixture which has the same composition as it vapors and boils at constant temperature.

NB. Mixtures that deviate positively from Ideality are often obtained by mixing a polar and a non-polar solvent, example, methanol and cyclohexane. It is also observed that that the azeotrope has a higher composition of the most volatile component.

Examples of solution that show positive deviation are:-

- (1) Benzene and methanol,
- (2) Carbon disulfide and acetone,
- (3) Chloroform and ethanol.

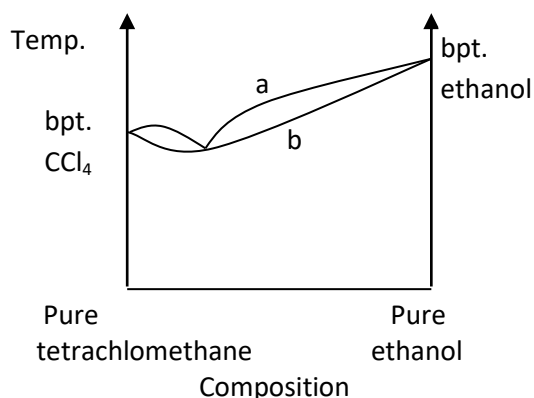
Formation of solution that deviates positively from Raoult's law is accompanied with **absorption of heat (cooling) and expansion in volume.**

#### Example 4

Ethanol (bpt.  $78.5^{\circ}\text{C}$ ) and tetrachloromethane (bpt.  $76.8^{\circ}\text{C}$ ) form an azeotropic mixture of boiling point  $65.0^{\circ}\text{C}$ .

- What is meant by azeotropic mixture? (2marks)
- Draw a boiling point diagram for the ethanol-tetrachloromethane mixture (2marks)

(You will notice that ethanol and tetrachloromethane mixtures deviate positively because the boiling point of the azeotrope is lower than that of either component; the boiling composition curve for a mixture that shows positive deviation is required)



Key

a = Vapor composition curve

b = Vapor composition curve

- Explain why ethanol and tetrachloromethane form an azeotropic mixture (2marks)

The forces of attraction between like molecules (i.e. ethanol molecules or tetrachloromethane molecules) are stronger than those between unlike molecules (ethanol -tetrachloromethane molecules probably because tetrachloromethane interferes with formation of hydrogen bond in ethanol while ethanol disrupts the van der Waal forces of tetrachloromethane. Therefore, molecules of each liquid in the mixture tend to escape into vapor phase more easily than those of pure components. This makes the total pressure of the mixture higher than that expected from Raoult's law.

### Trial 7

- (i) State Raoult's law (2marks)
- (ii) Draw the vapor pressure/composition curve for mixtures of methanol (more volatile) and cyclohexane and explain the shape of the curve with reference to Raoult's law (8marks)

### Trial 8

- (a) (i) Define the term constant boiling point mixture (2marks)
- (ii) Sketch a labeled diagram of the boiling point-composition for hydrochloric acid and water system. [The boiling points of water and hydrochloric acid are 100°C and 85°C respectively]
- (iii) Describe what would happen if a mixture of 10% hydrochloric acid
- (c) A constant boiling point mixture of hydrochloric acid has a density of 1.18gcm<sup>-1</sup>. Calculate the volume the acid needed to prepare one litre of 2M hydrochloric acid solution. (03marks)
- (d) The vapor of ethanol at 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for the mixture of and ethanol at 20°C. Calculate
- (i) The vapor pressure of the mixture. (04marks)
- (ii) The mole fraction of benzene in the vapor. (2marks)

### Trial 9

- (a) State Raoult's law.
- (b) Methanol and cyclohexane form a mixture that deviates from Raoult's law. The data below concerns a mixture of methanol and cyclohexane. The normal boiling points of cyclohexane and methanol are 81 and 65°C respectively.

Boiling point of the mixture (°C)	Mole fraction of methanol in the liquid mixture	Mole fraction of methanol in the vapor above mixture
70	0.12	0.27
60	0.31	0.47
55	0.50	0.56
57	0.82	0.69
61	0.94	0.83

- (i) Plot a boiling point-composition diagram for the mixture, labeling clearly the liquid-composition and vapor composition curves. (5marks)
- (ii) From your graph state the composition of the azeotropic mixture (1mark)
- (iii) Name the pure liquid obtained when a liquid mixture containing one mole of cyclohexane and nine moles of methanol is fractional distilled (1mark)
- (iv) State how the mixture deviates from Raoult's law. (1mark)

### Negative deviation

Negative deviation from ideality is said to occur when the vapor pressure of the mixture is lower than what it would be expected from calculations of Raoult's law.

$$\text{i.e. } P_{\text{total}} < X_A P_A^0 + X_B P_B^0$$

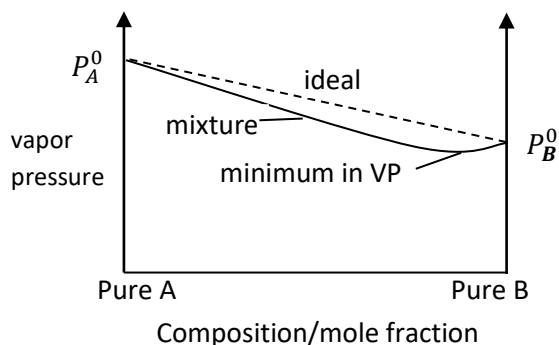
### Causes of negative deviation

Unlike molecules interact (attract) with one another *more strongly* than like molecules do.

$$\text{i.e. } A \leftrightarrow B > A \leftrightarrow A \text{ or } B \leftrightarrow B$$

In this case  $P_A < X_A P_A^0$  and  $P_B < X_B P_B^0$   
and therefore  $P_A + P_B < P_{\text{total}}(\text{Ideal})$

### Vapor pressure /composition diagram for a solution which deviate negatively (A more volatile than B)



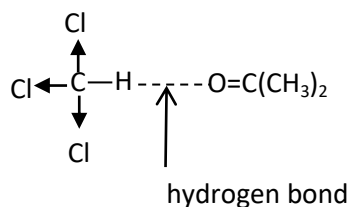
—— Actual

----- Ideal behavior

NB: minimum in vapor pressure forms towards the less volatile component.

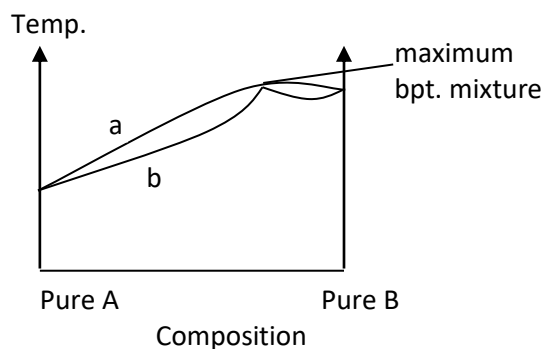
An example of a mixture showing negative deviation is that of propanone ( $\text{CH}_3\text{COCH}_3$ ) and chloroform ( $\text{CHCl}_3$ ); and water and hydrochloric acid.

Usually mixtures showing negative deviation are obtained by mixing two polar compounds. The negative deviation in this case is due to hydrogen bonding between  $\text{CHCl}_3$  and  $\text{CH}_3\text{COCH}_3$



Mixtures that deviate negatively from Raoult's law form a zeotropes with boiling points higher than those of either of their components.

### Boiling point versus composition for a mixture that deviates negatively at constant pressure (A more volatile than B)



Key

Formation of a solution that a = Vapor composition curve Raoult's law is accompanied with evolution of heat and contraction of volume. b = Vapor composition curve

### Reasons why azeotropes are not compounds

- (i) Can be separated by physical means
- (ii) Their composition varies with pressure.
- (iii) Cannot be represented by a chemical formula

### Methods of separating azeotropic mixture

1. Adding a substance that reacts and removes one component. e.g.  $\text{CaO}$  reacts and removes water from azeotrope of ethanol and water
2. Distillation with a third substance e.g. benzene in rectified spirit
3. Fractional crystallization
4. solvent extraction
5. adsorption

### Example 5

(a) State Raoult's (3marks)

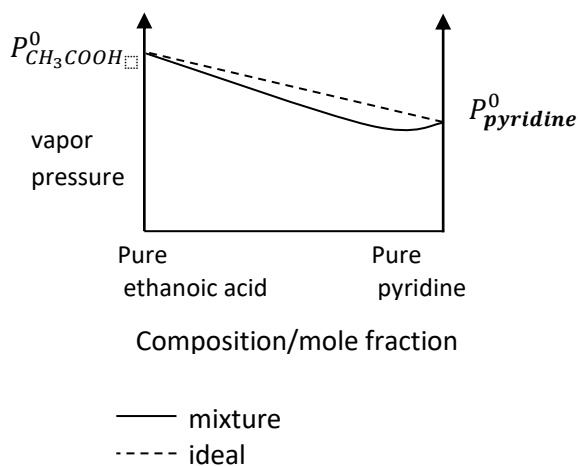
A mixture of ethanoic acid (bpt.  $118^{\circ}\text{C}$ ) and pyridine (bpt.  $123^{\circ}\text{C}$ ) show negative deviation from Raoult's law

(i) Draw the vapor pressure /composition curve for the mixture of ethanoic acid and pyridine and indicate the line for ideal behavior (4marks)

#### Solution

To draw the correct diagram, the following should be put into account

- ethanoic acid with lower boiling point has higher vapor pressure
- The minimum boiling point occurs to the composition containing more pyridine (the less volatile) than ethanoic acid.



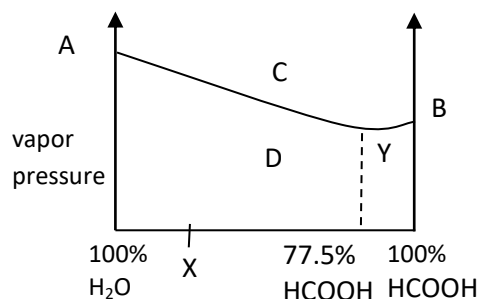
(ii) Explain the shape of the curve in relation to Raoult's law

- the curve for the mixture lies below the line for ideal behavior
- this is because the attraction between the molecules of ethanoic acid and those of pyridine are greater (stronger) than those between ethanoic acid-ethanoic acid or pyridine-pyridine molecules
- pyridine molecules are held by weak van der waal forces
- ethanoic acid molecules are associated with hydrogen bonds
- when ethanoic acid and pyridine are mixed, intermolecular hydrogen bonds are formed between ethanoic acid and pyridine molecules which are stronger than the bonds in pure or equal to those in pure ethanoic acid
- consequently, the escaping tendency of individual molecules of each component is reduced, leading to reduced vapor of solution of the mixture



### Trial 10

The diagram below shows the vapor pressure-composition for water-methanoic acid at constant temperature.



- (a)(i) What do the points A and B represent  
(ii) What does the curve AYB represent?  
(iii) What phases exist in areas C and D?
- (b) Explain the shape of the graph (4marks)
- (c) Explain the changes which would take place if a liquid of composition x was fractional distilled.

### Trial 11

- (a) State Raoult's law
- (b) A mixture of liquid Y and Z obeys Raoult's law. If the vapour pressure of Y and Z are  $9.50\text{kNm}^{-2}$  and  $3.20\text{kNm}^{-2}$  respectively at  $20^\circ\text{C}$ .
- (i) Calculate the composition of the vapour containing 0.5 moles of each liquid at  $20^\circ\text{C}$ . (04marks)
- (ii) State which of the two liquids is more volatile. Give a reason for your answers. (02marks)
- (c) The boiling points of y and Z are  $368^\circ\text{C}$  and  $395^\circ\text{C}$  respectively.
- (i) Sketch a labeled boiling point-composition diagram of the mixture of liquids (03marks)
- (ii) Using the diagram, describe how pure Z can be obtained from a mixture containing 50% Z. (05marks)
- (d) Explain why some liquids show negative deviations from Raoult's law. (03marks)
- (e) If the mixture of liquids Y and Z in (b) was to deviate negatively from Raoult's law, sketch a labeled boiling point-composition diagram for the mixture (02marks)

### Trial 12

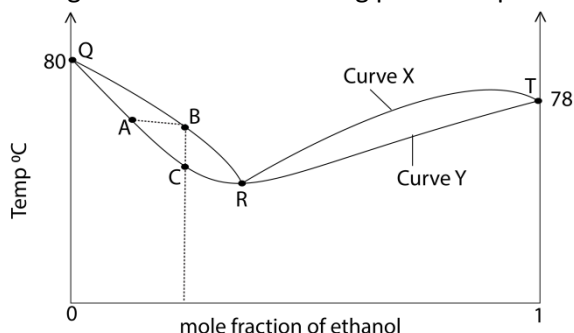
- (a) State three reasons why azeotropes are considered to be mixtures and not compounds ( 1 ½ marks)
- (b) The total vapour pressure of a mixture of propanone and trichloromethane and the mole fraction of trichloromethane at constant temperature are given in the table below

Mole fraction of trichloromethane	0.0	0.2	0.4	0.6	0.8	1.0
Total vapour pressure of mixture (mmHg)	347	305	267	244	256	293

- (i) Plot a graph of total vapour pressure of the mixture against the mole fraction of trichloromethane (03marks)
- (ii) Using the graph deduce how the mixture deviates from Raoult's law. Give a reason for your answer (02marks)
- (iii) Explain the causes of the deviation you have stated in (b)(ii) (1 ½ marks)
- (iv) Determine the composition of the azeotropes (01marks)

### Trial 13

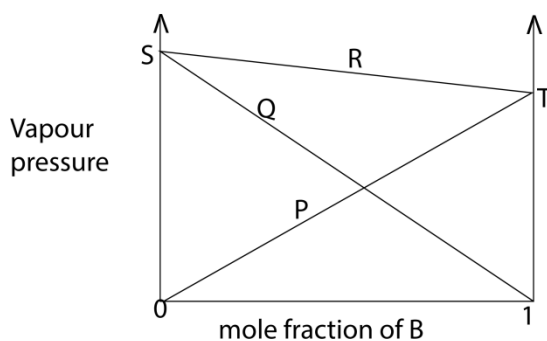
- (a) Explain why a solution containing 2.5g of glucose,  $C_6H_{12}O_6$ , in 100g of ethanol boils at  $83^\circ C$  at 760mmHg pressure whereas pure ethanol boils at  $78^\circ C$  at the same pressure. (3 ½ marks)
- (b) Using the data in (a), calculate the molar boiling point constant,  $K_b$  of ethanol. (4marks)
- (c) The figure below shows boiling point composition curve the benzene-ethanol system.



- (i) Identify curves A and Y, and point R (03marks)
- (ii) A mixture at point R was boiled, state what happened to its composition. (01 mark)
- (iii) State the relationship between A, B and C. (02marks)
- (iv) Explain the shape of curve Y, between T and R. (03 marks)
- (v) Draw a labeled diagram to illustrate the vapour pressure- composition diagram for benzene-ethanol system.

### Trial 14

- (a) State **three** properties of an ideal solution. (1 ½ marks)
- (b) The vapour pressure- composition curve an ideal solution of liquids A and b is shown below



- (i) Identify line P, Q, and R and points S and T (2 ½ marks)
- (ii) Draw a fully labeled boiling point- composition diagram for a mixture of liquid A and B.
- (iii) State what would be obtained as the distillate and the residue if a mixture containing 40% of A is fractional distilled. (02marks)
- (c) A mixture of benzene and methyl benzene form an ideal solution.
- (i) Calculate the vapour pressure of a solution containing 1.94g of benzene and 4.6g of methylbenzene at  $20^\circ C$ . [ the vapour pressure of pure benzene and pure methylbenzene at  $20^\circ C$  are 10.0kPa and 8.2 kPa respectively]
- (ii) Determine the composition of the vapour of the mixture (c)(i) above
- (d) Briefly describe what takes place during fractional distillation. (04marks)

### Trial 15

- (a) Define the term 'partial pressure.'
- (b) The vapour pressure of pure chloroform and carbon tetrachloride are 199.1 and 114.4mmHg respectively at 25°C.  
(Assume that a mixture of the two liquids behaves as an ideal solution and that it contains 0.96 moles of each pure liquid.)  
Calculate
- (i) The partial pressure of each component in the mixture (2 ½ marks)
- (ii) Total pressure ( ½ mark)
- (c) Calculate the percentage of carbon tetrachloride in the vapour in equilibrium with the liquid mixture (1mark)

### Trial 16

The vapour pressure of a solution containing 1 mole of liquid A and 4moles of liquid B is 0.750atmospheres at a certain temperature

The vapour pressure of pure A and pure B are 0.674 and 0.453 respectively at the same temperature.

- (a) Calculate the vapour pressure of the solution if it behaved as an ideal solution (03)
- (b) State how the solution deviates from Raoult's law. Give a reason for your answer. (1 ½ mark)

Suggested answers

### Trial 1

- (a) Distillation under reduced pressure occurs at reduced temperature thereby protecting heat labile substances from decomposition and it also saves energy.
- (b) Heat of vaporization is required to convert a liquid at its boiling points into vapor

### Trial 2

(a)  $PV = \frac{m}{Mr}RT$ ;  $P = 98\text{kNm}^{-2}$ ,  $T = 273 + 22 = 295^{\circ}\text{C}$ ,  $V = 50.8 \times 10^{-6} \text{ m}^3$ .

Then

$$1000 \times 9.8 \times \frac{50.5}{1000000} = \frac{0.108}{Mr} \times 8.314 \times 295$$

$$Mr = 532$$

(b)  $1.01 \times 10^5 \times \frac{20}{1000000} = \frac{0.1}{Mr} \times 8.314 \times 373$

$$Mr = 153$$

### Trial 3

- (i) Mole fraction of a compound in a mixture is the ratio of moles of the component to the total moles of components in the mixture.

- (ii) Formula mass of NaCl = 23 + 35.5 = 58.5g

$$\text{Moles of NaCl} = \frac{10}{58.3} = 0.17$$

$$\text{Formula mass of H}_2\text{O} = 1 \times 2 + 16 = 18\text{g}$$

$$\text{Moles of water} = \frac{100}{18} = 5.56$$

$$\text{Total moles} = 5.56 + 0.17 = 5.73$$

$$\text{Mole fraction of NaCl} = \frac{0.17}{5.73} = 0.03$$

- (iii) Mass of NaCl in 100g of water

100g contain 10g

$$100\text{g contain } \frac{10 \times 1000}{100} = 100\text{g}$$

Boiling point elevation

Since 1mole of NaCl dissociates into 2 moles of ions

58.5g (1mole) of NaCl produce an elevation of  $0.52 \times 2 = 1.04^{\circ}\text{C}$

$$100\text{g of NaCl produce an elevation of } \frac{100 \times 1.04}{58.5} = 1.8^{\circ}\text{C}$$

Boiling point of solution = boiling point of water + boiling point elevation

$$= 100 + 1.8 = 101.8^{\circ}\text{C}$$

### Trial 4

- (a) (i) Raoult's law states that the partial pressure of a component in a mixture is a product of mole fraction and its vapor pressure of pure component.

(ii) An ideal solution is a solution that obeys Raoult's law, it has uniform forces of attraction between like and unlike molecules; its formation produces no change in temperature and volume.

(iii) Formula mass of heptane,  $C_7H_{16} = 12 \times 7 + 16 = 100$

$$\text{Moles of heptane} = \frac{50}{100} = 0.5$$

Formula mass of octane,  $C_8H_{18} = 12 \times 8 + 18 = 118$

$$\text{Moles of octane} = \frac{38}{118} = 0.3$$

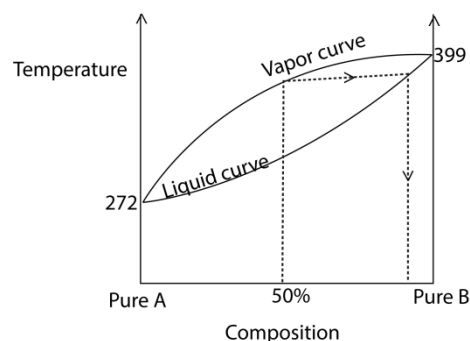
$$\text{Total mole} = 0.5 + 0.3 = 0.8$$

$$\text{Total vapor pressure} = \frac{0.5}{0.8} \times 473.2 + \frac{0.3}{0.8} \times 139.8 = 348.175$$

$$\text{Mole fraction of octane} = \frac{52.435}{348.175} = 0.15$$

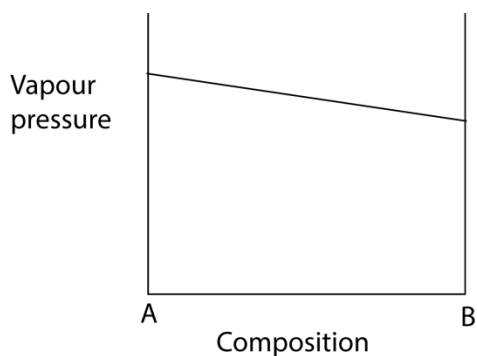
### Trial 5

(i)



(ii) When the mixture that contain 50% is distilled, the residue retains high proportion of B. continued distillation of the residue finally produces pure B as the final residue.

(iii)



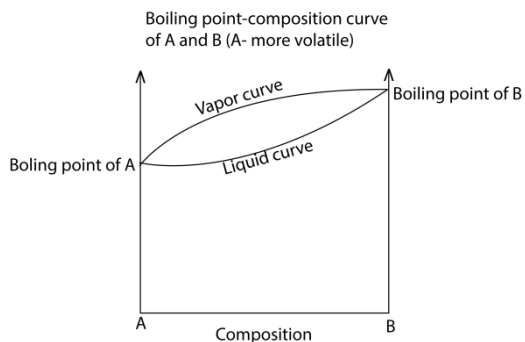
### Trial 6

(a)(i) Raoult's law states that the partial pressure of a component in a mixture is a product of mole fraction and its vapor pressure of pure component.

Limitation of Raoult's law

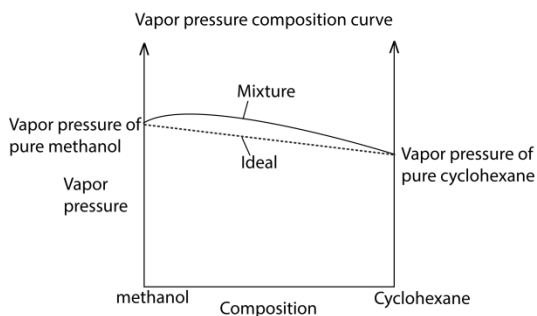
- There must be uniform attraction between like and unlike molecules
- Formation of mixtures that obey Raoult's law should not involve change in temperature nor volume.

(ii)



- (ii) On fractional distillation the more volatile component is obtained as a distillate while the residue is the less volatile component.

### Trial 7

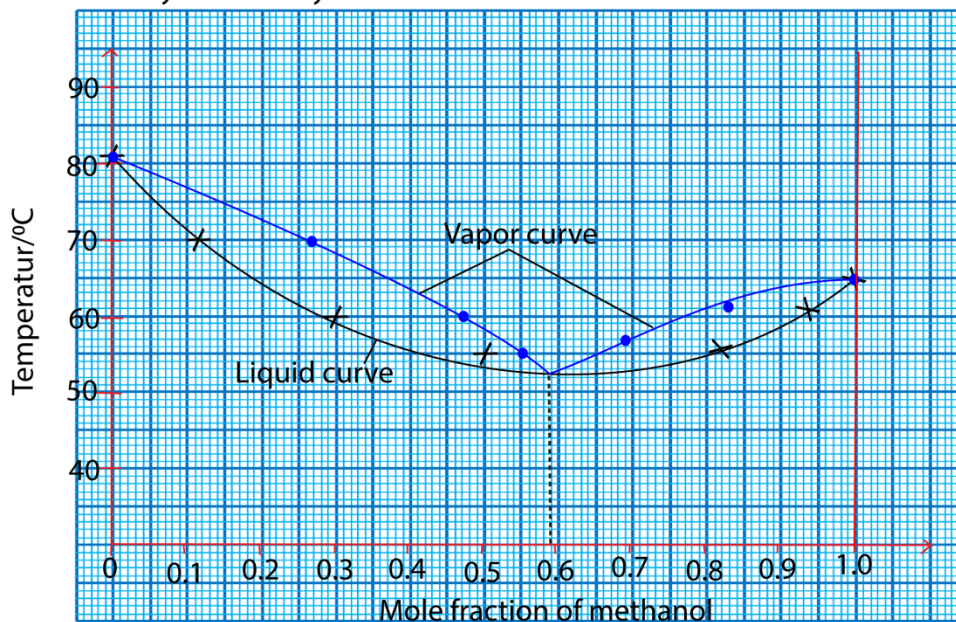


The vapor pressure of the mixture is higher than expected because cohesive forces are higher than adhesive forces. This promotes evaporation of either components.

### Trial 8

(i)

A plot of boiling point -composition curve of methanol and cyclohexane system



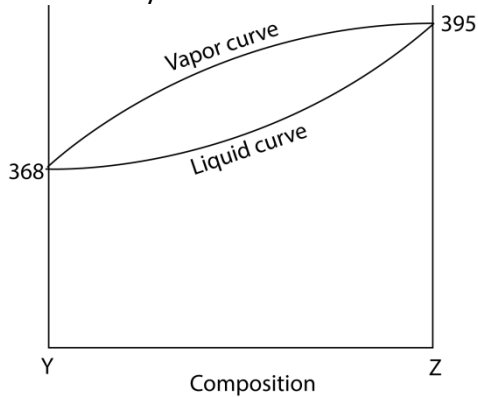
- (i) Percentage of methanol in azeotrope = 59
- (ii) Methanol
- (iii) Positive deviation

**Trial 10**

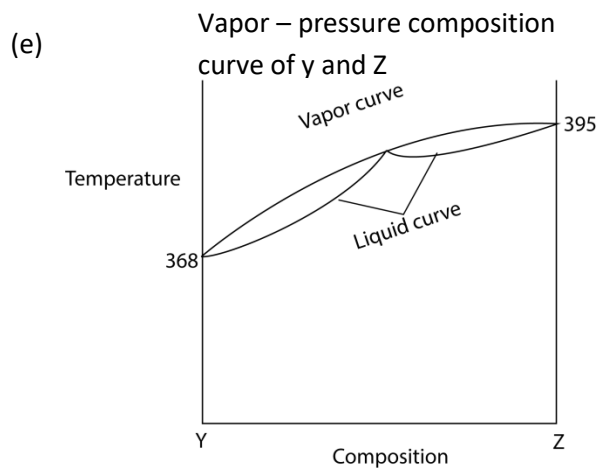
- (a) (i) A – vapour pressure of pure water  
B – Vapor pressure of methanoic acid
- (ii) vapor pressure of the mixture
- (iii) C- vapor  
D – liquid
- (b) Vapor pressure of the mixture is less than ideal because adhesive forces are higher than cohesive forces which reduce evaporation and vapor pressure.
- (c) Distillate: water  
Residue: azeotrope

**Trial 11**

- (b) (i) % of Y in vapor = 75 and that of Z is 25
- (c) (i) Vapor – pressure composition curve of y and Z

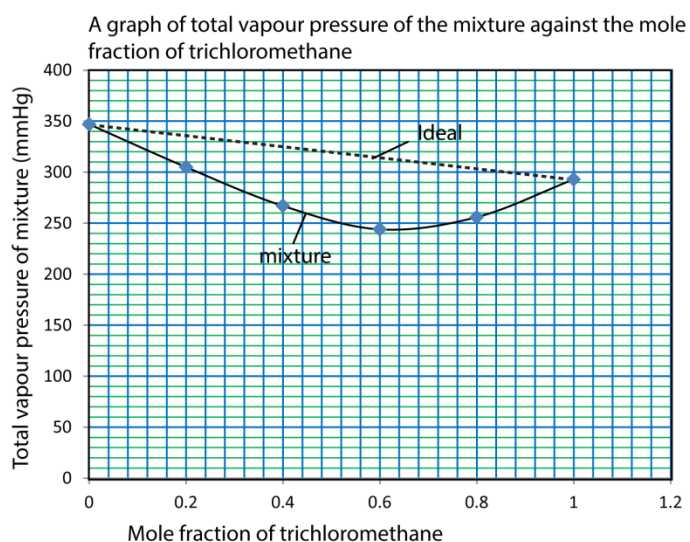


- (ii) When the mixture that contain 50% is distilled, the residue retains high proportion of Z. continued distillation of the residue finally produces pure Z as the final residue.
- (d) Adhesive forces are stronger than cohesive forces which reduce the rate of evaporation, vapor pressure and increase the boiling point



### Trial 12

(i)



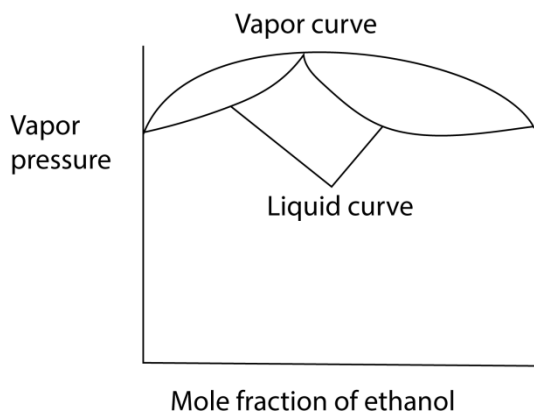
- (ii) Negative deviation because vapor pressure of the mixture is less than ideal
- (iii) Adhesive forces are stronger than cohesive forces which reduces the rate of evaporation of either component
- (iv) Mole fraction  $f$  trichloromethane in azeotrope = 0.5

### Trial 13

- (a) The nonvolatile glucose molecules occupy part of the surface of ethanol reducing evaporation tendency of ethanol molecules and vapor pressure of the solution. Thus, the solution has to be heated to a temperature higher than the boiling point of the pure ethanol in order to boil.
- (b) Relative formula mass of glucose,  $C_6H_{12}O_6 = 12 \times 6 + 12 \times 1 + 16 \times 6 = 180$   
 Boiling point elevation =  $83 - 78 = 5^\circ C$   
 Mass of glucose in 100g of ethanol  
 100g contain 2.5g  
 1000g of ethanol contains 25g  
  
 Boiling point elevation constant  
 25g cause boiling point elevation of  $5^\circ C$   
 180g of glucose cause elevation  $K_b = 36^\circ C mol^{-1} kg^{-1}$ .

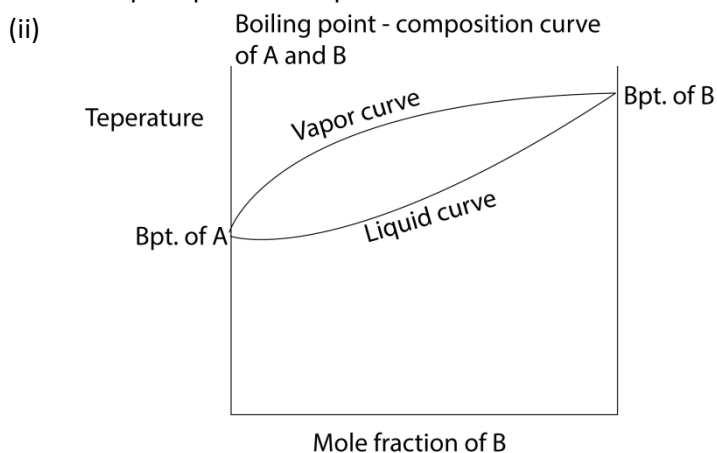


- (c) (i) X = vapor curve, Y = liquid curve, R = azeotrope point  
(ii) Composition does not change  
(iii) A liquid of composition A boils to give vapor of composition B which cools to give a liquid of same composition C  
(v)



#### Trial14

- (a) Has uniform force of attraction between like and unlike molecules  
Its formation involves no change in mass  
Its formation involve no change in volume  
(b) (i) Q- partial pressure of A  
P – partial pressure of B  
R – total vapour pressure of the mixture  
S – vapor pressure of pure A  
T – Vapour pressure of pure B



- (iii) Distillate is A while the residue is B

- (b)(i) partial pressure of chloroform = 99.8mmHg  
Partial pressure of carbon tetrachloride = 57.2mmHg  
(iii) Total pressure = 157 mmHg  
(c) 36%

Trial 16

(a)  $P_t = 0.5$

(b) Deviates positively because the vapor pressure solution is higher than what is expected from Raoult's law.