ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 6: PHYSICAL EQUILIBRIA

PART I: RAOULT'S LAW AND DEVIATIONS

1. (a) State three reasons why azeotropes are considered to be mixtures and not compounds.

   (b) The total vapour pressure of mixture of propanone and 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 the mixture (mmHg)	347	305	267	244	256	293

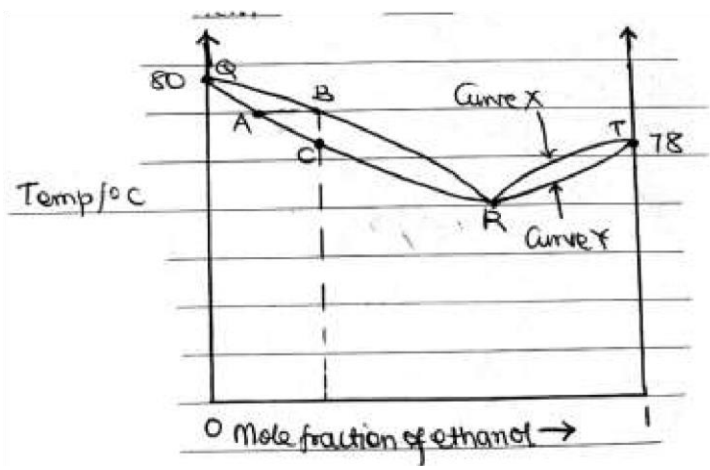
   (i) Plot a graph of total vapour pressure of the mixture against the mole fraction of trichloromethane

   (ii) Using your graph, deduce how the mixture deviates from Raoult's law. Give a reason for your answer

   (iii) Explain the causes of the deviation you have stated in b (ii)

   (iv) Determine the composition of the azeotrope

2. (a) The graph below shows the boiling point – composition diagram for benzene – ethanol system



   (i) Identify curves X and Y and point R.

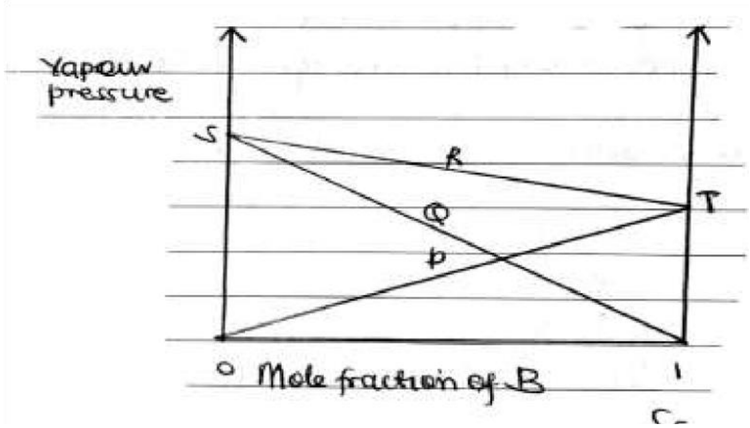
   (ii) A mixture at point R was boiled, state what happened to its composition

   (iii) State the relationship between A, B and C

   (iv) Draw a labelled diagram to illustrate the vapour pressure – composition diagram for the benzene – ethanol system.

3. (a) State three properties of an ideal solution

(b) The vapour pressure – composition diagram for an ideal solution of liquids A and B is shown below.



(i) Identify lines P, Q and R and the points S and T.

(ii) Draw a fully labelled boiling point – composition diagram for a mixture of liquids A and B

(iii) State what would be obtained as the distillate and the residue if a liquid mixture containing 40% of A is fractionally distilled

(c) A mixture of benzene and methylbenzene form an ideal solution

(i) Calculate the vapour pressure of a solution containing 1.95g of benzene and 4.6g of methylbenzene at 20ºC. [the vapour pressure of pure benzene and methylbenzene at 20ºC are 10.0kPa and 8.2kPa respectively] (ii) Determine the composition of the vapour of the mixture in (i) above

(d) Briefly describe what takes place during fractional distillation.

4. (a) The vapour pressure of a solution containing 1 mole of liquid A and 4 moles of liquid B is 0.750 atm at a certain temperature. The vapour pressure of pure A and pure B are 0.674 and 0.453 atm respectively at the same temperature.

(i) Calculate the vapour pressure of the solution if it behaved as an ideal solution

(ii) State how the solution deviates from Raoult's law and give a reason

(b) (i) State Raoult's law

(ii) Explain why some solutions do not obey Raoult's law.

5. (a) Explain what is meant by the term ideal solution.

(b) At standard atmospheric pressure, hydrochloric acid and water form a constant boiling point mixture having a boiling point of 110ºC and a composition of 20% by mass of hydrochloric acid.

(i) Define a constant boiling mixture

(ii) Sketch a labelled diagram of the boiling point – composition for hydrochloric acid and water system. [boiling point of water and hydrochloric acid are 100 and 85ºC respectively]

(c) A constant boiling mixture of hydrochloric acid and water has a density of 1.18gcm^{-3}. Calculate the volume of the acid needed to prepare one litre of 2M hydrochloric acid solution

(d) The vapour pressure of ethanol at 20ºC is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for a mixture of benzene and ethanol at 20ºC. Calculate

(i) The vapour pressure of the mixture

(ii) The mole fraction of benzene in the vapour phase

6. (a) Define the term partial pressure

(b) The vapour pressure of pure chloroform and carbon tetrachloride are 199.1 and 114.5 mmHg respectively at 25ºC. Assuming that the mixture behaves ideally. Calculate

(i) The partial pressure of each component in the mixture

(ii) The total pressure.

(c) Calculate the percentage of carbon tetrachloride in the vapour in equilibrium with the liquid mixture containing 0.4 mole fraction of chloroform

7. (a) State Raoult's law

(b) A mixture of ethanoic acid (boiling point 118ºC) and pyridine (boiling point 123ºC) show negative deviation from Raoult's law

(i) Draw the vapour pressure – composition diagram for the mixture of ethanoic acid and indicate the line for the ideal behaviour

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

8. (a) Heptane and octane form an ideal solution

(i) Explain what is meant by the term '**ideal solution**'

(ii) State Raoult's law

(iii) Calculate the vapour pressure of a solution containing 50g of heptane and 30g of octane. The vapour pressure of heptane and octane at this temperature are 473.2 and 139.8Pa respectively

(b) Compound A (boiling point 372ºC) and compound B (Boiling point 399ºC) form an ideal solution.

(i) Sketch a labelled boiling point – composition diagram for the mixture

(ii) Using the diagram, describe and explain how pure B can be obtained from a mixture containing 50% compound B.

9. (a) Explain what is meant by the term ideal solution

(b) Propanone and trichloromethane form a mixture that deviates negatively from Raoult's law.

(i) Explain why this mixture deviates negatively from Raoult's law.

(ii) Sketch a labelled diagram for the vapour pressure – composition for the mixture of propanone and trichloromethane (the boiling of propanone is lower than that of trichloromethane)

(iii) Describe what would happen if a mixture of trichloromethane and propanone was fractionally distilled

10. (a) Ethanol (boiling point 78.5ºC) and tetrachloromethane (boiling point 76.8ºC) form an azeotropic mixture of boiling point 65.0ºC and 38% ethanol by composition

(i) What is an **azeotropic mixture**?

(ii) Draw a well labelled boiling point – composition diagram for the ethanol – tetrachloromethane mixture

(iii) Explain why ethanol and tetrachloromethane form an azeotropic mixture?

(b) Describe the changes that take place when a mixture containing 45% ethanol is fractionally distilled.

11. (a) State Raoult's law

(b) Methanol and cyclohexane form a mixture that deviates positively from Raoult's law

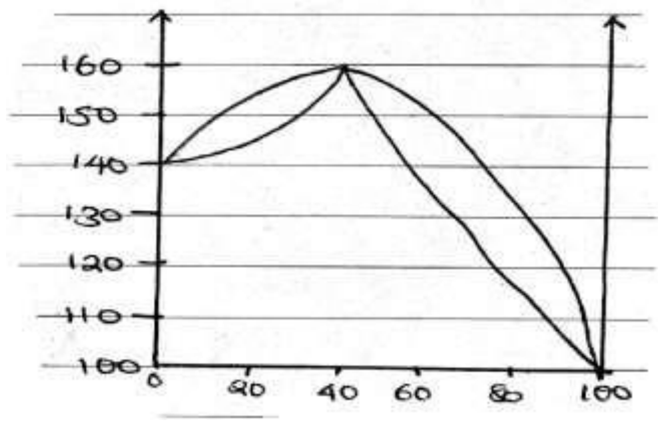
(i) Explain why mixtures may deviate positively from Raoult's law

(ii) Draw a vapour pressure – composition diagram for the methanol – cyclohexane mixture (the vapour pressure of cyclohexane is higher than that of methanol)

(iii) If a constant boiling mixture of methanol and cyclohexane is contains 42% methanol. Draw a well labelled boiling point – composition diagram for the system

(iv) Describe the changes that take place when a mixture containing 60% cyclohexane is fractionally distilled.

(b) The boiling point – composition diagram for a mixture of water and a substance X, which is miscible with water is shown below



(i) State how the mixture deviates from Raoult's law

(ii) Explain how pure X can be obtained from a mixture containing 50% water.

(iii) What name is given to a mixture containing 40% of X

(iv) Name one substance that would behave in a different way from water

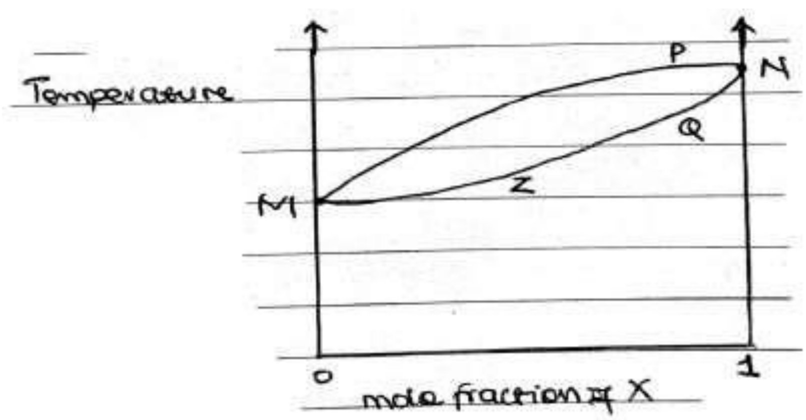
12. (a) State Raoult's law

(b) A liquid mixture of A and B obeys Raoult's law. The vapour pressures of A and B are $10.00kNm^{-2}$ and $2.92kNm^{-2}$ respectively at 20ºC.

(i) Calculate the composition of the vapour of a mixture containing 0.5 mole fraction of liquid A at 20ºC

(ii) Which of the liquids is more volatile? Give a reason for your answer.

(c) The diagram below shows the boiling point – composition diagram of a mixture of liquids X and Y.



(i) Identify the curves P and Q

(ii) Describe what happens when the liquid mixture of composition Z is boiled

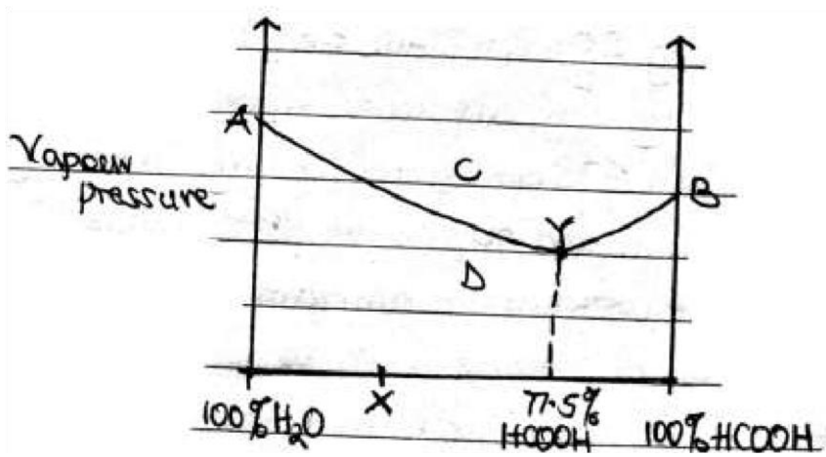
(iii) Explain how the principle in c (ii) can be used to separate liquid mixtures by fractional distillation

13. (a) The vapour pressures of methanol and water are 125.9 and 23.8mmHg respectively at 20ºC. When mixed, the two liquids form an ideal mixture. Calculate

(i) The vapour pressure of a mixture containing 21.0g of methanol and 89.0g of water at 20ºC.

(ii) The composition of the vapour above the mixture

(b) The diagram below shows the vapour pressure – composition diagram for water – methanoic acid system.



(i) What do the points A and B represent?

(ii) What does the curve AYB represent?

(iii) What phases exist in the area C and D

(iv) Explain the shape of the graph

(v) Explain the changes that would take place if a liquid of composition X was fractionally distilled

14. (a) Calculate the composition of the mixture AB which boils at 90ºC and 760 mmHg. The saturated vapour pressures of A and B are 948 and 369 mmHg. Assume A and B obey Raoult's law

(b) Calculate the composition of the vapour obtained when the liquid mixture in (a) boils

15. (a) State Raoult's law (b) What is

(i) An ideal solution

(ii) Partial vapour pressure

(c) An ideal solution was made by dissolving 2.84g of butanol and 0.98g of propanol. The mixture was vaporised in a $2dm^3$ closed vessel at 87ºC. Calculate the total pressure of the system at 87ºC.

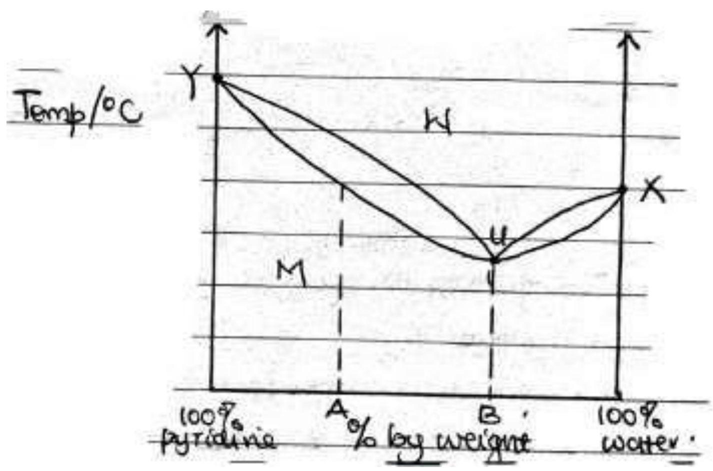
(d) A solution containing 50g of heptane and 38g of octane boils at 103ºC at 760mmHg. The saturated vapour pressure of heptane and octane are 957 and 378mmHg respectively. The normal boiling points of heptane and octane are 98 and 120ºC respectively. Sketch a labelled diagram to show

(i) The variation of the vapour pressure with composition (ii) The variation of boiling points of the mixture with composition (e) (i) Calculate the composition of the vapour at 103ºC.

(ii) Briefly describe how the mixture in (d) can be separated into pure components and explain the principles behind their separation

(iii) Give the application of fractional distillation

16. (a) The diagram below givens the boiling point – composition curve of pyridine and



(i) What does the points W, M, U, Y and X represent?

(ii) What do the upper and lower curves represent?

(b) (i) Name the type of deviation from Raoult's law shown.

(ii) State two characteristics of the mixture at U

(iii) Explain why the mixture at U has a minimum boiling point

(c) Explain carefully what happens when a mixture at each of the following is steam distilled

(i) A (ii) B

17. (a) The table below shows the partial vapour pressures for a two-component mixture of propanone and trichloromethane at 35ºC for a range of mole fractions of trichloromethane

Mole fraction of trichloromethane	0.0	0.2	0.4	0.6	0.8	1.0
Partial pressure of trichloromethane (mmHg)	0	35	82	142	219	293
Partial pressure of propanone (mmHg)	347	270	185	102	37	0

(i) Plot a graph to show how this system deviates from Raoult's law

(ii) Name the type of deviation shown by the system

(iii) State the cause of such a deviation and the characteristics of such a system showing this deviation

(b) What are the requirements for a system to obey Raoult's law

(c) Methanoic acid and water are miscible in all proportions. They form a maximum boiling mixture containing 77.5% methanoic acid which boils at 108ºC. The boiling point of methanoic acid is 101ºC

i) Sketch a labelled diagram if the mixture of methanoic acid and water showing the variation of the boiling points with composition

ii) Describe briefly what happens when a mixture containing 40% methanoic acid is distilled

iii) Suggest one method by which methanoic acid may be obtained from the mixture.

18. (a) Amino benzene and amino pentane form an idea mixture. (i) What is an ideal mixture?

(ii) Sketch the temperature – composition curves for the mixture.

(iii) Describe what happens when a mixture containing 15% amino benzene is distilled

(b) State Raoult's law

(c) Components A and B are miscible in all proportions and form an ideal mixture.

(i) Show graphically the relationship between the vapour pressure of the components with composition

(ii) At a fixed temperature, the vapour pressures of A and B are $2.5 \times 10^4 Pa$ and $6.5 \times 10^3 Pa$ respectively

(d) The boiling point of 2-methylpropan-2-ol and propan-1-ol are 109 and 82ºC respectively. The two compounds form an ideal solution

(i) Sketch a boiling point-composition diagram and use it to explain the changes that will take place when a mixture containing 20% propan-1-ol is fractionally distilled

(ii) Explain the effect of increasing the concentration of 2-methylpropan-2-ol on the boiling point of the mixture

19 (a) (i) Explain what is meant by the term non-ideal solution

(ii) State the two types of deviations from Raoult's law and explain their causes

(b) The boiling point of nitric acid and water are 87 and 96ºC respectively at atmospheric pressure. The nitric acid – water system forms a constant boiling mixture having a boiling point of 122ºC and composition of 63% by mass nitric acid

(i) Explain what is meant by the term constant boiling point mixture

(ii) Sketch a labelled boiling point – composition diagram for the nitric acid – water system

(iii) State and explain the deviation from Raoult's law

(c) (i) What changes take place when nitric acid is added to water

(ii) Explain the changes that take place when a mixture containing 25% nitric acid is distilled

(iii) Name a pair of liquids which show positive deviation

20. (a) Explain what is meant by fractional distillation

(b) When a mixture of ethanol and water is fractionally distilled, it forms an azeotrope boiling at 78ºC containing 4% water. The boiling point of ethanol and water are 80 and 100ºC respectively.

(i) What is meant by an azeotropic mixture

(ii) State one method of removing the small amount of water in the azeotrope (iii) Why does water – ethanol system deviate from Raoult's law?

(iv) Draw a boiling point – composition diagram and use it to explain the changes that take place when a mixture containing 80% water is fractionally distilled

(c) Methanol – ethanol solutions are ideal. If the vapour pressure of ethanol and ethanol at 60ºC are 8.5×10^4 and 4.8×10^4 Nm^{-2} respectively. Calculate the volume compositions of the vapour over a mixture of 80g methanol and 69g of ethanol at 60ºC. (d) The data below was obtained for the benzene – methylbenzene system

Boiling point (ºC)	110	107	100	95	90	85	80
Mole fraction of benzene in liquid	0	0.06	0.19	0.32	0.5	0.73	1.0
Mole fraction of benzene in vapour	0	0.19	0.48	0.65	0.79	091	1.0

(i) Plot an accurate boiling point-composition diagram for the system

(ii) Calculate the ratio of saturated vapour pressure of pure benzene to the total vapour pressure of the system at 100ºC

(iii) Explain how this mixture deviates from Raoult's law

21. (a) The table below shows the variation in the vapour pressure of the mixture of A and B at 25ºC with composition of B

Mole fraction of B	0.0	0.2	0.4	0.6	0.8
Total vapour pressure (Pa)	427	395	372.5	355	362.5

The vapour pressure of pure B at 25ºC is 400Pa

(i) Plot a vapour pressure – composition diagram for the above system

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

(iii) Name the type of deviation. Give a reason for your answer

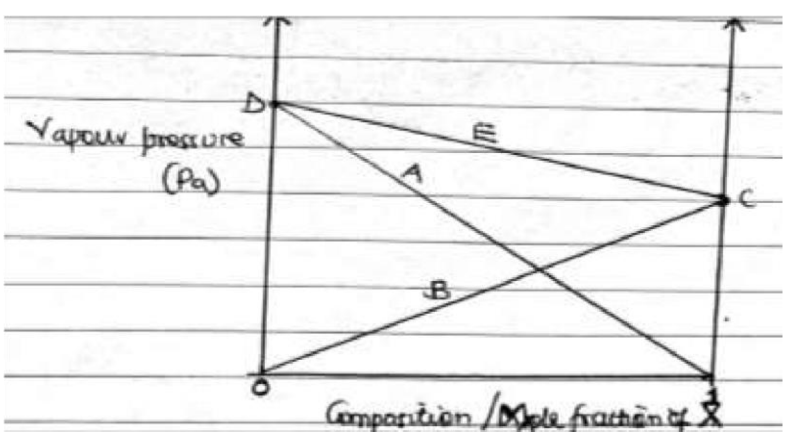
(iv) Explain why at a composition of mole fraction of 0.64 of A, the system shows a minimum vapour pressure.

(b) (i) Draw a boiling point – composition diagram for the system and label all the parts

(ii) Describe the changes that occur when a mixture of 0.2 mole fraction of B is
fractionally distilled

(iii) Describe the different ways of separating azeotropic mixtures

22. The graph below shows the variation of the vapour pressure of a mixture of components X and Y that show an ideal behaviour.



(a) Name the lines represented by the letters A, B, and C

(b) Name the points C and D

(c) Identify how the solution deviates from Raoult's law. Explain.

(d) Along CD, the vapour pressure of the system increases. Explain.

23. (a). When a mixture of water and methanol is distilled, a constant boiling mixture containing 85% methanol is obtained at 70°C (*the boiling point of pure water and methanol are 100°C and 75°C respectively*)

(i). Draw a boiling point – composition diagram for the mixture of methanol and water (ii). Explain the shape of diagram

(iii). Describe what would happen if a mixture containing less than 80% methanol was fractionally distilled

(b). (i). Calculate the vapour pressure of a solution containing 18.5g of a non-volatile

solute X in 30g of solvent Y at 298K. (*The molecular masses of X and Y are 280 and 74 respectively. The vapour pressure of Y is 1.2×10^4 at 298K*)

(ii). Explain the effect of increasing concentration of X on the boiling point of Y.

24. (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 kNm^{-2} and 3.20 kNm^{-2} respectively at 20°C.

(i). Calculate the composition of the vapour containing 0.5 mol of each liquid at 20°C

(ii). State which of the two liquids is more volatile. Explain your answer.

(c). The boiling points of liquid **Y** and **Z** are 368°C and 395°C respectively.

(i). Sketch a labelled boiling point – composition diagram of the mixture of the liquids

(ii). Using the diagram, describe how pure liquid **Z** can be obtained from a mixture containing 50% **Z**

(d). Explain why some liquids show negative deviation from Raoult's law

(e). If the mixture of liquids **Y** and **Z** in (b) was to deviate negatively from Raoult's law, sketch a labelled boiling point – composition diagram for the mixture.

PART II: IMMISCIBILITY AND STEAM DISTILLATION

1 (a) (i) What is meant by the term steam distillation

(ii) Draw a diagram of the set-up of apparatus that can be used to purify a substance by steam distillation

(b) (i) State three properties of a substance that enables it to be purified by steam distillation

(ii) Explain how the properties you have named in b(i) enable the substance to be purified by steam distillation

(iii) State the advantages of isolating the substance by steam distillation

(c) The vapour pressure of water ($V.P_H2O$) and that of substance A ($V.P_A$) at different temperatures are given in the table below

Temperature /ºC	20	40	60	80	100
$V.P_{H2}O$ (atm)	0.22	0.26	0.30	0.35	0.39
$V.P_A$ (atm)	0.35	0.42	0.49	0.56	0.63

(i) On the same axes plot a graph of vapour pressure against temperature for water and substance A

(ii) When substance A was steam distilled at 1 atm pressure, the distillation temperature was 97ºC and the distillate obtained contained 4.29g of substance A and 1.1g of water. Using your graph in c(i), calculate the relative molecular mass of A

2. When an amine Z was steam distilled at 98ºC and 760mmHg pressure, the distillate contained 25.5g of water and 7.4g of Z. Calculate the relative formula mass of Z. (the vapour pressure of water at 98ºC is 720mmHg)

3. (a) State the effect on the vapour pressure of water and the total vapour pressure of the system when a small amount of the following substances are separately added to water at 25ºC.

Substance added to water	Effect on	
	Vapour pressure of water	Total vapour pressure of the system
Sodium chloride		
Propanone		

Tetrachloromethane		

(b) Explain each of your answers in above

(c) An organic compound X was steam distilled at 95ºC at 760mmHg pressure. If the distillate contained 0.8g of water by mass. Calculate the relative formula mass of X (the vapour pressure of water at 95ºC is 732.5mmHg)

4. (a) State three conditions that can enable components of a liquid mixture to be separated by steam distillation

(b) When a mixture of two liquids A and B was steam distilled at 96ºC and 774mmHg pressure, the distillate contained 55% by mass A. calculate the molecular mass of A (the vapour pressure of water is 634mmHg at 96ºC)

5. The vapour pressure (V.P) of water and an immiscible liquid X at different temperatures are given in the table below.

Temperature (ºC)	92	94	96	98	100
V.P of X (kPa)	6	8	12	15	17
V.P of H_2O (kPa)	74	80	88	94	101

(a) On the same axes, plot graphs of vapour pressure against temperature

(b) (i) Determine the vapour pressures of the mixture of X and water at the temperatures given in the table above

(ii) On the same axes of the graph in (a) (i), plot a graph of vapour pressure of the mixture versus temperature

(c) The distillate obtained from the mixture at 101kPa contained 1.6g of water and 1.1g of X. calculate the relative molecular mass of X using the information from the graph

(d) (i) Explain the principles of separation of mixtures by steam distillation (ii) State any two advantages of steam distillation

6. (a) Substance A was steam distilled at 80ºC and 760mmHg and the distillate contained 90.8% by mass A. (the vapour pressure of water at 80ºC is 240mmHg). Calculate the formula mass of A

(b) (i) Explain what is meant by the term steam distillation.

(ii) When a compound Y was steam distilled at 96ºC, the distillate contained 74% by mass water. The vapour pressure of water at this temperature is 730mmHg. Calculate the molecular mass of Y

(c) When compound Z was steam distilled at atmospheric pressure and 86ºC, the distillate contained 85% by mass water. Calculate the relative molecular mass of Z. (vapour pressure of water at this temperature is 740mmHg)

7. (a) The melting point of 4-nitrophenol is much higher than that of 2-nitrophenol. The two compounds can be separated by steam distillation.

(i) Explain why the melting point of 4-nitrophenol is higher than that of 2nitrophenol

(ii) Explain the principles of steam distillation

(iii) Describe how a mixture of 2-nitrophenol and 4-nitrolphenol can be separated by steam distillation

(b) When substance W was steam distilled at 93ºC and 750mmHg, the distillate contained 55% by mass of W. calculate the relative molecular mass of Y. (the vapour pressure of water at 93ºC is 654mmHg)

8. The vapour pressure of water and that of an immiscible liquid at different temperature are given below

Temperature /°C	92	93	94	95	96	97	98	99	100
VP of X /kPa	6	8	8.2	10.0	12	12.2	14	16	16.2
VP of H_2O/ kPa	74	78	81	84	88	91	94	98	102

(a). Construct a graph including the vapour pressure curve of the mixture of water and X

(b). After distilling at 101 kPa for some time, the distillate was found to contain 1.00 g of water and 0.48g of X. By using the graphs you have drawn, calculate the relative formula mass of X

(c). Describe how the composition of distillate change during distillation

(d). Draw a labelled diagram showing the arrangement of the apparatus of steam distillation

9. (a). State the conditions for steam distillation

(b). State the advantages of steam distillation over fractional distillation

(c). Substance A distils with steam at 98.3°C under pressure of 753mmHg. Calculate the percentage of A by mass in the distillate. (The vapour pressure at 98.3°C is
715mmHg; A = 128)

10. (a). Explain what is meant by the term steam distillation

(b). A mixture of naphthalene ($C_{10}H_8$) and water distils at 93.3°C and 755mmHg. Calculate the percentage by mass of naphthalene in the distillate. (the vapour pressure of water at 98.3°C is 715mmHg)

(c). Steam distillation is one of the methods used for the separation of a component from a liquid mixture.

(i). State the requirements for a component to be separated by steam distillation

(ii). A mixture of substance Y was steam distilled at 760mmHg and 98°C. the distillate contained 85% by mass of water. If the vapour pressure of pure water is 734mmHg at 98°C. Calculate the molecular mass of Y.

11. Bromobenzene and water are immiscible.

(a). Explain why at a pressure of 760 mmHg, pure bromobenzene boils at 155°C whereas a mixture of bromobenzene and water boils at 95.5°C.

(b). Calculate the ratio by mass of bromobenzene and water in the distillate in (a). vapour pressure of water at 95.5° is 655mmHg) (H=1; C=12; O=16; Br=80)

(c). Briefly describe how a pure sample of bromobezene can be obtained from the distillate in (a).

12. Aniline is prepared in the laboratory by the reduction of nitrobenzene using tin and concentrated hydrochloric acid. The mixture is then treated with sodium hydroxide and aniline is isolated by steam distillation.

(a). What is steam distillation

(b). Explain the principles behind the isolation of a substance by steam distillation. (c). Describe briefly how you would perform steam distillation in the laboratory (d). What is the advantage of using steam distillation to isolate substances?

(e). At 760mmHg, steam distillation of a certain liquid of formula mass 45 takes place at 96°C. if the vapour pressure of water at the same temperature is 658 mmHg. Calculate the percentage composition by mass.

13. (a). The following data was obtained for the steam distillation of bromobenzene at
760mmHg

Temperature /°C	90	92	94	96	98	100
V.P of water (mmHg)	526	567	611	658	707	760
V.P of bromobenzene (mmHg)	96	106	114	123	132	141

(i). Plot a graph of vapour pressure against temperature
(ii). Use the graph to calculate the maximum percentage of bromobenzene by mass that can be steam distilled
(iii). What is the temperature of steam distillation?
(iv). Explain how bromobenzene can be isolated from the distillate?

14. (a). What is partial vapour pressure?
(b). Aniline and water are immiscible liquids and the mixture boils at a temperature below that of either liquid.
(i). Explain why this is so
(ii). Sketch a graph to show how the vapour pressure of the system varies with temperature
(iii). Briefly describe how the behaviour of the system would differ if the liquids were miscible
(c). At $100.3kNm^{-2}$, steam distillation of nitrobenzene takes place at 98°C. If the vapour pressure of water at the same temperature is $93.6kNm^{-2}$. Calculate the composition of the distillate as a percentage by mass
(d). At 723mmHg, steam distillation of compound takes place at 98°C. the ratio of the mass of the compound to the mass of water in the distillate is 0.188. if the vapour pressure of water at the same temperature is 712mmHg. Calculate the relative formula mass of X

15. The boiling point of amino benzene and a mixture of amino benzene – water is 183 and 97°C respectively.
(a). Explain the difference in the boiling points.
(b). Nitrobenzene distils in steam at a temperature of 96°C and an external pressure of 760mmHg. The distillate contains 40% by mass nitrobenzene.
(i). Calculate the relative formula mass of nitrobenzene if the vapour pressure of wat at 96°C is 723mmHg.
(ii). State the application of steam distillation
(iii). State the advantages of using steam distillation

16. (a). When compound X was steam distilled at 97°C and 101kPa. The distillate contained 1.00g of water and 0.48g of X. the vapour pressure of water at this temperature is 89.3kPa. calculate the relative formula mass of X

(b). A compound Y which is insoluble in water forms a mixture which boils at 370K at a pressure of 101.325kPa. The vapour pressure of water at this temperature is 96240Pa. if the molecular mass of Y is 125. Calculate the percentage by mass of Y in the distillate.

(c). A mixture containing substance Q was steam distilled at a pressure of 760mmHg and at a temperature of 90°C. If the distillate contained 45% by mass of water. Calculate the vapour pressure of Y at 95°C.

Determination of K_D of ammonia between trichloromethane and water

Procedure

- A given volume of a standard solution of ammonia is shaken with a given volume of a mixture of water and trichloromethane in a stoppered separating funnel at a given temperature for about 15minutes. This ensures that equilibrium is attained.
- The mixture allowed to stand to let the layers separate out. Equal volumes of either layer are pipetted and separately titrated with a standard solution of HCl using phenolphthalein indicator. Ammonia reacts with HCl according to the equation

$$NH_3(aq) + HCl\ (aq) \longrightarrow NH_4Cl(aq)$$

- The volume of HCl required to reach the end point is noted and the concentration of ammonia in either layer can be calculated. The value of K_D is obtained from the expression.

$$\boldsymbol{K_D} = \frac{[\boldsymbol{Ammonia}]\ \boldsymbol{in\ trichloromethane}}{[\boldsymbol{Ammonia}]\ \boldsymbol{in\ water}}$$

- Ammonia is much more soluble in water than trichloromethane and the partition coefficient of Ammonia between the two solvents at a given temperature gives the number of times ammonia is more soluble in water than trichloromethane.

Determination of K_D ethanoic acid between tetrachloromethane and water.

Procedure

- A known volume of CCl_4 and a known volume of water are put in a separating funnel.
- A known volume of a standard solution of ethanoic acid is added to the mixture. The funnel is stoppered and shaken for the equilibrium to be attained at a given temperature.
- The mixture is then allowed to stand to let the two layers separate out and equal volumes of either layer are pipetted and titrated separately with a standard solution of

sodium hydroxide using phenolphthalein as the indicator.

- Ethanoic acid reacts with sodium hydroxide according to the equation.

  $CH_3CO\bar{O}H(aq) + NaOH(aq) \longrightarrow CH_3CO\bar{O}Na^+(aq) + H_2O(l)$

- The volume of sodium hydroxide required to reach the end point for the separate layers is noted and the concentration of ethanoic acid in either layer is then determined from which the partition coefficient of ethanoic acid can be calculated as.

$$K_D = \frac{[Ethanoic\ acid]\ in\ tetrachloromethane}{[Ethanoic\ acid]\ in\ water}$$

- Ethanoic acid is much more soluble in tetrachloromethane than water and the K_D value obtained is an indicator of the number of times ethanoic acid is more soluble in the organic layer than in water

Determination of KD of iodine between tetrachloromethane and water.

Procedure;

- A given mass of iodide is shaken with a given volume of a mixture of tetrachloromethane and water in a stoppered separating funnel at a given temperature until the equilibrium of iodine between the two layers is attained.
- The mixture is allowed to stand to let the two layers separate and equal volumes of each layer are pipetted in separate conical flasks and separately titrated with a standard solution of sodium thiosulphate using starch indicator.
- The volume of standard sodium thiosulphate required to reach end point is noted for each layer.
- Sodium thiosulphate reacts with iodine according to the equation

  $I_2(aq) + 2S_2O_3^{2-}(aq) \longrightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

- The partition ratio of iodine between tetrachloromethane and water is then determined.

Note:

Iodine is a covalent solute, non-polar with limited interaction between its molecules and water so it has a very low solubility in water.

Assignment

1. $50cm^3$ of 0.1M ammonia solution was shaken to equilibrium with $50cm^3$ of $CHCl_3$ in a stoppered bottle at 25℃. $25cm^3$ of aqueous layer reacted completely with $24cm^3$ of 0.1M HCl solution. calculate the concentration of NH_3 in;
   a) $CHCl_3$ layer
   b) Aqueous layer at equilibrium
   c) K_D for NH_3 between $H_2O$and $CHCl_3$ at 25^0c
2. In an experiment to determine the K_D of NH_3 between water and $CHCl_3$, $50cm^3$ of NH_4OH was shaken with $250cm^3$ of $CHCl_3$ until equilibrium was established; and the number of moles of NH_3 in each layer was determined. The experiment was repeated several times using aqueous ammonia of different concentration and the results are given below

Amount of NH_3 in $50cm^3$ of water (moles)	0.0065	0.0070	0.0095	0.014	0.019	0.025	0.028
Amount of NH_3 in $250cm^3$ of $CHCl_3$	0.0005	0.001	0.002	0.003	0.004	0.005	0.006

a) Plot a graph of concentration of NH_3 in water against concentration of NH_3 in trichloromethane.

b) Use your graph to determine K_D of ammonia between water and trichloromethane.

Applications of the partition law

a) Solvent extraction

- This is a technique of extracting a solvent from one solvent system to another solvent system with both solvents being immiscible, solute maintaining its molecular state and temperature remaining constant.
- Solvent extraction can also be defined as the isolation of organic compounds from aqueous solution in which the organic compound is immiscible by extracting it using another solvent in which the extracted compound is more soluble.

NOTE: Its more efficient to use smaller portions of the organic solvent.

Conditions of solvent extraction

- ✓ Solvents must be immiscible
- ✓ Temperature must be constant
- ✓ Solute must be more soluble in the extracting organic solvent
- ✓ Solute must not react in solvent

Example

1. a) 60cm^3 of an aqueous solution containing 0.3g of compound Y was shaken with 30cm^3 of ethoxyethane and the mixture allowed to stand. Calculate the mass of Y which was extracted into the ethoxyethane layer.(K_D of Y between ethoxyethane and water is 4.7)

b) The aqueous solution in (a) was extracted with two successive 15cm^3 of ether, calculate the mass of Y that was extracted by ether and comment on your answer.

Space for solution

Assignment

1. An aqueous solution contains 0.2g of asprine ($C_9H_80_4$) in $50cm^3$ of solution. To this solution was added $20cm^3$ of Diethyl ether. The mixture was shaken and allowed to reach equilibrium at 25^0c. At this temperature, the K_D of $C_9H_8\ 0_4$ between diethyl ether and water is 4.7

a) Calculate the mass of $C_9H_80_4$ that remain s in the aqueous layer.

b) If the extraction is carried out using two successive $10cm^3$ portion of ethoxyethane, determine the mass of $C_9H_80_4$ that remain unextracted.

2. a) (i) Explain what is meant by the term solvent extraction.

   ii) State two conditions for solvent extractions.

c) Calculate the mass of aniline [$C_6H_5NH_2$] that can be extracted from 100cm^3 of water containing 3g of aniline by using 20cm^3 of benzene [K_D of aniline between benzene and water is 10]

b) Ion exchange

- ✓ is the type of partition of ionic compounds
- ✓ ***Ion exchange resin is a polymer which removes undesirable cations or anions and replaces them with other cations or anions.***
- ✓ Cation exchangers contain reactive hydrogen ions which may exchange with other cations like Na^+, Ca^{2+}, or Mg^{2+} in a reversible reaction. E.g R(CH2) $_n$ C-00H, $-SO_3H$ and R(CH2)$_n$ OH.
- ✓ Anion exchangers contain basic OH which are exchanged for other anions like chloride or sulphate e.g. secondary, tertiary and quaternary amino groups.
- ✓ Ion exchange can be used in purification of water in the following ways;

(i). Water may be softened by ion exchange by removing the Ca^{2+} or Mg^{2+}

$NaR(s) + Ca^{2+} \longrightarrow CaR_2(s) + Na^+ (aq)$ where R- resin

(ii). Water is then further purified by using both cations and anion exchange to form de-ionized water.

This is a two-step process;

(a) A cation exchanger removes cations replaces them with H^+

$-SO_3H^+(aq) + Na^+(aq) \longrightarrow -SO_3Na^+(aq) + H^+(aq)$

(b). Anion exchanger removes cations and replaces them with OH anion

$R0H + Y^-(aq) \longrightarrow RY(s) + {}^-OH$

d) Determination of solubility and equilibrium constants

- ✓ Knowing the solubility of iodine in CS_2 and the partition coefficient, solubility of iodine in water can be determined from;

$$K_D = \frac{Solubility\ of\ iodine\ in\ pure\ water}{Solubility\ of\ iodine\ in\ CS_2}$$

Example

Some iodine was dissolved in 0.3M potassium iodide solution and the solution was shaken with CS_2 until equilibrium was established. The concentration of iodine in both layers was then determined by titration. The solubility of iodine in pure H_2O and CS_2 are given in the table below

Concentration (M)	Aqueous layers	Organic layer
	0.044	0.13
Concentration (M)	Pure H2O $4X10^{-4}$	CS2 0.234

i) Determine the K_D of iodine between water and CS_2.

ii) Calculate the equilibrium for the reaction.

Space for solution

e) Determination of formula of complex ion

Determination of formula of the complex formed btn excess ammonia and copper (ii) ion i.e $[Cu(NH_3)_n]^{2+}$

Procedure

- A known volume of excess ammonia solution is added to a glass flask containing an equal volume of solution of Cu^{2+} with known concentration of, X mol dm^{-3}.
- Resultant deep blue solution (complex, $[CU(NH_3)_n{}^{2+}]$) formed is shaken with trichloromethane and the mixture is allowed to settle so as to reach equilibrium.
- A known volume of the organic layer is pipetted into a conical flask, titrated with a standard solution of Hydrochloric acid using methyl orange.
- The volume of Hydrochloric acid required for complex neutralization is noted, concentration of ammonia in the trichloromethane layer is then calculated, Y mol dm^{-3}
- Procedure is repeated with aqueous layer and the total concentration of ammonia in the aqueous layer determined, Z mol dm^{-3}

Results

- ✓ Portion coefficient of ammonia between water and chloroform = K_D
- ✓ Concentration of Cu^{2+} = Xmoldm^{-3}
- ✓ Concentration of NH_3 in the organic layer =Y moldm^{-3}
- ✓ Original concentration of ammonia in the aqueous layer= Z moldm^{-3}

Treatment of result

Examples

1. $25cm^3$ of excess ammonia solution was added to $25cm^3$ to 0.1M $CuSO_4$ solution. The resulting deep blue solution was shaken with $50cm^3$ of $CHCl_3$ and the mixture allowed to settle .$50cm^3$ of the $CHCl_3$ layer required $25.5cm^3$ of 0.05M of HCl for neutralization. $20cm^3$ of the aqueous layer was neutralized by $33.3cm^3$ of 0.5M HCl. (KD between water and trichloromethane = 25). Find the formula of the complex formed.

Space for solution

NOTE: Leave about 4 pages for more example