QUESTIONS

Question 1

Can azeotropes be separated into pure components by fractional distillation? Explain.

Ouestion 2

Why in constructing boiling temperature of the solution against composition curve, liquid phase curve lies below the vapour phase curve while in the vapour pressure of solution against composition curve, the vapour phase curve lies below the liquid phase curve.

Question 3

State whether the following statements are true or false. In each case give reason(s) to support your answer.

- (i) Azeotropes are compounds and not mixtures.
- (ii) Raoult's law of ideal solutions is applicable both to the liquid and vapour phase compositions.

Ouestion 4

- (i) Is the aqueous methanol solution ideal or non-ideal solution? Explain.
- (ii) What is the molality of an aqueous methanol solution whose mole fraction is 0.2?

Question 5

State Konowaloff's rule.

Question 6

Explain why we cannot prepare absolute alcohol by fractional distillation.

Question 7

In a binary solution obeying Raoult's law, can the liquid and the vapour phases have the same composition? Explain.

Question 8

Azeotropes can be said to be similar to compounds. Justify.

Question 9

What is zeotrope?

Question 10

What type of deviation is shown by a mixture of ethanol and acetone? Give reason.

Question 11

Fractional distillation of a particular liquid binary mixture leaves behind a liquid consisting of both components in which the composition does not change as the liquid is boiled off. Is this behaviour characteristic of a maximum or a minimum boiling point azeotrope?

Ouestion 12

Is steam distillation used to isolate limonene from lemon? Explain.

Question 13

(i) What general name is given to binary mixture which show deviation from Raoult's law and whose components cannot be separated by fractional distillation.

(ii) How many types of such mixture are there? Name them with an example in each case.

Ouestion 14

List down four conditions of which the compound to be separated by steam distillation must fulfill.

Question 15

Partition law helps to study different aspects of chemistry. List down any three applications of distribution law.

Ouestion 16

Differentiate between zeotropic mixture and azeotropic mixture.

Ouestion 17

Write down three factors which determine the value of partition coefficient?

Ouestion 18

Why very dilute solutions are regarded as ideal solutions irrespective to the nature of the solute and solvent?

Question 19

- (i) Define ideal solution.
- (ii) What type of liquids form ideal solutions?

Question 20

Define azeotrope. What type of azeotrope is formed by positive deviation from Raoult's law? Give an example.

Question 21

A solution of chloroform and acetone is an example of maximum boiling azeotrope. Explain why?

Question 22

Solution can be classified in several categories based on number of factors. One factor which is commonly considered in classifying solution is the physical state.

- (i) How many types of solutions are formed?
- (ii) Write briefly about each type with an example.
- (iii) Give an example of solid solution in which the solute is a gas.

Ouestion 23

- (i) Define boiling point of liquid?
- (ii) How boiling point is affected by external pressure?

Question 24

What role does the molecular interaction play in a boiling point of a solution of alcohol and water?

Ouestion 25

Benzene and toluene are both mainly non-polar compounds. If instead of toluene, an equivalent chemical amount of a polar compound like benzoic acid were dissolved in benzene, how would you expect the partial pressure of benzene above the solution to deviate from the partial pressure of benzene above an ideal solution(if at all)? Explain.

When liquid A is mixed with liquid B to form a solution at room temperature, the solution becomes warm to the touch. Does this suggest a positive or negative deviation from Raoult's law? Explain.

Ouestion 27

Volatile hydrocarbons are not used in the brakes of automobile as lubricants, but non-volatile hydrocarbons are used as lubricants. Explain.

Ouestion 28

Explain why the boiling point of immiscible solution is less than either of the component.

Question 29

Define the following terms:

- (i) Saturated vapour pressure
- (ii) Raoult's law
- (iii) Azeotropic point
- (iv) Ideal solution

Ouestion 30

Components of binary mixture of two liquids A and B were being separated by distillation. After sometime, separation of components stopped and composition of vapour phase became same as that of liquid phase. Both components start coming in the distillate. Explain why this happened.

Question 31

Ethanol and water form an azeotropic mixture which boils at 78.1°C with 95.6% ethanol. The boiling point of pure ethanol and water are 78.4°C and 100°C respectively.

- (i) Draw a temperature-mole fraction phase diagram of ethanol-water solution.
- (ii) What happens when a solution of less than 50% ethanol is boiled?
- (iii) How pure ethanol may be obtained from the azeotropic mixture?

Question 32

- (i) State Nernst's distribution law.
- (ii) List any three limitations of the distribution law.

Briefly explain how the law stated in (i) above is useful in daily life

Ouestion 33

- (i) What is the solvent extraction?
- (ii) Explain two conditions for solvent for solvent extraction to be more successful.

Question 34

- (i) What are immiscible liquids
- (ii) Outline two important characteristics of immiscible liquid system

Question 35

The following data have been obtained on the distribution of phenol between water and chloroform.

| C ₁ | 0.094 | 0.163 | 0.254 | 0.436 |
|----------------|-------|-------|-------|-------|
|----------------|-------|-------|-------|-------|

| C_2 | 0.254 | 0.761 | 1.850 | 5.430 |
|-------|-------|-------|-------|-------|
|-------|-------|-------|-------|-------|

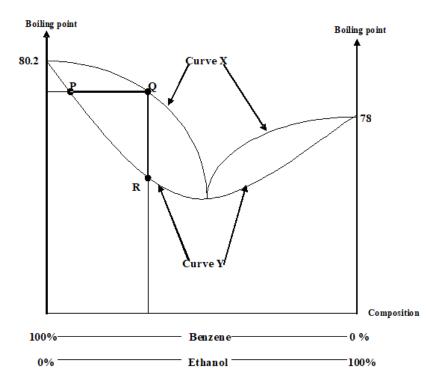
Where C_1 is the molar concentration in the aqueous layer and C_2 is the molar concentration in the chloroform layer; what conclusion do you draw from these results regarding the molecular condition of phenol in the chloroform solution?

Question 36

Liquid immiscible with water can be efficiently separated from their mixture with water through steam distillation. State any two conditions necessary for steam distillation to be efficient.

Question 37

The diagram below illustrates the boiling point-composition relationship for benzene – ethanol system.



- (a) What do the curves **X** and **Y** represent?
- (b) What is the relation between P, Q and R
- (c) From the above boiling point-composition diagram, sketch labelled diagram to illustrate the vapour pressure-composition relationships for the benzene –ethanol system.

Question 38

- (i) State Raoult's law
- (ii) With reference to Raoult's law, distinguish positive deviation from negative deviation.

Question 39

Explain how an increase in temperature, increases vapour pressure of a liquid.

Question 40

Briefly explain the principle of solvent extraction.

Compare and contrast fractional distillation from steam distillation.

Question 42

- (i) Identify whether the mixture of nitric acid and water shows positive or negative deviation from Raoult's law.
- (ii) What interaction between nitric acid and water leads to this type of deviation?

Ouestion 43

Given the following result for the distribution of phenol between water and chloroform

| Concentration of phenol in water (g/dm ³) | 8.836 | 15.322 | 23.876 |
|---|--------|--------|---------|
| Concentration of phenol in chloroform | 23.876 | 71.534 | 173.900 |
| (g/dm^3) | | | |

- (i) Use the above result to deduce whether phenol exists in normal state or dimerises in chloroform
- (ii) Describe clearly the reason for the state of phenol in chloroform deduced in (i) above

Question 44

Explain why addition of 1mol of NaCl to 1L of water, increases the boiling point of water, while addition of 1mol of methyl alcohol to 1L of water decreases its boiling point.

Ouestion 45

Under what main condition does solution formed upon mixing two liquids **A** and **B** behave as ideal solution? **Question 46**

Liquid **A** and **B** form an ideal solution when mixed together. If the boiling point of pure **A** is higher than the boiling point of pure **B** at 1 atmospheric pressure. Sketch:

- (a) A vapour-composition curve for the solution of liquid **A** and **B**
- (b) A temperature –composition curve for the solution of liquids **A** and **B**
- (c) Explain what will happen when an equimolar solution of mixture **A** and **B** is distilled at atmospheric pressure of 1atm.

Ouestion 47

Raoult's law only really works for ideal solutions. An ideal solution is defined as one which obeys Raoult's law

How do the following affect how ideal a solution is?

- (i) The concentration of the solution.
- (ii) The forces between the particles in the solution.

The vapour pressures of several solutions of water-propanol (CH₃CH₂CH₂OH) were determined at various compositions, with the following data collected at 45°C:

| X _{H2} 0 | Vapour pressure mmHg |
|-------------------|----------------------|
| 0 | 74.0 |
| 0.15 | 77.3 |
| 0.37 | 80.2 |
| 0.54 | 81.6 |
| 0.69 | 80.6 |
| 0.83 | 78.2 |
| 1.00 | 71.9 |

Based on the above data, answer the following questions:

- (a) Are solution of water and propanol ideal? Explain.
- (b) Predict the sign of enthalpy of solution, ΔH_{soln} , for water-propanol solutions.
- (c) Are the interactive forces between propanol and water molecules weaker than, stronger than, or equal to the interactive forces between the pure substances? Explain.
- (d) Which of the solutions in the data would have the lowest normal boiling point? What special name is given for this solution?

Question 49

A liquid is in equilibrium with its vapour in a sealed container at a fixed temperature. The volume of the container is suddenly increased.

- (i) What is the initial effect of the change on vapour pressure?
- (ii) How do rates of evaporation and condensation change initially?
- (iii) What happens when equilibrium is restored finally and what will be the final vapour pressure?

Question 50

- (i) State Raoult's law of volatile liquids.
- (ii) Give any three examples of ideal solutions.
- (iii) Give two main assumptions for Raoult's law to be valid?

Question 51

For each system, compare the intermolecular interactions in the pure liquids with those in the solution to decide whether the solution will be approximately ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:

- (i) cyclohexane and ethanol
- (ii) methanol and acetone
- (iii) n-hexane and isooctane

Ouestion 52

For each of the following liquid mixture; classify the mixture as ideal solution, non-ideal solution with positive deviation or non-ideal solution with negative deviation:

- (i) Benzene and n-hexane
- (ii) Trichloromethane and acetone
- (iii) Ethylene glycol and carbon tetrachloride
- (iv) Acetic acid and propanol

Alcohol dissolves in water to give a solution that boils at a lower temperature than pure water while table salt dissolves in water to give a solution that boils at a higher temperature than pure water. Explain this fact in terms of vapour pressure.

Question 54

What is wrong with each of the following statements:

- (i) When polar liquids are mixed together, the resulting mixture is always ideal solution.
- (ii) Boiling point of any solution containing two volatile liquids always lies between boiling points of the pure liquids.
- (iii) Solution containing alcohol and water is appropriately separated into its pure components by simple fractional distillation.

Ouestion 55

When two volatile liquids are mixed to form solution, the heat change for the process may be either be zero, positive or negative. Explain clearly each of the three scenarios

Question 56

Vapour pressure is an important physical property of substance. Knowing vapour pressure of substance at **given** temperature help us to know volatility of the substance.

- (i) How is vapour pressure related to intermolecular forces?
- (ii) Why in measurement of vapour pressure, temperature must be 'given'?
- (iii) Explain how vapour pressure is related to volatility.

Ouestion 57

Identify the solute and solvent in each of the following solutions:

- (i) Seawater
- (ii) 50/50 mixture of antifreeze and water
- (iii) Air
- (iv) Carbonated water
- (v) Bronze

Question 58

Ethyl benzoate is liquid with a boiling point of 213°C. It is virtually insoluble in water

(a) The vapour pressures of water and ethyl benzoate at 99°C are:

Ethyl benzoate 2.34kPa Water 97.76kPa

What can you say about the boiling point of the mixture at atmosphere pressure (101.325kpa)?

Ouestion 59

Explain clearly what is wrong with each of the following statements:

- (i) Ideal solution is the solution which obeys Raoult's law.
- (ii) Non-ideal solution with positive deviation are warm to the touch.

Question 60

List down five limitations of partition law.

Question 61

Give at least two examples of each of the following:

- (i) Ideal solution
- (ii) Non-ideal solution with negative deviation
- (iii) Non-ideal solution with positive deviation

(iv) Solid solution

Ouestion 62

Explain the behaviour of ideal solution on fractional distillation.

Question 63

- (i) How is distribution law modified when the solute undergoes dissociation in one of the solvent?
- (ii) What would happen if the solute is completely dissociated in one of the solvent?

Question 64

Give at least two advantages of steam distillation.

Ouestion 65

Compared to other methods, steam distillation is said to be cheap. Give two reasons to support this statement.

Ouestion 66

List down at least three differences between fractional distillation and steam distillation.

Question 67

Give an example of each of the following:

- (i) Gas solution in which the solute is liquid.
- (ii) Gas solution in which the solute is solid.
- (iii) Liquid solution in which the solute is gas.
- (iv) Solid solution in which the solute is liquid.

Solid solution in which the solute is solid too

Question 68

Explain why the concept of ideal solution is just hypothetical.

Ouestion 69

Mention at least three examples of substances which can be separated by steam distillation.

Ouestion 70

In what case, steam distillation needs to done under reduced pressure. Explain.

Question 71

List down at least three applications of steam distillation.

Question 72

Vapour pressure of a liquid does not depend upon the size of the container. Explain.

Question 73

What is steam distillation?

Ouestion 74

Why is an increase in temperature observed on mixing chloroform and acetone?

Mixture of ethoxyethane, $(C_2H_5O)_2O$ and trichloromethane, CHCl₃ do not obey Raoult's law; they have higher boiling points than expected. Explain this observation in terms of the intermolecular forces present in the pure liquids and in the mixture.

Ouestion 76

Predict the deviation from Raoult's law when two liquids are mixed and the heat of the solution is small. Give an explanation to support your prediction

Question 77

State and explain Raoult's law.

Question 78

Why are deviations from the ideal behaviour predicted by Raoult's law more common for solutions of liquids than are deviations from the ideal behaviour predicted by the ideal gas law for solutions of gases?

Question 79

- (i) Derive Nernst's distribution law.
- (ii) Give any four applications of Nernst's distribution law.

Ouestion 80

Explain how temperature affects vapour pressure of pure liquid.

Ouestion 81

A mixture of chlorobenzene and bromobenzene forms nearly ideal solution but a mixture of chloroform and acetone does not. Why?

Question 82

What will happen to the boiling point of the solution on mixing two miscible liquids showing negative deviation from Raoult's law? Explain.

Ouestion 83

Which type of deviation is shown by the solution formed by mixing cyclohexane and ethanol? Explain.

Question 84

Give at least three examples of compounds which can be separated by steam distillation.

Ouestion 85

Why all gas-gas solutions are considered to be ideal?

Ouestion 86

Azeotrope has fixed composition like compounds. However the azeotrope is usually regarded as a mixture and not as a compound. Explain.

Question 87

A 'solution' is made by dissolving ice in water. Is the solution ideal or non-ideal? Explain

Question 88

Not component of all kind of solutions can be separated by simple fractional distillation method. Viability of the method depend on how the solution behave with respect to Raoult's law.

(i) Which kind of solutions whose components may be separated by simple fractional distillation?

| (ii) | What feature possible? | do t | hese | solutions | (mentioned | in (i) | above) | possess | that | makes | the | separation |
|------|------------------------|------|------|-----------|------------|--------|--------|---------|------|-------|-----|------------|
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SOLUTIONS

Question 1

No.

Explanation

For mixture to be separated into pure components by fractional distillation, vapour composition should change compared to liquid composition upon boiling. Azeotropes boil at constant temperature making the vapour composition the same as liquid composition and hence they cannot be separated by fractional distillation.

Question 2

To condense a vapour of given composition to get its corresponding liquid at given pressure, lower temperature (liquid phase is below vapour phase) is needed while in condensing the vapour at given temperature, higher pressure (liquid phase is above the vapour phase) is needed.

Question 3

(i) True

Reason:

Unlike compounds azeotropes consists of different molecules of different substances. Furthermore, components of azeotropic mixture can be separated by physical methods like azeotropic distillation. Also, components of azeotropic mixture react independently; for example, only water in alcohol-water azeotrope reacts with CaO leaving alcohol unreacted.

(ii) True

Reason:

For a solution to obey Raoult's law in liquid phase, the intermolecular forces in pure liquids must be equal to intermolecular forces in the solution such that $P_A = X_A P_A^o$ and $P_B = X_B P_B^o$. Also, the vapour phase of the solution must behave exactly as ideal gas such that it obeys Dalton's law of partial pressure, that is $P_{soln} = X_A P_A^o + X_B P_B^o$

Question 4

(i) Ideal solution

Explanation:

Like water, methanol possess intermolecular hydrogen bonding accounted by presence of OH group. It is also bonded to very small non-polar (CH₃) group and thus making its polarity and strength of intermolecular forces very similar to those of water and hence even after mixing the two compounds in the solution, strength of intermolecular forces between methanol and water in the solution will remain the same making the solution ideal.

(ii) The mole fraction of 0.2 means that number of moles of methanol in 1 mol of the solution is 0.2mol.

And number of moles of water = (1 - 0.2)mol = 0.8mol

Using
$$m = n \times M_r = 0.8 \text{mol} \times 32 \text{gmol}^{-1} = 25.6 \text{g} = 0.0256 \text{kg}$$

The molality =
$$\frac{n_{su}}{m_{sv} \text{ in kg}} = \frac{0.2 \text{mol}}{0.0256 \text{ kg}} = 7.8125 \text{mol/kg}$$

Molality of the solution is 7.8125mol/kg.

Question 5

When an ideal solution is boiled at given temperature, the vapour phase is always richer in the more volatile component as compared to the solution phase.

Question 6

Due to the formation of azeotropic mixture, any attempt to separate alcohol from alcohol-water mixture by fractional distillation, will end up with distillate of the azeotrope containing 96% alcohol and pure water as residue. So absolute alcohol cannot be prepared by fractional distillation unless suitable dehydrating agent like CaO is introduced to the distillate to eliminate water.

Ouestion 7

No.

Explanation:

Ideal solution boils in such a way that the vapour formed is richer in one component which is more volatile. So always vapour phase has more of the component with high vapour pressure compared to liquid phase and hence vapour composition will normally be different to liquid composition.

Question 8

Azeotropes are similar to compounds in the following manner:

- ✓ They have fixed composition.
- ✓ They boil at fixed temperature without changing their composition.
- ✓ They cannot be separated into their respective pure components by simple distillation.

Question 9

Zeotropic mixture is the liquid mixture whose vapour composition is not the same as the liquid composition at given temperature. Is the mixture like benzene-toluene mixture with liquid components that have different boiling points and therefore can be separated by fractional distillation.

Question 10

Positive deviation.

Reason:

With hydrogen bonds, ethanol is more polar than acetone which has no hydrogen bonds. Thus, when acetone is mixed to ethanol, it tends to weakens the hydrogen bonds in ethanol and hence the intermolecular forces of attraction in the ethanol-water solution become smaller than intermolecular forces of attraction in ethanol leading to the positive deviation from Raoult's law.

Ouestion 11

Non-ideal solution of negative solution has higher boiling point than the expected one if the solution would be ideal. Consequently it attains azeotropic composition in liquid phase of which the liquid mixture has maximum boiling point. Hence the explained behaviour is the characteristic of a maximum boiling azeotrope.

Question 12

Yes.

Explanation:

Limonene is high boiling liquid which decomposes at high temperature. So steam distillation is used to obtain essential oils as the distillation (boiling) of immiscible mixture of the oil and water occurs at lower temperature.

Question 13

- (i) Azeotrope (or azeotropic mixture)
- (ii) Two; namely:
 - 1. Minimum boiling azeotrope/positive azeotrope, example ethanol-water mixture containing $95.6\% \left(\frac{m}{m}\right)$ ethanol.
 - 2. Maximum boiling azeotrope/negative azeotrope, example nitric acid-water mixture containing $68\% \left(\frac{m}{m}\right)$ nitric acid.

Question 14

- 1. Must be immiscible in water.
- 2. Must not decompose at the temperature of steam.
- 3. Must have fairly high vapour pressure at 100°C
- 4. Its impurities must be non-volatile.

Question 15

- 1. Study of association of a solute
- 2. Study of dissociation of a solute
- 3. Study of complex ions
- 4. Solvent extraction
- 5. Distribution of indicators

Question 16

Zeotropic mixture is the liquid mixture whose vapour composition is not the same as the liquid composition at given temperature while azeotropic mixture is the liquid mixture whose vapour composition is the same as liquid composition at given temperature. Thus zeotropic is the mixture with liquid components that have different boiling points and therefore can be separated by fractional distillation while azeotropic mixture boils at constant temperature and cannot be separated by fractional distillation.

Ouestion 17

- 1. Temperature
- 2. Nature of solute
- 3. Nature of solvents

Ouestion 18

In very dilute solution there are much more solvent-solvent forces of attraction than solvent-solute forces of attractions (as number of solvent molecules is too large compared to number of solute molecular) and hence intermolecular forces of attraction in the solution become almost equal to intermolecular forces of attraction in pure liquids.

- (i) An ideal solution is the solution which obeys Raoult's law exactly over the entire range of concentration.
- (ii) Ideal solutions are formed by mixing the two components which are identical in molecular size, in structure and have almost identical intermolecular forces. In these solutions, the intermolecular forces between the components in the solution are of same magnitude as the intermolecular forces in pure components.

Definition: Is the constant boiling point liquid mixture whose composition does not change on distillation.

Type: Minimum boiling azeotrope.

Example: A mixture of ethanol and water containing 95.6% ethanol forms minimum boiling azeotrope.

Question 21

The solution of chloroform and acetone has lower vapour pressure than ideal solution because of intermolecular hydrogen bonds between chloroform and acetone molecules in the solution which are stronger intermolecular forces than dipole-dipole forces in pure chloroform and acetone. As a result, total vapour pressure becomes less than the corresponding ideal solution of same composition (i.e. negative deviations). Therefore, the boiling points of solutions are increased and form maximum boiling azeotropes.

Question 22

- (i) There are three types.
- (ii)

1. Gaseous solution

This is the solution in which the solvent is a gas.

In these solutions; the solute may be liquid, solid or gas. For example, a mixture of oxygen and nitrogen gas is a gaseous solution.

2. Liquid solution

This is the solution in which the solvent is a liquid.

In these solutions, the solute may be gas, liquid or solid. For example a solution of sodium chloride in water is a liquid solution

3. Solid solution

This is the solution in which the solvent is a solid.

The solute in this solution may be gas, liquid or solid. For example, a solution of copper in zinc is a solid solution.

(iii) Hydrogen in palladium (in which hydrogen gas is a solute and the solid is solvent)

- (i) Boiling point of a liquid is the temperature at which vapour pressure of the liquid is equal to the atmospheric (external) pressure.
- (ii) Increase in external pressure increases boiling point and vice versa.

In pure alcohol and water, the molecules are held tightly by strong hydrogen bonding. Then interaction between molecules of alcohol and water is weaker than alcohol-alcohol and water –water interaction. As result, when alcohol and water are mixed, the intermolecular interactions become weaker and the molecules can easily evaporate. This increases the vapour pressure of the solution which in turn lowers the boiling point of resulting solution.

Question 25

Raoult's law holds for an ideal solution. So the partial pressure of benzene in benzene-toluene mixture (where by both components of the mixture are non-polar, making the solution ideal) is given by the following formula: $P_{benzene} = X_{benzene} P_{benzene}^{\circ}$

Adding a polar compound (benzoic acid) to a non-polar solvent (benzene) will result in an increased intermolecular force of attraction between the polar solute and the non-polar solvent relative to the intermolecular forces of attraction between the non-polar solute and the non-polar solvent. This will reduce partial pressure of benzene, giving a negative deviation from Raoult's law.

Question 26

Negative deviation from Raoult's law.

Explanation:

The solution being warm to touch suggests that the process of mixing A and B is exothermic. This means that the interaction created between A and B are stronger than A-A and B-B interactions which are broken in the mixing process thus making the process exothermic in overall. The exothermic nature of the mixing process is indicating a negative deviation from Raoult's law.

Ouestion 27

The vapour pressure of volatile hydrocarbons is very high and therefore they get evaporated, leaving behind the system. Due to this they are not used as lubricants in automobiles unlike non-volatile hydrocarbon which have low vapour pressure.

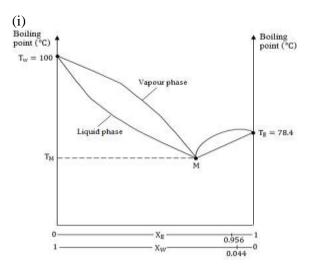
Question 28

In immiscible solution each liquid exerts pressure independently thus making the vapour pressure of the solution greater than either of the two components and hence boiling point will be less than either of the two.

- (i) Saturated vapour pressure is the vapour pressure of the liquid in equilibrium with excess liquid at **given temperature.**
- (ii) Raoult's law is the law that relate the partial vapour pressure of a particular component in ideal solution to its mole fraction.
- (iii) Azeotropic point is the boiling point of the azeotropic mixture.
- (iv) Ideal solution is the mixture of substances of similar chemical structures and polarities.

The separation of components stopped due to formation of azeotropic mixture in the distillate. Also the formation of azeotropic mixture in the distillate suggest that the binary mixture of A and B is the non-ideal solution of positive deviation.

Question 31



Where: T_w is the boiling point of pure water

T_E is the boiling point of pure ethanol

T_M is the boiling point of azeotropic mixture (azeotropic point)

M is the azeotropic mixture

X_E is the mole fraction of ethanol

X_W is the mole fraction of water

- (ii) The solution will boil in such a way that the vapour formed is richer in ethanol until its percentage in the collector rises to 95.6%. Finally on successive distillation and condensation the filtrate in the collector will be azeotropic mixture with 95.6% ethanol and the residue in the distillation flask will be pure water.
- (iii) By introducing suitable dehydrating agent like calcium oxide (CaO) so as to remove water which is only 4.4%.

- (i) When non-volatile solute is introduced into the container containing two immiscible solvents mixture, the solute tends to distribute itself in such a way that there is a fixed ratio of concentration of solute in the two solvents, provided that the molecular state of the solute remains the same in the two solvents and temperature is kept constant.
- (ii) Distribution law is not applicable when:
- 1. The temperature is not kept constant.
- 2. The molecular state of the solute in the two solvents is not the same. (If the solute undergoes either association or dissociation in one of the solvent).

- 3. The distribution of solute in the two solvents is not at equilibrium.
- 4. The solute concentration in the two solvents is high.
- 5. The solvents are miscible.

(iii) The law is applied in solvent extraction to remove impurities; in liquid chromatography to separate solutes and also in determination of solubility of substances like solubility of drugs in water and other solvents.

Question 33

(i) Is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent(extractive solvent) which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents.

(ii)

First condition: The solute must be more soluble in extractive solvent than in the first solvent. That is, to ensure that greater amount of solute goes to extractive solvent, the partition coefficient between extractive solvent and first solvent, K_d should be large.

Second condition: The volume of extractive solvent should be divided into small portions (partitions) rather than using the whole large volume at once. That is, greater amount of solute is extracted by having larger number of portions of volume of extractive solvent.

Question 34

- (i) Are liquids which do not mix at all so that they tend to form separating layer when they are mixed. These are liquids like water and benzene whose intermolecular forces differ much.
- (ii)

1. Vapour pressure

Vapour pressure of the immiscible liquid mixture is the arithmetic summation of vapour pressure of individual pure components.

2. Intermolecular forces

Intermolecular forces in pure liquids is different to intermolecular forces in the solution.

(Liquids which form immiscible mixture have different intermolecular forces).

| C ₁ | 0.094 | 0.163 | 0.254 | 0.436 |
|--------------------------|-------|-------|-------|-------|
| C_2 | 0.254 | 0.761 | 1.850 | 5.430 |
| $\frac{C_1}{C_2}$ | 0.370 | 0.214 | 0.137 | 0.080 |
| $\frac{C_1}{\sqrt{C_2}}$ | 0.187 | 0.187 | 0.187 | 0.187 |

Thus $\frac{C_1}{\sqrt{C_2}}$ = constant, suggesting that two molecules of phenol associate in the chloroform solution to form a dimer.

Hence phenol exists as dimer in the chloroform solution.

Question 36

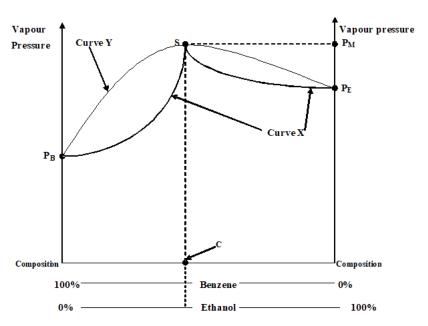
- 1. The liquid must be immiscible with water and the solution should boil to a temperature close to $100^{\circ}C$
- 2. The vapour pressure of liquid (at temperature close to 100°C) should be greater than that of water.
- 3. The molar mass of the liquid should be large compared to that of water.

Question 37

(a) Curve x represent vapour phase of the solution

Curve y represent liquid phase of the solution

- (b) \mathbf{Q} is the vapour formed after distillation (boiling) of liquid \mathbf{P} at given temperature and \mathbf{R} is the liquid formed after condensation of vapour \mathbf{Q} .
- (c) A sketched graph to illustrate the vapour pressure composition relationship for benzene ethanol system



Question 38

- (i) Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.
- (ii) Real vapour pressure of non-ideal solution with negative deviation is smaller than that predicted by Raoult's law.

Increase in temperature **increases concentration** and **speed** of vapour particles leading to **more frequent collisions** between vapour particles and walls of the container and hence greater vapour pressure.

Question 40

Solvent extraction is the method of removing (extracting) a solute from a certain solvent by introducing the second solvent(extractive solvent) which is immiscible to the first one and then allowing the solute to distribute itself in the two solvents. The layer of extractive solvent is then removed with significant amount of the solute and on successive extractions which are done by introducing fresh extractive solvent again and again, the solute is finally completely removed from the first solvent (or very small amount remain in the first solvent).

Ouestion 41

Similarity: They both separate components of the mixture based on the boiling point.

Difference: Steam distillation separates thermally unstable component of the mixture which is immiscible to water while fractional distillation separates thermally stable components of miscible liquid mixture. Steam distillation is therefore takes place at temperature below the boiling point of components while fractional distillation takes place at boiling point of components.

Question 42

- (i) Negative deviation.
- (ii) Ion-ion interactions.

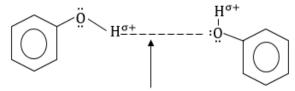
Question 43

(i) Let C_1 and C_2 be concentration of phenol in water and chloroform respectively.

| C_1 | 8.836 | 15.322 | 23.876 |
|--------------------------|--------|--------|---------|
| C_2 | 23.876 | 71.534 | 173.900 |
| $\frac{C_1}{C_2}$ | 0.370 | 0.214 | 0.137 |
| $\frac{C_1}{\sqrt{C_2}}$ | 1.808 | 1.812 | 1.811 |

Since $\frac{C_1}{C_2}$ is not constant while $\frac{C_1}{\sqrt{C_2}}$ is constant of approximated value of 1.8, phenol dimerises in chloroform

(ii) Dimerization of phenol is possible due to very strong hydrogen bonding existing between its molecules when the phenol is in chloroform.



Hydrogen bonding to enable the dimerisation

NaCl is non-volatile solute; introducing it in water, lowers the vapour pressure of water and hence the boiling point is increased.

On another hand, methanol is less polar liquid than water; introducing it in water weakens intermolecular forces between water molecules, increasing its vapour pressure and hence boiling point is decreased.

Question 45

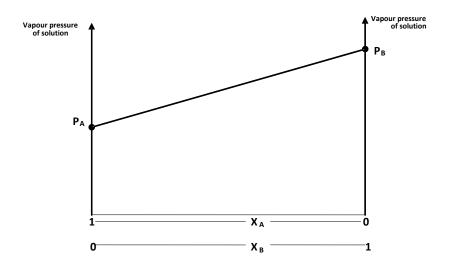
Intermolecular forces in A and B should be equal in such a way that intermolecular forces in the solution is equal to intermolecular forces in pure A and pure B.

$$A \dots A = B \dots B = A \dots B$$

Where; represents intermolecular forces.

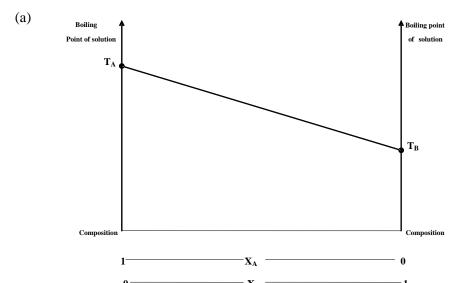
Question 46

(a)



Where P_A is the vapour pressure of pure A

 P_B is the vapour pressure of pure B



Where T_A is the boiling point of pure A

 T_B is the boiling point of pure B

(c) The solution will boil in such a way that the vapour formed is richer in $\bf B$ (more volatile component). So on successive distillation and condensation the pure $\bf B$ is obtained as distillate in collector and pure $\bf A$ remain in the distillation flask as residue.

Question 47

- (i) Decrease in concentration makes the solution more ideal while increase in concentration makes the solution to deviate more from ideal behaviour.
- (ii) If the intermolecular forces in the solution are similar to intermolecular forces in pure components the solution will be more ideal while different intermolecular forces in the solution compared to those present in the pure components makes the solution to show greater deviation from ideal behaviour.

Question 48

(a) Not ideal solution.

Explanation

An ideal solution would have a vapour pressure at any mole fraction of H_2O between that of pure propanol and pure water (between 74torr and 71.9torr). The vapor pressures of the solution are not between these limits so it is not an ideal solution.

- (b) From the data, the vapour pressures of the various solutions are greater than in the ideal solution (positive deviation from Raoult's law). This occurs when the intermolecular forces in solution are weaker than the intermolecular forces in pure solvent and pure solute. This will cause the solution making process endothermic (positive) and hence the enthalpy of solution (ΔH_{soln}) will be positive.
- (c) Weaker.

Explanation

The interactions between propanol and water molecules are weaker than between the pure substances since the solution exhibits a positive deviation from Raoult's law.

(d) When $X_{H_2O} = 0.54$ the vapour pressure is highest as compared to the other solutions. Since a solution boils when the vapour pressure of the solution equals the external pressure, then the solution with $X_{H_2O} = 0.54$ should have the lowest normal boiling point; this solution will have a vapour pressure equal to 1 atm at a lower temperature as compared to the other solutions.

Special name: Azeotropic mixture (minimum boiling azeotrope).

- (i) If the volume of the container is suddenly increased, then the vapour pressure would decrease initially. This is because the amount of vapour remains the same, but the volume increases suddenly. As a result, the same amount of vapour is distributed in a larger volume.
- (ii) Since the temperature is constant, the rate of evaporation also remains constant. When the volume of the container is increased, the density of the vapour phase decreases. As a result, the rate of collisions of the vapour particles also decreases. Hence, the rate of condensation decreases initially.
- (iii) When equilibrium is restored finally, the rate of evaporation becomes equal to the rate of condensation. In this case, only the volume changes while the temperature remains constant. The vapour pressure depends on temperature and not on volume. Hence, the final vapour pressure will be equal to the original vapour pressure of the system.

Question 50

- (i) Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.
- (ii)
- 1. Propanol-ethanol solution
- 2. Toluene-benzene solution
- 3. Heptane-hexane solution
- (iii)
 - 1. Intermolecular forces between the components in the solution is the same as those intermolecular forces in pure components.
 - 2. The gaseous phase of the solution act as an ideal gas where the use ideal gas law is applicable.

- (i) Liquid ethanol contains an extensive hydrogen bonding network, and cyclohexane is non-polar with Van-der-Waals dispersion forces. Because the cyclohexane molecules cannot interact favorably with the polar ethanol molecules, they will disrupt the hydrogen bonding. As a result, the intermolecular interactions in the solution will be weaker than those intermolecular interactions in pure ethanol and pure cyclohexane leading to a higher vapour pressure than predicted by Raoult's law and hence the solution will be non-ideal with positive deviation.
- (ii) Methanol contains an extensive hydrogen bonding network. With the polar acetone molecules, it create intermolecular interactions in the solution which are stronger than the intermolecular interactions in pure components. This makes the real vapour of solution to be lower than that predicted by Raoult's law and hence the solution will be non-ideal with negative deviation.
- (iii) Hexane and isooctane are both non-polar molecules. Thus the predominant intermolecular forces in both liquids are London dispersion forces. So in the solution the intermolecular interactions will be similar to those intermolecular forces in the pure liquids. As result, the real vapour pressure of the solution will be almost the same as that predicted by Raoult's law and hence the solution will be approximately ideal.

- (i) Ideal solution
- (ii) Non-ideal solution with negative deviation
- (iii) Non-ideal solution with positive deviation
- (iv) Non-ideal solution with negative deviation

Question 53

An alcohol-water solution has a higher vapour pressure than that of pure water because alcohol is a volatile solute and therefore contributes significantly to the vapour of the solution. This high vapour pressure accounts for the lower boiling point in alcohol-water solution.

On another hand, a salt-water solution has a lower vapour pressure than that of pure water because salt is a non-volatile solute and solute-solvent interaction decrease the vapour of the solution. This low vapour pressure accounts for the higher boiling point in salt-water solution.

Ouestion 54

- (i) Polar liquid may form partially miscible mixture which are normally behaving as non-ideal solution with positive deviation. For example, ethanol and water are both polar liquid but the ethanol-water mixture is non-ideal solution with positive deviation. Also some polar liquids like sulphuric acid ionises in the polar solvent, water, resulting to ion-ion interactions in the solution and hence the solution becomes non-ideal with negative deviation.
- (ii) The given statement does not hold for any solution. Non-ideal solution with positive deviation has the boiling point which lower than either of the pure component while non-ideal solution with negative deviation has boiling point which is higher than either of the pure component.
- (iii) Simple fractional distillation cannot be used to get pure water and pure ethanol from the mixture due to the formation of azeotropic mixture as the ethanol-water mixture is non-ideal solution.

Question 55

Zero heat change: This occurs when strength of intermolecular forces in pure liquid is equal to that in solution such that the energy absorbed in breaking intermolecular forces in pure liquid is equal to the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are ideal solution.

Positive heat change: This occurs when strength of intermolecular forces in solution are smaller than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is greater than the energy evolved in forming intermolecular forces in the solution. As result, solution under this category are non-ideal solution with positive deviation.

Negative heat change: This occurs when strength of intermolecular forces in solution are higher than those in pure liquid such that the energy absorbed in breaking intermolecular forces in pure liquid is smaller than the energy evolved in forming intermolecular forces in the solution. As result, solutions under this category are non-ideal solution with negative deviation.

Question 56

(i) Vapour pressure becomes smaller as intermolecular forces becomes stronger.

- (ii) Vapour pressure is temperature dependent whereby it increases as temperature increases and hence it becomes necessary to state temperature at which vapour pressure has been measured.
- (iii) High vapour pressure of a substance implies that smaller temperature raise is needed to increase the vapour pressure to atmospheric pressure and thus lower boiling point and hence high volatility of the substance.

(i) **Solute:** salts. **Solvent:** water.

(ii) Solute: ethylene glycol. Solvent: water.

(iii) Solute: Oxygen (and all other minor components). Solvent: Nitrogen gas

(iv) Solute: carbon dioxide. Solvent: water.

Solute: tin. Solvent: copper

Question 58

A liquid boils when its vapour pressure becomes equal to the atmospheric pressure. At 99°C, the total pressure is 100.1kPa (2.34kPa + 97.76kPa) which is slightly less than the atmospheric pressure. That means that it is close to, but below its boiling point.

Pure water must have a vapour pressure of 101.325kPa at 100°C (normal boiling point of water).

The combined water and ethyl benzoate vapour pressure reach 101.325kPa at temperature less than 100°C (boiling point of immiscible liquid mixture is less than either of the two components) and hence the mixture must boil somewhere between 99°C and 100°C.

Ouestion 59

- (i) For the solution to be ideal it must obey Raoult's law over the **entire range of concentration (at any concentration)**. Even non-ideal solution may obey Raoult's if the solution is very dilute.
- (ii) Formation of non-ideal solution with positive deviation is endothermic process and thus the solution becomes cold to touch. If the solution is warm to touch it must be non-ideal solution with negative deviation whose formation is exothermic process.

Ouestion 60

- 1. Constant temperature
- 2. Same molecular state
- 3. Equilibrium concentration
- 4. Dilute solution
- 5. Non miscibility of solvents

Question 61

- (i) Benzene-toluene and methanol-ethanol solution.
- (ii) Hydrochloric acid solution (HCl-water solution) and acetone-chloroform solution.
- (iii) Ethanol-water solution and benzene-phenol solution.
- (iv) Hydrogen-platinum solution and copper-zinc solution (brass alloy).

Question 62

Ideal solution boils in such a way that, the vapour formed is richer in one component which more volatile. So on successive distillation and condensation pure component which more volatile is found in the collector

as the distillate and pure component which less volatile remains in the distillation flask as the residue. Hence non-ideal solution can be separated into its pure component by fractional distillation.

Question 63

(i) It is modified to $K_d = \frac{C_1}{C_2(1-\alpha)}$ where C_1 is the concentration of the solute in the first solvent where the solute exist in its normal molecular state,

 C_2 is the original concentration (before dissociation) of the solute in the second solvent where it dissociates, α is the degree of dissociation of the solute in the second solvent where it dissociates.

(ii) The distribution coefficient would be undefined $(K_d = \infty)$

Question 64

- 1. It avoids thermal decomposition
- 2. Its equipment is relatively inexpensive
- 3. It generates products which are free from organic solvents
- 4. It does not involve subsequent separation steps
- 5. It requires less fuel for extraction of oil

Ouestion 65

- 1. Its equipment is inexpensive
- 2. It requires less fuel for extraction of oil

Question 66

- 1. In steam distillation vapourisation is normally done by means of steam whereas direct heating is used to vapourise component in fractional distillation.
- 2. Steam distillation is used to separate components in a heat sensitive mixture whereas the fractional distillation is a technique useful in separating the hydrocarbon fractions in crude oil.
- 3. In steam distillation only one step of distillation and condensation is used whereas there is successive (repetition of) distillation and condensation in the fractional distillation.

In steam distillation components are distilled at temperatures below their actual boiling points whereas in fractional distillation, the components are distilled at their boiling points

Question 67

- (i) Water in air (humidity)
- (ii) Camphor in nitrogen gas
- (iii) Carbon dioxide in water
- (iv) Mercury in zinc (zinc amalgam)
- (v) Carbon in iron (steel)

Ouestion 68

This is because there is no solution which is exactly ideal; every solution deviates from Raoult's law to some extent at certain concentration. To be exactly ideal, the intermolecular forces of attraction in pure components must be exactly the same which is impossible (only molecules of the same substance have exactly the same intermolecular forces).

Question 69

1. Orange oil

- 2. Eucalyptus oil
- 3. Camphor oil
- 4. Benzene
- 5. Toluene
- 6. Xylene

When the substance to be isolated is such temperature sensitive that it decomposes at much low temperature.

Explanation

Steam distillation is used in isolation of substances like organic compounds which decompose before boiling as their normal boiling point are above their decomposition temperature. When the substances are very sensitive to heat (they decompose at much lower temperature), then steam distillation is applied under reduced pressure, therefore reducing the boiling point of the mixture (operating temperature) even further.

Question 71

- 1. Extraction of eucalyptus oil from eucalyptus
- 2. Extraction of citrus oils from lemon

Extraction of oils used in perfumes from various plant material

Question 72

Vapour pressure is measured when the liquid in the container is at equilibrium with vapour. Using container of larger volume means the liquid has more surface to evaporate and therefore there are more vapour at equilibrium resulting to the same collision frequency between vapour and container's walls despite the increase in volume and hence equilibrium vapour pressure remains constant. Analogously, container of smaller volume means less surface area for liquid to evaporate resulting to the same vapour pressure despite the decrease in volume.

Question 73

Is a separation process for temperature sensitive materials which is immiscible to water of which distillation is carried in a current of steam. It is the method mainly used to separate organic compounds (especially aromatic compounds like xylene) which have tendency to decompose at high temperature.

Ouestion 74

The intermolecular forces in pure chloroform molecules and pure acetone are dipole-dipole interactions. But on mixing, the chloroform and acetone molecules, they start forming intermolecular hydrogen bonds which are stronger than dipole-dipole interactions resulting in the release of energy and hence the increase in temperature.

Question 75

Having higher boiling point than expected means that intermolecular forces in the solution are stronger than those present in pure liquid components suggesting negative deviation from Raoult's law. This is due to the fact that intermolecular forces in pure ethoxyethane molecules and pure trichloromethane are dipole-dipole interactions. But on mixing, the ethoxyethane and trichloromethane molecules, they start forming intermolecular hydrogen bonds which are stronger than dipole-dipole interactions resulting to higher boiling point of the solution.

Question 76

Prediction: Small deviation from Raoult's law (Almost ideal solution).

Explanation:

Small heat of solution means that amount of heat evolved in forming intermolecular forces in the solution is almost the same to the amount of heat absorbed in breaking intermolecular forces in pure components. This implies that the strength of intermolecular forces in pure components is similar to strength of intermolecular forces in the solution which in turn implies that the solution is relatively ideal with almost zero deviation from Raoult's law.

Raoult's law states that: Partial vapour pressure of a particular constituent (component) in a solution which contains two or more volatile miscible liquids is the product of its mole fraction and its vapour pressure of the pure liquid at given temperature.

The law relates the partial vapour pressure of a particular component in ideal solution to its mole fraction. It's only applicable for ideal solution and by combining it with Dalton's law of partial pressure, vapour pressure of ideal solution can be determined.

Thus for the solution which contains two volatile liquids, say A and B:

By Raoult's law;
$$P_A = X_A P_A^0$$
 and $P_B = X_B P_B^0$

And by Dalton's law of partial pressures:

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

Hence
$$P_{soln} = X_A P_A^o + X_B P_B^o$$

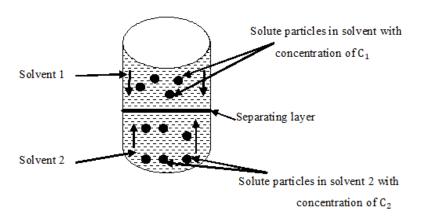
Question 78

For liquid solution to obey exactly Raoult's law, the intermolecular forces of attraction in pure components must be exactly the same which is impossible unless those components are of the same substance whose 'mixture' will no longer be a solution. So the deviation of solution from Raoult's law is compulsory.

On another hand, for gas solution to obey ideal gas law, intermolecular forces between gas molecules must be absent and size of individual gas molecules must be neglected. The two conditions are relatively easily met in small gases and also when there is high temperature and low pressure and hence it is easier to find gas solution which obey ideal gas law than finding the liquid solution which obeys Raoult's law.

Question 79

(i) Consider the following diagram:



The rate of diffusion of solute particles from one solvent to another in directly proportional to the concentration of the solute in the solvent

So if:

 R_1 is the rate of diffusion of the solute from the solvent 1 to solvent 2

 R_2 is the rate of diffusion of the solute from the solvent 2 to solvent 1

Then $R_1 \propto C_1$ or $R_1 = K_1C_1 \dots (i)$ (K_1 is the constant for proportionality)

And $R_2 \propto C_2$ or $R_2 = K_2C_2 \dots \dots (ii)(K_2 \text{ is the constant for proportionality})$

After certain time of diffusion, the equilibrium will be established where; $R_1 = R_2$

Thus at equilibrium:
$$K_1C_1 = K_2C_2$$
 or $\frac{K_2}{K_1} = \frac{C_1}{C_2}$

But $\frac{K_2}{K_1}$ gives another constant which is known as the partition coefficient, K_d

Hence
$$K_d = \frac{\text{Concentration of solute in the solvent 1}}{\text{Concentration of solute in the solvent 2}}$$

(ii)

- 1. Solvent extraction
- 2. Partition chromatography
- 3. Release of drug from dosage form
- 4. Passage of drug through membranes
- 5. Preservation of emulsions and creams
- 6. Formation of solubilized system

Question 80

Vapour pressure of the liquid is increased by increase in temperature.

Explanation:

When the temperature is increased, the number of vapour (gas) particles and their velocity are also increased which in turn increases both collision frequency and collision intensity between vapour particles and walls of the container and hence the vapour pressure is also increased.

Question 81

Like in their respective pure component, there are dipole-dipole interactions between bromobenzene and chlorobenzene in the solution with similar strength as that acting between pure bromobenzene molecules and chlorobenzene molecules. This makes the solution nearly ideal solution unlike in chloroform-acetone solution where there are intermolecular hydrogen bonds between chloroform and acetone molecules in the solution which are stronger intermolecular forces than dipole-dipole forces in pure chloroform and acetone leading to negative deviation from Raoult's law.

Question 82

Boiling point will be greater than either of the pure liquid.

Explanation:

Intermolecular forces in non-ideal solution with negative deviation are stronger than intermolecular forces in pure liquid components making vapour pressure of the solution less than that predicted by Raoult's law and hence higher boiling point for the solution.

Question 83

Positive deviation from Raoult's law.

Explanation:

Cyclohexane being less polar tend to weakens intermolecular hydrogen bonds in ethanol which is more polar and consequently intermolecular forces between cyclohexane and ethanol molecules in the solution are weaker than in pure ethanol leading to positive deviation from Raoult's law.

Question 84

- 1. Benzene
- 2. Toluene
- 3. Xylene
- 4. Nitrobenzene

Question 85

Gas molecules in both pure form and mixture form in the solution are fast moving and are very far apart such that intermolecular forces between them negligible and hence the solution becomes ideal.

Question 86

This is because, unlike compounds azeotropes consists of different molecules of different substances. Furthermore components of azeotropic mixture can be separated by physical methods like azeotropic distillation. Also components of azeotropic mixture react independently; for example, only water in alcoholwater azeotrope reacts with CaO leaving alcohol unreacted.

Question 87

The solution is ideal.

Explanation:

Ice (solid water) and liquid water have the same chemical structure of water. Their mixture is actually the one thing of pure substance which is water, and hence in solution terms the 'mixture' is exactly ideal solution.

- (i) **Type:** Ideal solution
- (ii) **Feature:** Its composition change on distillation (On distillation, the vapour formed is richer in one component which is more volatile as compared to liquid composition).