

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

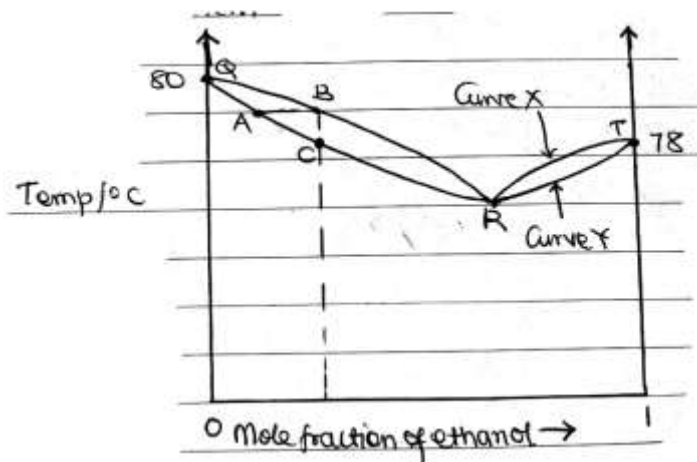
CHAPTER 6: PHYSICAL EQUILIBRIA

PART I: RAOULT'S LAW AND DEVIATIONS

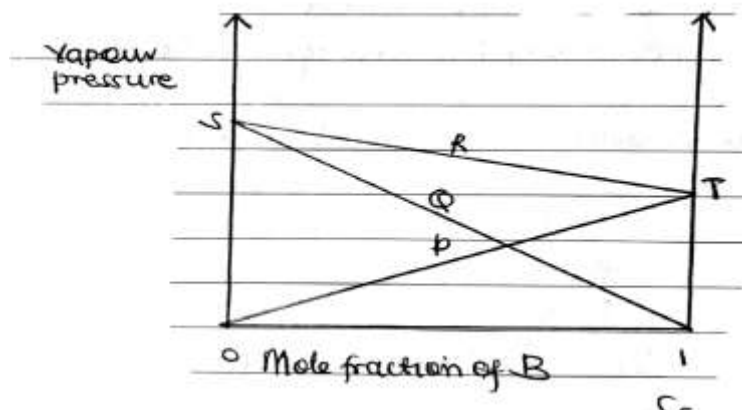
1. (a) State three reasons why azeotropes are considered to be mixtures and not compounds.
(b) The total vapour pressure of mixture of propanone and trichloromethane at constant temperature are given in the table below

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



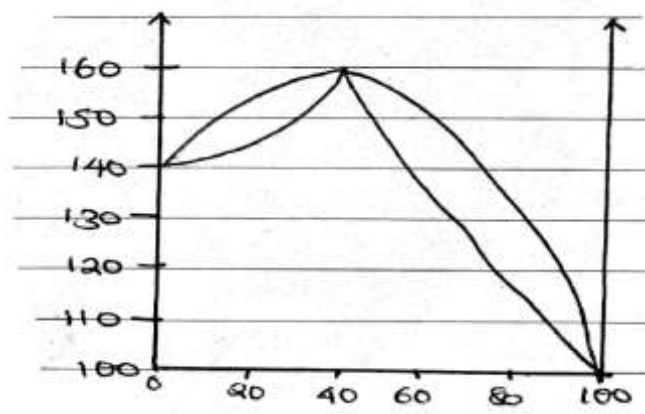
- (i) Identify curves X and Y and point R.
(ii) A mixture at point R was boiled, state what happened to its composition
(iii) State the relationship between A, B and C
(iv) Draw a labelled diagram to illustrate the vapour pressure – composition diagram for the benzene – ethanol system.
3. (a) State three properties of an ideal solution
(b) The vapour pressure – composition diagram for an ideal solution of liquids A and B is shown below.



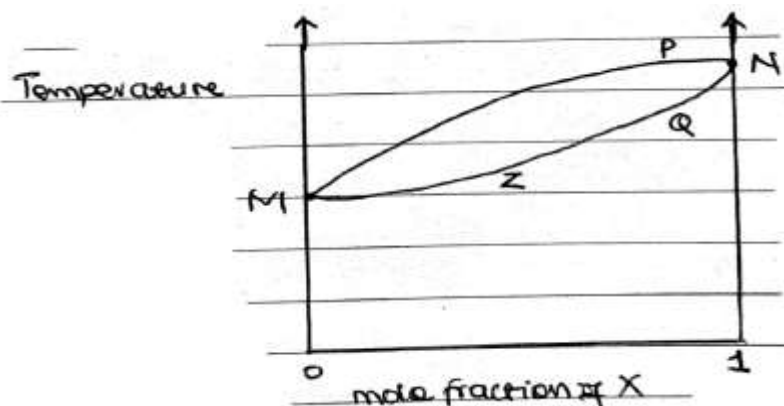
- (i) Identify lines P, Q and R and the points S and T.
 - (ii) Draw a fully labelled boiling point – composition diagram for a mixture of liquids A and B
 - (iii) State what would be obtained as the distillate and the residue if a liquid mixture containing 40% of A is fractionally distilled
 - (c) A 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 20°C. [the vapour pressure of pure benzene and methylbenzene at 20°C 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. Give a reason for your answer.
- (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 110°C 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 85°C 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 20°C is 43.6mmHg while that of benzene at the same temperature is 75.2mmHg. The mole fraction of benzene is 0.09 for a mixture of benzene and ethanol at 20°C. 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 25°C. 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 118°C) and pyridine (boiling point 123°C) 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 372°C) and compound B (Boiling point 399°C) 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 78.5°C) and tetrachloromethane (boiling point 76.8°C) form an azeotropic mixture of boiling point 65.0°C 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
- Explain why mixtures may deviate positively from Raoult's law
 - Draw a vapour pressure – composition diagram for the methanol – cyclohexane mixture (the vapour pressure of cyclohexane is higher than that of methanol)
 - If a constant boiling mixture of methanol and cyclohexane is contains 42% methanol. Draw a well labelled boiling point – composition diagram for the system
 - 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

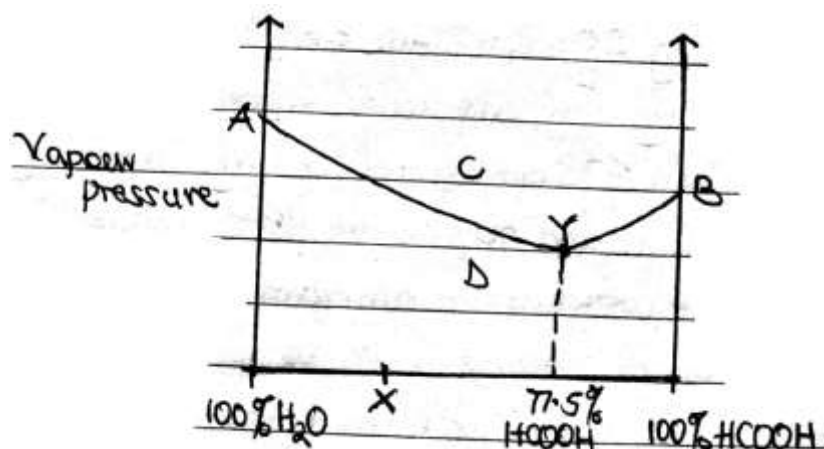


- State how the mixture deviates from Raoult's law
 - Explain how pure X can be obtained from a mixture containing 50% water.
 - What name is given to a mixture containing 40% of X
 - Name one substance that would behave in a different way from water
12. (a) State Raoult's law
- (b) A liquid mixture 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 20°C .
- Calculate the composition of the vapour of a mixture containing 0.5 mole fraction of liquid A at 20°C
 - 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.



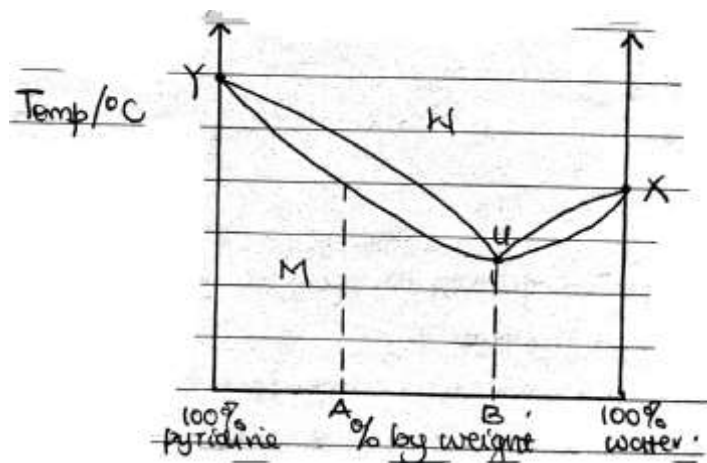
- (i) Identify the curves P and Q
- (ii) Describe what happens when the liquid mixture of composition Z is boiled
- (iii) Explain how the principle in c (ii) can be used to separate liquid mixtures by fractional distillation

13. (a) The vapour pressures of methanol and water are 125.9 and 23.8mmHg respectively at 20°C. 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 20°C.
 - (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 90°C 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
- An ideal solution
 - 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 87°C . Calculate the total pressure of the system at 87°C .
- (d) A solution containing 50g of heptane and 38g of octane boils at 103°C 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 120°C respectively. Sketch a labelled diagram to show
- The variation of the vapour pressure with composition
 - The variation of boiling points of the mixture with composition
- (e) (i) Calculate the composition of the vapour at 103°C .
- (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 gives the boiling point – composition curve of pyridine and



- What does the points W, M, U, Y and X represent?
 - What do the upper and lower curves represent?
- (b) (i) Name the type of deviation from Raoult's law shown.
- State two characteristics of the mixture at U
 - 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
- A
 - B

17. (a) The table below shows the partial vapour pressures for a two component mixtures of propanone and trichloromethane at 35°C 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 108°C. The boiling point of methanoic acid is 101°C
- (i) Sketch a labelled diagram of 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 ideal 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 $2.5 \times 10^4 \text{ Pa}$ and $6.5 \times 10^3 \text{ Pa}$ respectively
- (d) The boiling point of 2-methylpropan-2-ol and propan-1-ol are 109 and 82°C 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 96°C respectively at atmospheric pressure. The nitric acid – water system forms a constant boiling mixture having a boiling point of 122°C 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 78°C containing 4% water. The boiling point of ethanol and water are 80 and 100°C 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 60°C are 8.5×10^4 and $4.8 \times 10^4 \text{ Nm}^{-2}$ respectively. Calculate the volume compositions of the vapour over a mixture of 80g methanol and 69g of ethanol at 60°C.

(d) The data below was obtained for the benzene – methylbenzene system

Boiling point (°C)	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	0.91	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 100°C
 (iii) Explain how this mixture deviates from Raoult's law

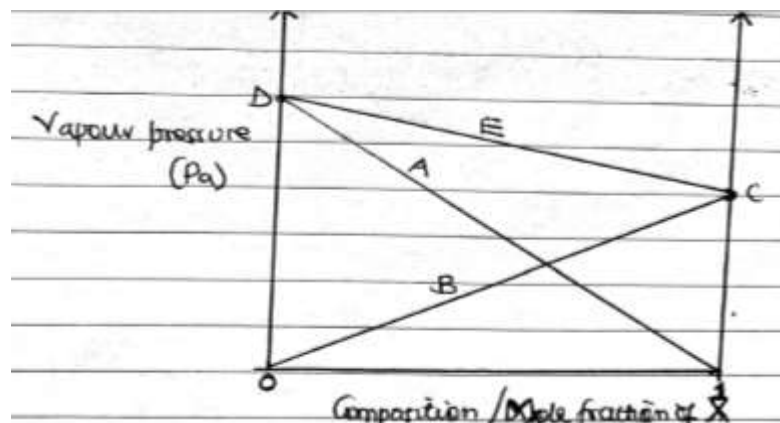
21. (a) The table below shows the variation in the vapour pressure of the mixture of A and B at 25°C with composition of B

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 25°C 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 ($V.P_{H_2O}$) and that of substance A ($V.P_A$) at different temperatures are given in the table below

Temperature /°C	20	40	60	80	100
$V.P_{H_2O}$ (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 97°C 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 98°C 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 98°C 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 25°C.

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 95°C 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 95°C 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 96°C and 774mmHg pressure, the distillate contained 55% by mass A. calculate the molecular mass of A (the vapour pressure of water is 634mmHg at 96°C)
5. The vapour pressure (V.P) of water and an immiscible liquid X at different temperatures are given in the table below.

Temperature (°C)	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 80°C and 760mmHg and the distillate contained 90.8% by mass A. (the vapour pressure of water at 80°C 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 96°C, 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 86°C, 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 2-nitrophenol
- (ii) Explain the principles of steam distillation
- (iii) Describe how a mixture of 2-nitrophenol and 4-nitrophenol can be separated by steam distillation
- (b) When substance W was steam distilled at 93°C and 750mmHg, the distillate contained 55% by mass of W. calculate the relative molecular mass of Y. (the vapour pressure of water at 93°C 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.

PART III: IMMISCIBILITY AND PARTITION RATIO (DSITRIBUTION CONSTANT)

1. (a). What is meant by the term **partition ratio**?
- (b). Describe how the partition ratio for iodine between tetrachloromethane and water can be determined
- (c). 50 cm³ of a solution containing 0.966g of iodine in tetrachloromethane was shaken with 50 cm³ of water
 - (i). Calculate the amount of iodine that was retained in the tetrachloromethane layer (the K_D of iodine between tetrachloromethane and water is 85.25)
 - (ii). Explain how your answer in c(i) would be affected if the iodine solution in the tetrachloromethane was shaken with aqueous potassium iodide instead of water
- (d). Cobalt(II) ions form a complex, $[Co(NH_3)_n]^{2+}$. The table below shows the results of partition of ammonia between 0.1M cobalt(II) sulphate and trichloromethane

$[NH_3](0.1M CoSO_4)$	0.72	0.94	1.19	1.43	1.70	1.92
$[NH_3](CHCl_3)$	0.01	0.03	0.05	0.07	0.09	0.11

- (i). Plot a graph of $[NH_3](0.1M CoSO_4)$ against $[NH_3](CHCl_3)$
 - (ii). Determine the value of n in $Co(NH_3)_n^{2+}$
2. (a). Write the electronic configuration of copper
- (b). State two properties which show that copper is a transition element
- (c). Excess ammonia was shaken with an equal volume of trichloromethane and a 0.05M aqueous solution of copper(II) sulphate and allowed to stand. Some ammonia formed a complex with copper ($[Cu(NH_3)_n]^{2+}$). At equilibrium, the concentration of ammonia in the trichloromethane layer and aqueous layer were 0.021 mol l⁻¹ and 0.725 mol l⁻¹ respectively. (The partition ratio K_D of ammonia between water and trichloromethane is 25). Calculate
 - (i). The concentration of free ammonia in the aqueous layer
 - (ii). The concentration of ammonia that formed the complex with copper
 - (iii). That value of n in the complex.
3. (a). State the **distribution law**.
- (b). Describe how the distribution constant for butane-1,4-dioic acid between water and ethoxyethane can be determined
- (c). 100 cm³ of a solution contains 30g of substance Z. calculate the mass of Z extracted by shaking with
 - (i). 100 cm³ of ethoxyethane
 - (ii). Two 50 cm³ portions of ethoxyethane (the distribution constant of Z between ethoxyethane and water is 5)

- (d). Briefly describe how the distribution constant can be used to determine the formula of the complex formed between copper(II) ions and ammonia
4. (a). 100 cm³ of an aqueous solution containing 20g of W was shaken once with 50cm³ of ether. Calculate
- The mass extracted by ether
 - The mass of W the would be extracted by shaking the solution twice with 25 cm³ of ether
- (b). 50.0g of substance Y was dissolved in water to make 100 cm³ of solution. The partition ratio of Y between water and ether is 0.2. Calculate the mass of Y extracted by shaking the 100 cm³ of solution with
- 500 cm³ of ether
 - Two successive portions of 250 cm³
5. (a). State the **distribution law**
- (b). Under which conditions is the law in (a) valid
- (c). 100 cm³ of a solution containing 10g of compound Q was shaken with 100 cm³ of benzene. The partition constant of Q between benzene and water is 12.25. calculate the mass of Q left in water.
- (d). State the applications of partition of solutes.
6. The table below shows the distribution of ammonia in a 0.1M copper(II) ions and trichloromethane.

$[NH_3](0.1M CuSO_4) / \text{moll}^{-1}$	0.84	1.08	1.32	1.56	1.8
$[NH_3](CHCl_3) / \text{moll}^{-1}$	0.02	0.03	0.04	0.05	0.06

- Plot a graph of $[NH_3](0.1M CuSO_4)$ against $[NH_3](CHCl_3)$
 - Determine the distribution constant, K_D , of ammonia between aqueous copper(II) ions and chloroform
 - State what value of K_D , you have determined indicates about the distribution of ammonia
 - Determined the number of moles of ammonia that react with copper(II) ions
 - Write the equation for the reaction between ammonia and copper(II) ions
7. 1.00dm³ of an aqueous solution contains 5.00g of butanoic acid. Calculate the mass butanoic acid extracted when the solution was shaken with
- 50 cm³ of solvent Q
 - Twice with 25cm³ of solvent Q (the K_D butanoic acid between water and Q is 5)
8. (a). A copper ore was dissolved in excess concentrated ammonia and the solution made up to 1dm³. The resultant solution was shaken with trichloromethane and left to settle. 50cm³ of the organic layer needed 25.0cm³ of 0.05M hydrochloric acid for complete neutralisation. 25cm³ of the aqueous layer was neutralised with by 40cm³ of 0.5M hydrochloric acid.
- Write equation for the reaction between copper(II) ions and ammonia
 - Calculate he concentration of copper(II) ions in moldm⁻³. (the distribution constant of ammonia between water trichloromethane in 25)

9. (a). Explain what is meant by the term **distribution law** and mention its limitations
 (b). An aqueous solution containing 0.06g of iodine in 500cm³ of water was shaken with 200cm³ of tetrachloromethane and the mixture allowed to stand for some time. Calculate the mass of iodine extracted by tetrachloromethane (the partition ratio for distribution of iodine between tetrachloromethane and water is 85)
 (c). The aqueous solution in (b) was extracted with two successive 100cm³ of tetrachloromethane. Calculate the mass of iodine remaining in the aqueous layer.
 (d). Comment on your results in (b) and (c)
 (e). State two applications of partition of solutes
10. (a). Write an expression for the distribution of ammonia between water and trichloromethane
 (b). 100 cm³ of a solution containing 0.171g of ammonia in trichloromethane was shaken with 100cm³ of water until equilibrium was attained at room temperature. Calculate the number of moles of ammonia in the trichloromethane layer. (the distribution constant of ammonia between water and trichloromethane at room temperature is 27.5)
11. (a). Explain what is meant by the term **distribution constant**.
 (b). Describe how the distribution constant of ethanoic acid between water and butanol can be determined
 (c). When 100cm³ of an aqueous solution containing 30g of ethanoic acid were shaken with 50cm³ of butanol, 12g of ethanoic acid remained in the aqueous layer. Calculate the distribution constant of ethanoic acid between water and butanol
 (d). The aqueous solution of ethanoic acid in (b) was shaken twice with 25cm³ portions of butanol. Calculate the mass of ethanoic acid extracted.
 (e). State two application of the partition law.
12. (a). Define the term partition ratio and state its units
 (b). Briefly describe how the partition ratio for the distribution of iodine between water and trichloromethane can be determined
 (c). (i). 60cm³ of an aqueous solution containing 0.3g of a compound Y was shaken with 30cm³ of ethoxyethane and the mixture allowed to stand. Calculate the mass of Y that was extracted into the ethoxyethane layer. (the partition of Y between ethoxyethane and water is 4.7)
 (ii). The aqueous solution in c (i) was extracted with two successive 15cm³ portions of ether. Calculate the mass of Y that was extracted by ether.
 (c). The table below shows the results of partition of aminomethane between trichloromethane and 0.1M nickel(II) sulphate solution.

$\frac{[CH_3NH_2](0.1M NiSO_4)}{[CH_3NH_2](CHCl_3)}$ / mol l ⁻¹	0.87	1.10	1.33	1.57	1.8
$\frac{[CH_3NH_2](CHCl_3)}{[CH_3NH_2](0.1M NiSO_4)}$ / mol l ⁻¹	0.02	0.03	0.04	0.05	0.06

- (i). Plot a graph of $[CH_3NH_2](0.1M NiSO_4)$ against $[CH_3NH_2](CHCl_3)$
 (ii). Determine the number of moles of aminomethane that has formed a complex with nickel(II) ions
 (iii). Write equation for the reaction between nickel(II) ions and aminomethane

13. 20 cm³ of 0.1M iodine solution in aqueous potassium iodide was vigorously shaken with in a separating funnel with 20cm³ of tetrachloromethane. The colour of tetrachloromethane gradually changed to purple and finally dark purple.
- (i). Explain the role of potassium iodide solution in this experiment.
 - (ii). Explain the observed colour changes in the tetrachloromethane layer.
- (b). 10cm³ of the tetrachloromethane layer reacted with 18cm³ of 0.02M thiosulphate solution
- (i). Write the equation for the reaction that took place
 - (ii). Determine the distribution constant for iodine between the two solvents
 - (iii). State the factors that affect the value of the distribution constant
- (c). Describe the applications of the distribution ratio.
14. (a). Explain what is meant by the following terms
- (i). Distribution constant
 - (ii). Solvent extraction
- (b). Describe briefly how the distribution constant for butanedioic acid between water and trichloromethane can be determined
- (c). The distribution coefficient of a compound A between ethoxyethane and water is 90. An aqueous solution of A with a volume of 500cm³ contains 5.0g. Calculate the mass of A that will be extracted by using
- (i). 100cm³ of ethoxyethane
 - (ii). Two successive portions of 50.0cm³ of ethoxyethane
- (d). State three conditions under which partition ratio is valid
15. (a). State the **distribution law**
- (b). State three applications of the distribution law
- (c). 0.0005 moles of a complex $[Co(NH_3)_n]^{3+}$ was treated with excess sodium hydroxide and the ammonia liberated was absorbed in 50cm³ of 0.5M sulphuric acid. The excess acid remaining after absorption required 20.0cm³ of 0.01M sodium hydroxide for neutralisation
- (d). The table below shows the partition of ammonia between 0.1M copper(II) sulphate and tetrachloromethane.

$[NH_3](0.1M CuSO_4) / \text{mol}^{-1}$	0.86	1.10	1.57	1.80	2.40
$[NH_3](CCl_4) / \text{mol}^{-1}$	0.02	0.03	0.05	0.06	0.08

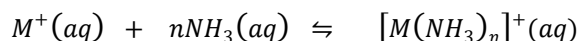
- (i). Plot a graph of the concentration of $[NH_3](0.1M CuSO_4)$ against $[NH_3](CCl_4)$
 - (ii). Determine the intercept on the vertical axis
 - (iii). Determine the value of x in the complex $[Cu(NH_3)_x]^{2+}$
16. (a). The table below shows the results obtained for the distribution of benzoic acid between benzene and water.

$[Benzoic\ acid]_{\text{water}} (\text{mol}^{-1})$	0.86	1.10	1.57	1.80	2.40
$[Benzoic\ acid]_{\text{benzene}} (\text{mol}^{-1})$	0.02	0.03	0.05	0.06	0.08

- (i). Plot a suitable graph and determine the value of distribution constant K_D for benzoic acid between benzene and water
- (ii). Calculate the mass of aniline that can be extracted from 100cm³ of water containing 2g of aniline by using 20cm³ of benzene. (the partition ratio of aniline between benzene and water is 10)
17. (a). Describe briefly how you would determine the partition ratio for iodine between water and carbon tetrachloride at room temperature
- (b). State and explain how the distribution of iodine would be affected by the addition of potassium iodide to the aqueous layer in (a)
- (c). 50cm³ of an aqueous solution containing 5.08g l⁻¹ of iodine was shaken with 50cm³ of chloroform. The mixture was left to stand for some time. 25cm³ of the organic layer required 12.5cm³ of sodium thiosulphate using starch indicator for a complete reaction. Calculate the partition ratio of iodine between chloroform and water. ($I=127$)
- (d). Industrially, silver is extracted from molten lead using molten zinc which is insoluble in lead. The solubility of silver is 300 times greater in zinc than it is in an equal volume of lead. Calculate the percentage of silver extracted using 0.01dm³ of molten zinc and 0.2dm³ of molten lead containing 5g of silver.
- (e). Briefly describe how partition ratio is used in the study of complexes
18. (a). Explain the term **solvent extraction**
- (b). Calculate the mass of compound X that can be extracted from 100cm³ of aqueous solution containing 40g of X by extracting with
- (i). 100cm³ of ether
- (ii). Two successive portions of 50cm³ of ether.
- (iii). Comment on your answers in (i) and (ii)
(the K_D of X between ether and water is 5)
- (c). Some iodine was dissolved in 0.3M potassium iodide solution and the solution was shaken with carbon disulphide until an equilibrium was established. The concentration of iodine in both layers was determined by titrating with a standard solution of sodium thiosulphate and found to be 0.044 in the aqueous layer and 0.13 in the carbon disulphide layer. The solubility of iodine in pure water and carbon disulphide are 4×10^{-4} and 0.234 moldm⁻³ respectively. Calculate the
- (i). Partition coefficient, K_D for iodine between water and carbon disulphide
- (ii). The equilibrium constant for the reaction
- $$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq)$$
19. (a). What is meant by the term **partition ratio**?
- (b). An experiment to investigate the distribution of ammonia between an aqueous layer of 0.2M copper(II) ions and chloroform was performed. An equilibrium was established and the results are as shown.

$[NH_3](0.1M CuSO_4) / \text{moll}^{-1}$	0.86	1.10	1.57	1.80	2.40
$[NH_3](CHCl_3) / \text{moll}^{-1}$	0.02	0.03	0.05	0.06	0.08

- (i). Plot a graph of $[NH_3](0.1M CuSO_4)$ against $[NH_3](CHCl_3)$
 - (ii). Determine the distribution constant, K_D for ammonia between water and carbon trichloride
 - (iii). Determine the value of **y** in $[Cu(NH_3)_y]^{2+}$
- (c). The following results were obtained in an experiment to determine the distribution constant, K_D for ammonia between water and trichloromethane. 10cm³ of the aqueous layer required 21.6cm³ of 0.5M hydrochloric acid while the organic layer required 18.8cm³ of 0.046M hydrochloric acid.
- (i). Calculate the partition ratio, K_D
 - (ii). Why is ammonia more soluble in water than trichloromethane?
- (b). When 0.05M aqueous solution of copper(II) sulphate was allowed to reach equilibrium with excess ammonia, and trichloromethane, the aqueous layer was found to contain 0.725M of ammonia and the tetrachloromethane layer was 0.021M of ammonia. Using your results of K_D in (c), calculate
- (i). The concentration of free ammonia in the aqueous layer
 - (ii). The value of **n** in the complex $[Cu(NH_3)_n]^{2+}$
20. (a). State
- (i). Partition law.
 - (ii). **three** limitations of the law.
- (b). Describe an experiment to determine the partition coefficient of phenol between ethoxyethane and water
- (c). An aqueous solution contains 10g of phenol per litre. When 100cm³ of this solution is shaken with 20cm³ of ethoxyethane, the ethoxyethane layer extracts 0.8g of phenol. Calculate mass of phenol extracted when 500cm³ of the aqueous layer was shaken with
- (i). 50cm³ of the ethoxyethane.
 - (ii). two successive 25cm³ portions of the ethoxyethane.
21. (a). To 1 dm³ of a solution of 0.045M copper(II) sulphate solution was added excess ammonia, tetrachloromethane and the mixture was allowed to settle. 25.0cm³ of the tetrachloromethane layer required 12.5cm³ of 0.05M hydrochloric acid for complete reaction. 25.0cm³ of aqueous layer required 20.0cm³ of 1M hydrochloric acid for complete reaction. If the distribution constant for ammonia between water and tetrachloromethane is 25. Calculate the value of n in the formula $[Cu(NH_3)_n]^{2+}$
- (b). Ions of a metal M react with excess ammonia to form a complex according to the equation



25cm³ of ammonia solution was added to 25cm³ of 0.1M aqueous solution of metal M ions, followed by 50cm³ of trichloromethane. The mixture was shaken and allowed to reach equilibrium. The aqueous layer required 27.5cm³ of 1.0M nitric acid while the trichloromethane layer required 18.0cm³ of 0.05M nitric acid for complete reaction. Calculate the value of **n** in $[M(NH_3)_n]^+(aq)$ (the distribution constant of ammonia between water and trichloromethane at room temperature is 25)