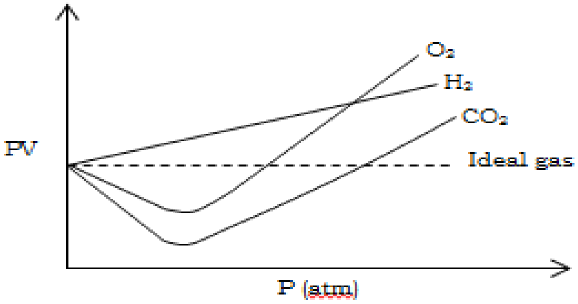
ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 1: MATTER

1. 1.86g of a compound X contains carbon, hydrogen, and nitrogen only. On combustion, X liberated 5.28g of carbon dioxide gas and 224cm^3 of nitrogen at s.t.p.
   (a) Determine the empirical formula of X
   (b) When vaporized, 0.2g of X occupied 81cm^3 at 184.1°C and 101325Pa. determine the molecular formula of X

2. A certain volume of a gaseous hydride of silicon of formula Si_nH_{2n+2} diffused through a narrow hole in 17.08s. The same volume of carbon dioxide diffused through the hole under identical conditions in 20.0s.
   (a) Determine the relative formula mass of the hydride
   (b) Determine the molecular formula of the hydride. ($Si = 28, O = 16$)

3. (a) State what is meant by the term ideal gas
   (b) Explain how liquefaction of a gas can be affected by
   (i) Pressure
   (ii) Temperature
   (c) The curves below show deviations of some gases from the ideal behaviour



   (i) State why hydrogen shows a small deviation from the ideal behaviour compared to other gases
   (ii) Compare the deviations of oxygen and carbon dioxide from the ideal behaviour
   (d) A gas Q contains 30.43% nitrogen and the rest being oxygen. 0.23g of Q occupied 154.11cm^3 at 150°C and 840mmHg. Determine the
   (i) Empirical formula of Q
   (ii) Molecular formula of Q
   (*1 mole of a gas occupies 24dm^3 at 25°C and 760mmHg*)

4. When 0.45g of compound Q made if carbon, oxygen and hydrogen atoms only was burnt, 0.44g of carbon dioxide and 0.09g of water was formed. The relative molecular mass of Q is 90. Determine the
   (i) Empirical formula of Q
   (ii) Molecular formula of Q

5. A sample of concentrated ammonia solution was placed at one end 'A' of a 0.8m glass tube held horizontally. At the other end 'B' was placed a sample of concentrated hydrochloric acid and both ends of the tube sealed. When the tube was left for some time, a whit ring was formed inside the tube.
   (a) Write equation for the formation of the white ring
   (b) Calculate the distance between B and the white ring

6. (a) A compound W, on combustion gave 0.629g of carbon dioxide and 0.257g of water. Determine the empirical formula of W
   (b) When 0.10g W was vaporized, it occupied a volume of 53.3cm^3 at s.t.p. Determine the
   (i) Molecular mass of W
   (ii) Molecular formula of W
   (c) 0.1g of Y occupied 22.1cm^3 when vaporized at 20°C and 766mmHg. Determine the molecular mass of Y

7. A compound Q contains 62.1% carbon and 10.3% hydrogen and the rest being oxygen. The vapour density of A is 2.59×10^{-3}gcm^{-3} at s.t.p.
   (a) Determine the
   (i) Empirical formula of Q
   (ii) Molecular formula of Q
   (b) Write down the structural formulae of all the possible isomers of Q

8. Compound R contains cobalt 24.8%, chlorine 29.8% and water 45.4%. Determine the
   (a) Empirical formula of R
   (b) Molecular formula of R
   $(Co = 58.9, Cl = 35.5, RFM\ of\ R\ is\ 237.9)$

9. A compound P contains 52.2% carbon and 13.0% hydrogen and the rest being oxygen.
   (a) Determine the empirical formula of P
   (b) When vaporized, 0.1g of P occupied 78.8cm^3 at 157 °C and 740mmHg. Determine the
   (i) Formula mass of P
   (ii) Molecular formula of P
   (c) Write the structural formulae of all the possible isomers of P

10. A chloride of beryllium Z, contains 11.25% beryllium and 88.75% chlorine. Determine the
   (a) Empirical formula of Z
   (b) Molecular formula of Z

11. (a) State Graham's law of diffusion.
   (b) A certain volume of oxygen diffused through a porous membrane in 120s. Under the same conditions, the same volume of a gas X diffused in 112s. calculate the formula mass of X

12. When 4.90g of an organic compound X, containing carbon and hydrogen only was burnt in oxygen, 15.78g of carbon dioxide and 5.38g of water were formed. Calculate the empirical formula of X.

13. When 8.8g of a hydrocarbon Z was burnt in excess air, 14.4g of water and 13.44dm^3 of carbon dioxide were produced at s.t.p. determine the
    (a) Empirical formula of Z
    (b) Molecular formula of Z
    (c) Write the structural formula for all the possible isomers of Z
    (Vapour density of Z is 22)

14. (a) An organic compound W contains carbon, hydrogen and oxygen only. On combustion. 0.463g of W gave 1.1g of carbon dioxide and 0.563g of water. Determine the empirical formula of W
    (b) When vaporized, 0.1g of W occupied 54.5cm^3 at 208°C and 98.3kPa. determine the molecular formula of W

15. A compound X, vapour density 58, contains carbon 62.07% and hydrogen 10.34% and rest being oxygen. Determine the
    (i) Empirical formula of X
    (ii) Molecular formula of X

16. (a) A gaseous hydrocarbon Y contains 44.4% carbon, 51.9% nitrogen and the rest being hydrogen. Determine the empirical formula of Y.
    (b) 50ml of Y diffused through a porous plug in 25s. under similar conditions, the same volume of hydrogen gas diffused in 6.8s. determine the molecular mass and hence formula of Y

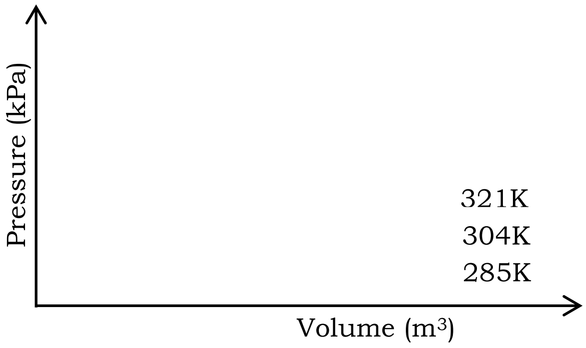
17. When 142cm^3 of a hydrocarbon Q of molecular mass 58 was exploded with excess oxygen and cooled to room temperature, the residual gas was 649cm^3. After addition of concentrated potassium hydroxide, the volume decreased to 126cm^3. Determine the molecular formula of Q

18. When 0.155g of an organic compound T was burnt in in excess oxygen, 0.220g of carbon dioxide and 0.153g of water were formed.
    (a) Determine the empirical formula of T
    (b) When vaporized, 0.225g of T occupied 119.11cm^3 at 127°C and 760mmHg. Determine the
    (i) Molecular mass of T
    (ii) Molecular formula of T
    (Molar gas volume at s.t.p is 22.4dm^3)

19. A gaseous hydrocarbon P contains 92.3% carbon.
    (a) Calculate the empirical formula of P
    (b) 0.13g of P occupies 112cm^3 at s.t.p. Calculate
    (i) The formula mass of P
    (ii) Molecular formula of P

20. (a) An organic compound H contains carbon 80%, hydrogen 6.7% and the rest being oxygen. Calculate the empirical formula of H
   (b) 0.5g of H when vaporized at 150°C and 760mmHg occupied 144.6cm^3. determine the molecular formula of H

21. (a) The diagram below shows the isothermals of a gas.
   (i) What is the critical temperature of the gas
   (ii) Which isothermal almost represents an ideal gas
   (iii) What does the region ABC represent
   (b) State two conditions for liquefying a gas



22. 1.18g of a compound P on vaporization occupied 300cm^3 at s.t.p.
   (a) Calculate the formula mass of P
   (b) The empirical formula of P is C_2H_4O. Determine the molecular formula of P

23. A certain organic liquid K contains 54.5% carbon, 36.4% oxygen and 9.1% hydrogen. If the formula mass of K is 44, determine the
   (a) Empirical formula of K
   (b) Molecular formula of K

24. An organic compound R contains 40% carbon, 6.77% hydrogen and the rest being oxygen. If the molecular mass of the compound is 180. Calculate the
   (a) Empirical formula of R
   (b) Molecular formula of R

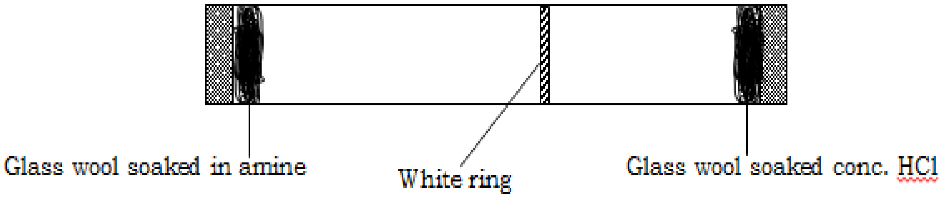
25. 1.5g of a compound, A, containing carbon, hydrogen and oxygen gave 2.2g of carbon dioxide and 1.8g of water on complete combustion in excess pure oxygen. Calculate the empirical formula of A.

26. 2.5g of an organic, Z, which contains carbon, hydrogen and oxygen only, gave on combustion 2.0g of carbon dioxide and 1.3g of water. Calculate the empirical formula of Z.

27. The combustion of a hydrocarbon X gave 8.8g of carbon dioxide and 4.5g of water, if the molecular mass of X is 58. Determine the
   (a) Empirical formula of X
   (b) Molecular formula of X

28. Under the same conditions of temperature and pressure, nitrogen diffuses 1.42 times as fast as a gaseous hydrocarbon Q, which contains 85.7% carbon. Calculate the
   (a) Molecular mass of Q
   (b) Molecular formula of Q

29. Two pieces of glass wool, one soaked in an amine ($C_nH_{2n+1}NH_2$) and the other in conc. Hydrochloric acid were placed at the opposite ends of a 1.0m glass tube as shown below.



After some time, a white ring was seen 0.52m from the end at which the amine was place. Calculate the
   (a) Molecular mass of the amine.
   (b) Molecular formula of the amine

30. (a) Oxygen diffuse through a small hole in 0.935 times faster than gas X. calculate the formula mass of X
   (b) Gas X contains 57% oxygen and the rest being carbon
   (i) Determine the molecular formula of X
   (ii) Write an equation for the reaction between X and copper(II) oxide.

31. 0.60g of hydrogen and 9.0g of nitrogen and 10.2g of oxygen were put in 2dm^3 container at 25°C. Calculate the total pressure in the container. ($R = 8.314 J mol^{-1} K^{-1}$)

32. A vessel contains 10.0g of oxygen at 25°C and a pressure of 4.8atm. Calculate the
   (a) __ Volume of the vessel ($R = 0.082 latm\ mol^{-1} K^{-1}$)
   (b) The final pressure when 0.8mol of hydrogen was added to into the vessel at 25°C without changing the volume.
   (c) The pressure of the gas in the vessel, if the mixture was exploded an allowed to cool to 25°C.

33. A compound was analysed and found to have 66.7% carbon, 11.1% hydrogen and the rest being oxygen. Determine the
   (a) Empirical formula of X
   (b) Molecular formula of X

34. A compound Z contains carbon, hydrogen and oxygen. Element analysis shows that 54.5% is carbon and 9.09% is hydrogen.
   (a) Calculate the empirical formula of X
   (b) 0.524g of Z occupies 148cm^3 at 20°C and 740mmHg. Determine the molecular formula of Z.

35. (a) Complete combustion of 7.05g of organic compound Z containing carbon hydrogen and oxygen gave 17.8g carbon dioxide and 9.27g of water. Calculate the empirical formula of Y
    (b) When vaporized, at 760mmHg and 400K, 0.225g of Y occupied 100cm^3. Calculate the molecular formula of Y.

36. 0.236g of an organic compound Y on combustion gave 0.528g of carbon dioxide and 0.324g of water. If 0.295g of Y at s.t.p gave 56cm^3 of nitrogen gas and the molecular weight of Y is 59, determine the molecular formula of Y

37. 15cm^3 of a gaseous hydrocarbon P were exploded with 105cm^3 of oxygen. After cooling, the residual gas occupied 75cm^3. On addition of potassium hydroxide solution, there was a contraction in volume to 30cm^3. Determine the molecular formula of P

38. 50.0cm^3 of gas W effused through a tiny aperture in 146s. the same volume of carbon dioxide under the same conditions effuses in 11.5s. calculate the molecular mass of W

39. It takes 2½ minutes for 25.0cm^3 of hydrogen to effuse through a pin hole. Find the time taken for the same volume of oxygen gas under the same conditions to effuse through the same pinhole

40. A gaseous alkane diffused through a porous partition at a rate of 2.56cms^{-1}. Helium diffuses through the same partition under the same conditions at a rate of 8.49cm^{3}s^{-1}. Determine the molecular formula of the alkane.

41. 20cm^3 of a gaseous hydrocarbon X were exploded with 120cm^3 of oxygen. After explosion and cooling to room temperature, the volume of gas remaining was 90cm^3 and this volume decreased to 50cm^3 on treatment with aqueous potassium hydroxide. Determine the molecular formula of X

42. 10cm^3 of a gaseous hydrocarbon P was mixed with 33cm^3 of oxygen. The mixture was exploded and after cooling to room temperature, the resultant volume of the gas was 28cm^3. On addition of concentrated potassium hydroxide, the volume decreased to 8cm^3. Determine the formula of P

43. A mixture of 10cm^3 of a gaseous hydrocarbon and 100cm^3 of excess oxygen was exploded. After explosion and cooling to room temperature, the volume of the residual gas was 75cm^3, which decreased to 35cm^3 on treatment with potassium hydroxide. Calculate the molecular formula of Q

44. When 10cm^3 of a hydrocarbon, C_xH_y, were exploded with excess oxygen and cooled to room temperature, there was a contraction in volume of 30cm^3. When the gaseous product was bubbled through potassium hydroxide solution, there was a further contraction in volume of 30cm^3. Determine the formula of the hydrocarbon

45. 10cm^3 of a hydrocarbon, C_aH_b was exploded with excess oxygen. When the mixture of the gaseous product was cooled to room temperature, 50cm^3 of steam condensed. When

the gaseous product was treated with potassium hydroxide solution, there was a contraction of 40cm^3. Determine the formula of the hydrocarbon.

46. 10cm^3 of a hydrocarbon X were exploded with excess oxygen and the mixture cooled to room temperature. On treatment with conc. potassium hydroxide solution, the volume decreased by 40cm^3. If the RFM of the hydrocarbon is 58, determine the molecular formula of X

47. When 10cm^3 of a hydrocarbon, Q, were exploded with excess oxygen and cooled to room temperature, the volume of the residual gases was 150cm^3. On treatment with potassium hydroxide solution, the volume decreased to 110cm^3. If the RFM of Q is 54, determine the formula of Q

48. 20cm^3 of a gaseous hydrocarbon M was exploded with excess oxygen and cooled to room temperature. When bubbled through conc. potassium hydroxide solution, a contraction in volume of 60cm^3 occurred. If the RMM of M is 42, determine the formula of M

49. (a) State Graham's law of diffusion

(b) The table below shows the times (t) taken for gases of different molecular mass (M_r) to diffuse through a narrow opening under similar conditions.

t(s)	25.00	34.23	41.67	47.62
M_r	16	30	44	58

Plot a graph of rate of diffusion, ($\frac{1}{t}$) against $\sqrt{\frac{1}{M_r}}$

(c) Using your graph in (b) above, find the molecular mass of a gas

(i) Whose rate of diffusion is 0.02ss^{-1}

(ii) That takes 38.42 seconds to diffuse

50. (a) For each of the information provided below, determine the molecular mass of an organic compound Z containing carbon, oxygen and hydrogen

(i) Oxygen diffuses 1.199 times faster than Z

(ii) 0.1g of Z when vaporized at 80°C and 890mmHg, it occupied a volume of 53.77cm^3

(iii) 25cm^3 of Z effuses through a small pore in 12.2 seconds. Under similar conditions, the same volume of oxygen takes 10.5 seconds

(b) 10cm^3 of the vapour of Z was mixed with 130cm^3 of oxygen, and the mixture exploded. On cooling to room temperature, the volume of the residual mixture was 125cm^3 which dropped to 105cm^3 on passing the mixture through conc. potassium hydroxide solution. Determine the molecular formula of Z.

51. (a) For each of the information provide, determine the molecular mas of K which contains only carbon, hydrogen and hydrogen.

(i) When 0.05g of K were vaporized, it occupied a volume of 39.5cm^3 at 27°C and 740mmHg

(ii) 17cm^3 of nitrogen diffuses through a porous plug in 8.2 seconds while under the same conditions, K takes 8.8 seconds

(iii) K diffuses 0.935 times faster than nitrogen

(b) 20cm^3 of K were exploded with 100cm^3 of oxygen and the mixture cooled to room temperature. The resultant gaseous volume was 102cm^3. This decreased by 20cm^3 after absorption with potassium hydroxide. Determine the molecular formula of K

52. (a) For each of the information provided, determine the molecular mass of M which contains only carbon, hydrogen and oxygen

(i) When 0.20g of M was vaporized, it occupied a volume of 107.54cm^3 at 115°C and 750mmHg.

(ii) A certain volume of carbon dioxide diffuses through a small opening in 13.8 seconds. The same volume of M diffuses through the same opening in 18.8 seconds under the same conditions.

(iii) Carbon dioxide diffuses 1.363 times faster than M

(b) 15cm^3 of the organic compound M were exploded with 155cm^3 of oxygen. And the mixture cooled to room temperature. The resultant gaseous volume was 140cm^3. On passing the mixture through potassium hydroxide solution, the volume of the mixture reduced to 95cm^3. Determine the formula of the organic compound.

53. (a) For each of the information provided, determine the molecular mass of compound A, that contains carbon, oxygen and hydrogen.

(i) 10.4cm^3 of hydrogen diffuses through a small plug in 23.2 seconds. Under the same conditions, the same volume of A takes 89.89 seconds.

(ii) When 0.05g of A was vaporized, it occupied 37.33cm^3 at s.t.p.

(iii) A diffuses 3.875 times slower than hydrogen under the same conditions.

(b) 10cm^3 of A were mixed with 120cm^3 of excess oxygen, exploded and cooled to room temperature. The gaseous residual volume was 125cm^3. When bubbled through potassium hydroxide solution, the volume decreased to 10cm^3. Determine the formula of A

54. (a) An organic compound R containing carbon, hydrogen and nitrogen only. 38.71% of the compound is carbon. On combustion, 0.51g of R gave 184.26cm^3 of nitrogen gas at s.t.p. Determine the empirical formula of R.

(b) When vaporized, 0.48g of R occupied a volume of 346.84cm^3 at s.t.p. determine the molecular formula of R

55. (a) An organic compound T contains carbon, hydrogen and nitrogen only. When 0.42g of the compound was burnt in excess oxygen, 0.596g of carbon dioxide was produced. When 0.51g of T were burnt, 184.26cm^3 of nitrogen gas were formed at s.t.p. determine the empirical formula of T.

(b) When vaporized, 0.48g of T occupied a volume of 4422.63cm^3 at 80°C and 770mmHg. Determine the molecular formula of T

56. (a) When 0.45g of an organic compound, L, containing carbon, hydrogen and nitrogen only was burnt completely, 199.5cm^3 of nitrogen were collected at 62°C and 760mmHg. When 0.25g of the organic compound was burnt in excess oxygen, 0.355g of carbon dioxide gas was produced. Determine the empirical formula of L

(b) 13.5cm^3 of hydrogen effuse through a narrow pore in 7.5 seconds. Under the same conditions, the same volume of L takes 66.4 seconds. Determine the molecular formula of L

57. (a) An amine P contains 53.33% carbon. When 0.12g of P was burnt in excess oxygen, 29.87cm^3 of nitrogen were produced at s.t.p. determine the empirical formula of P

(b) When vaporized, 0.1g of P occupied a volume of 67.93cm^3 at 102°C and 765mmHg. Determine the molecular formula of P

58. (a) When 0.41g of an amine Z was burnt in excess oxygen, 0.802g of carbon dioxide was formed, 102.04cm^3 of nitrogen at s.t.p. determine the empirical formula of Z

(b) When 0.1g of Z was vaporized, it occupied a volume of 49.78cm^3 at s.t.p. determine the formula of Z

59. (a) 0.215g of an amine K was burnt in excess oxygen, 0.42 g of carbon dioxide was produced. When 0.205g of K was completely burnt in oxygen, 62.72cm^3 of nitrogen were collected. At 67°C and 770mmHg. Determine the empirical formula of K

(b) Methane diffuses 1.6764 times faster the K under the same conditions and volume. Determine the formula of K

60. (a) When 0.40g of an amine X was burnt in excess oxygen, 1.135g of carbon dioxide and 48.17cm^3 of nitrogen were produced at s.t.p. determine the empirical formula of X

(b) When vaporized, 0.53g of X occupied a volume of 190.29 cm^3 at 150°C and 760mmHg. Determine the molecular formula of X.

61. (a) An amine W contains 77.42% carbon. When 0.22g of W was burnt in excess oxygen, 26.50cm^3 of nitrogen gas were collected at s.t.p. determine the empirical formula of W

(b) When vaporized, 0.22g of W occupied 52.99cm^3 at s.t.p. determine the molecular formula of W

62. (a) When 0.11g of an organic compound Y containing carbon, hydrogen and nitrogen was burnt in excess oxygen. 0.312g of carbon dioxide was produced 0.25g of the compound on combustion yielded 43.04cm^3 of nitrogen at 107°C and 740mmHg. Determine the empirical formula of Y

(b) 15cm^3 of carbon dioxide diffused through a porous plug in 42.8 seconds. The same volume of Y under the same conditions took 62.2 seconds to diffuse through the same hole. Determine the molecular formula of Y

63. (a) When 0.325g of an amine Z was burnt in excess oxygen, 469.68cm^3 of carbon dioxide and 39.14cm^3 of nitrogen were produced at s.t.p. determine the empirical formula of Z

(b) Carbon dioxide diffuses 1.4538 times faster than the vapour of Z under the same conditions. Determine the molecular formula of Z

64. (a) When 0.225g of an amine N was burnt in excess oxygen, 364.43cm^3 of carbon dioxide and 30.37cm^3 of nitrogen at 37°C and 770mmHg. Determine the empirical formula of N.

(b) The vapour of N under the same conditions diffuses 0.6879 times faster than carbon dioxide. Determine the molecular formula of N

65. (a) State

(i) Boyle's law

(ii) Graham's law of diffusion

(b) Explain the following

(i) Critical point

(ii) Compressibility factor

(b) (i) Show how the compressibility factor for a real gas varies with pressure at two different temperatures.

(ii) Explain the differences in behaviour of the gas at the two temperatures

(d) The time taken for equal volumes of two gases to diffuse under identical conditions was determined as below. Use it to determine the RFM of A

Gas	Oxygen	A
Time(s)	28.30	33.20

66. (a) When 0.368g of a compound Q, containing carbon and hydrogen was vaporized, it occupied 161.4cm^3 at 37°C and 760mmHg. Determine the RFM of Q

(b) When 142 cm^3 of Q were exploded with excess oxygen and cooled to room temperature, the volume of the residual gas was 694cm^3. After adding conc. potassium hydroxide, the volume decreased to 126cm^3. Determine the molecular formula of Q.

67. (a) When 0.1g of aluminium chloride was vaporised at 350°C and 1 atmosphere pressure, 19.2 cm^3 of vapour was formed.

(i). Calculate the relative molecular mass of aluminium chloride

(ii). Write the molecular formula of aluminium chloride in vapour state at 350°C.

68. (a) What is meant by the term critical temperature

(b) Explain why it is possible to liquefy a gas below its critical temperature.

(c) Use a P-V graph to describe how liquefaction occurs for a gas below its critical temperature

(d) Give two ways of liquefying a gas

(e) Explain why real gases deviate from the ideal behaviour

(c) (i) Name any two types of intermolecular forces

(ii) Give any two evidences for the existence of intermolecular forces.

69. (a) Distinguish between a real gas and an ideal gas

(b) The pressure and volume changes for a 0.02g of a vaporized substance Q at 25°C were as shown below.

Pressure (Nm^{-2})	2.2	5.4	6.3	8.5	10.10
Volume (m^3)	0.500	0.200	0.172	0.128	0.106

(i) Plot a graph of pressure against $\frac{1}{volume}$

(ii) Use your graph to determine the molecular mass of Q ($R = 8.314JK^{-1}mol^{-1}$)

(c) On analysis, it was found that Q contains carbon, hydrogen and oxygen only in the proportions of 52.17% carbon and 13.04% hydrogen.

(i) Determine the molecular formula of Q

(ii) Write the structural formulae of all the possible isomers and their IUPAC names.

69. A hydrocarbon Y contains 85.7% carbon and has a density of $2.5gl^{-1}$ at s.t.p.

(a) Calculate the empirical formula of Y

(b) Determine the molecular formula of Y

(c) Write the structural formulae of all the possible open chain isomers of Y

70. A compound M, relative molecular mass 93, burns with a sooty flame, and contains 77.42% carbon, 7.53% hydrogen and the rest being nitrogen. Determine the molecular formula of M

71. An alkane R, diffuses through a porous partition in 2 minutes. Under similar conditions, the same volume of oxygen diffuses in 1.75 minutes

(a). (i). Calculate the formula mass of R

(ii). Determine the molecular formula of R

(b). Write equations to show how R can be synthesized from propanone

72. 10cm^3 of a hydrocarbon P was exploded in 90cm^3 of oxygen. On cooling to room temperature, the residual gases occupied 70cm^3. When the residual gases were passed through potassium hydroxide solution, the volume reduces to 40cm^3. Determine the molecular formula of P

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 2: ATOMIC STRUCTURE

1. Complete the following equations for nuclear reaction
   (a) $^{239}_{94}Pu \ + \ ^{4}_{2}He \longrightarrow \ \ldots\ldots\ldots \ + \ 2\,^{1}_{0}n$
   (b) $\ldots\ldots\ldots \longrightarrow \ \propto \ + \ ^{234}_{90}Th$
   (c) $^{214}_{83}Bi \longrightarrow \ ^{239}_{94}Pu \ + \ \ldots\ldots\ldots + \ 2\,^{4}_{2}He$
   (d) $^{250}_{98}Cf \ + \ \ldots\ldots\ldots \longrightarrow \ ^{257}_{103}Lw \ + \ 4\,^{1}_{0}n$

2. (a) Complete the following equation for nuclear reactions
   (i) $^{27}_{14}Si \longrightarrow \ ^{27}_{13}Al \ + \ \ldots\ldots\ldots$
   (ii) $^{236}_{92}U \ + \ ^{1}_{0}n \longrightarrow \ ^{147}_{60}Nd \ + \ 2\,^{1}_{0}n \ + \ \gamma \ + \ \ldots\ldots\ldots$
   (b) When a radioactive isotope was left to stand, it decayed by 12.5% of its original value in 45 days. Calculate the half-life of the radioactive isotope.

3. Thorium undergoes nuclear decay according to the following equation.

$$^{232}_{90}Th \xrightarrow{\alpha} X \xrightarrow{\beta} Y \xrightarrow{\beta} Z$$

   (a) Identify the species X, Y and Z
   (b) 5g of thorium was left to decay. Calculate the mass of thorium that remained after 2.5×10^{10} years. (half-life of thorium is 1.4×10^{10} years)

4. (a) Complete the following equations for nuclear reactions.
   (i). $^{27}_{14}Si \longrightarrow \ ^{27}_{13}Al \ + \ \ldots\ldots\ldots$
   (ii). $^{241}_{95}Am \ + \ ^{4}_{2}He \longrightarrow \ ^{243}_{97}Bk \ + \ \ldots\ldots\ldots$
   (iii). $^{238}_{92}U \ + \ ^{1}_{0}n \longrightarrow \ ^{239}_{93}Np \ + \ \ldots\ldots\ldots$
   (b). In an experiment, the rate of radioactive decay of bromine decreased by 25% in 96 minutes. Calculate the half-life of bromine.

5. (a) State what is meant by the terms
   (i) Radioactivity
   (ii) Half-life
   (b) The table below shows data for radioactive decay of an element Z

Time (hours)	0.0	5.0	10.0	15.0	20.0	25.0	30.0
Activity (counts per minute)	25.00	23.00	21.25	19.50	18.00	16.50	15.25

   (i) Plot a graph of activity against time
   (ii) Determine the half-life of element Z
   (iii) Determine the decay constant and state its units

6. (a) Complete the following equation
   (i) $^{236}_{92}U \longrightarrow \ ^{92}_{36}Kr \ + \ ^{141}_{56}Ba \ + \ \ldots\ldots\ldots$
   (ii) $^{214}_{83}Bi \longrightarrow \ ^{0}_{-1}e \ + \ \ldots\ldots\ldots$

(b) The half-life for bismuth is 20 minutes. Determine the time taken for bismuth to decay b 75%

6 (a) (i) Define the term radioactivity

(ii) Name three types of radiations emitted during radioactivity and how they affect the nucleus of a radioisotope

(b) The table below shows how the mass of a radioactive protactinium varies with time

Mass of protactinium (g)	60.0	38.5	26.0	17.2	11.1
Time (s)	0	40	80	120	160

(i) Plot a graph of mass of protactinium against time

(ii) Use your graph to determine the half-life of protactinium

(iii) Calculate the radioactive decay constant for protactinium

(iv) Determine the time taken for 8g of protactinium to decay.

(c) Briefly describe how

(i) Carbon – 14 can be used to determine the age of archeological objects

(ii) Oxygen – 18 can be used to determine the mechanism for esterification of a monocarboxylic acid with a primary alcohol.

7 (a) (i) Plutonium, ${}^{216}_{84}Po$ undergoes radioactive decay to give elements X and Y according to the following equation

$${}^{216}_{84}Po \longrightarrow X + \beta \longrightarrow Y + \alpha$$

Write the

(i) Atomic number of X and Y

(ii) Mass number of X and Y

(b) Calculate the half-life of Y (decay constant of Y is $6.54 \times 10^{-4} min^{-1}$

8. Complete the following equation

(a) ${}^{27}_{13}Al + {}^{1}_{0}n \longrightarrow \dots\dots\dots\dots\dots\dots + {}^{4}_{2}He$

(b) $\dots\dots\dots\dots\dots\dots. \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He$

(c) ${}^{4}_{2}He + {}^{14}_{7}N \longrightarrow \dots\dots\dots\dots\dots\dots + {}^{1}_{1}H$

(d) ${}^{23}_{11}Na + {}^{2}_{1}D \longrightarrow \dots\dots\dots\dots\dots\dots + {}^{1}_{1}H$

9. The first three successive ionisation energies of element Y are 549, 1064 and 4226kJmol^{-1}.

(a) Explain the trend in the variation of the ionisation energies of Y

(b) State the group in the periodic table to which Y belongs

10. The first ionisation energies of some elements are shown in the table below

Elements	Ionisation energies (kJmol^{-1})			
	1st	2nd	3rd	4th
A	500	4600	6900	9500
B	740	1500	7700	10500
C	630	1600	3000	4800
D	900	1800	14800	21000
E	580	1800	2700	11600

(a) What

(a) What is meant by the term ionisation energy

(b) (i) State the element that is most likely to form an ion with a unit positive charge. Give a reason for your answer

(ii) Identify two elements that are in the same group of the periodic table

11. (a) Define the term isotope

(b) Describe the main steps involved in the operation of a mass spectrometer

(c) The table below shows the information from a mass spectrum of a lead sample

Isotope	204	206	207	208
Detector current (mA)	0.16	2.72	2.50	5.92

Calculate

(i) The relative abundance of the different isotopes of lead in this sample

(ii) The relative atomic mass of lead

(d) State two advantages of using a mass spectrometer over the depression of freezing point method of determining R.A.M

(e) The initial count of a radioactive nucleus was 680 per second. After 350 seconds, the count rate was 125 per second. Calculate the

(i) decay constant

(ii) half-life of the nucleus

12. (a) Complete the following equation for the nuclear reaction

(i) ${}^{35}_{17}Cl \;+\; {}^{1}_{0}n \longrightarrow {}^{1}_{1}H \;+\; \ldots\ldots\ldots\ldots$

(ii) ${}^{214}_{83}Bi \;+\; \longrightarrow 3\beta \;+\; 2\alpha \;+\; \ldots\ldots\ldots\ldots$

(iii) ${}^{2}_{1}H \;+\; {}^{10}_{5}B \longrightarrow {}^{1}_{0}n \;+\; \ldots\ldots\ldots\ldots$

(b) When a radioactive isotope was stored for 42 days, it retained $\frac{1}{8}$ of its original activity. Calculate the half-life of the isotope.

13. Complete the following equations for the nuclear reaction

(a) ${}^{239}_{94}Pu \;+\; {}^{1}_{0}n \longrightarrow {}^{91}_{39}Y \;+\; {}^{146}_{55}Cs \;+\; \ldots\ldots\ldots\ldots$

(b) ${}^{239}_{92}U \longrightarrow {}^{239}_{93}Np \;+\; \ldots\ldots\ldots\ldots$

(c) ${}^{226}_{88}Ra \longrightarrow {}^{4}_{2}He \;+\; \ldots\ldots\ldots\ldots$

14. (a) The first, second, third and fourth ionisation energies of an element Y are 736, 1451, 7740 and 10500 kJmol^{-1} respectively.

(i) State the group in the periodic table to which Y belongs. Give a reason for your answer.

(ii) Explain why the second ionisation energy is greater than the first ionisation energy.

(b) The mass spectrum of a naturally occurring Y is shown below

(i) Briefly describe how the mass spectrum was obtained.
(ii) State why the mass spectrum of Y shows three peaks
(iii) Calculate the RAM of Y

15. (a) Identify element X in the following equation for a nuclear reaction

$$^{235}_{92}U \quad + \quad ^{1}_{0}n \xrightarrow{\qquad\qquad} {}^{160}_{62}Sn \quad + \quad 4^{1}_{0}n \quad + \quad \ldots\ldots\ldots\ldots$$

(b) An element Y has three naturally occurring isotopes with isotopic masses and relative abundances as shown below

Isotopic mass	23.98	24.98	25.98
Relative abundance (%)	78.60	10.11	11.29

Calculate the RAM of Y

16. The mass spectrum of chlorine shows peaks at masses 70, 72, and 74. The heights of the peaks respectively are in the ratio of 9:6:1. Calculate
(a) The average atomic mass of chlorine
(b) The relative abundance of chlorine –35 and chlorine –37

17. The table below shows the ionisation energies of five lettered elements

Elements	Ionisation energies ($kJmol^{-1}$)			
	1st	2nd	3rd	4th
Q	500	4600	6900	9500
R	740	1500	7700	10500
T	630	1600	3000	4800
X	900	1800	14800	21000
Z	580	1800	2700	11600

(a) Which one of the elements is most likely to form an ion with a charge of +1. Give a reason for your answer
(b) State
  (i) Two elements which belong to the same group
  (ii) The group to which the elements you have named belong
(c) Write
  (i) The formula of the chloride of Z
  (ii) Equation for the reaction between the chloride of Z and water

18. (a) Complete the following equation for the decay of bismuth

$$^{214}_{83}Bi \xrightarrow{\qquad\qquad} {}^{0}_{-1}e \quad + \quad \ldots\ldots\ldots\ldots$$

(b) The half-life of bismuth is 19.7 minutes. Determine the time taken for 43% by mass of bismuth to decay

19. (a) Define the term RAM
(b) Explain how the RAM can be determined by mass spectrometer

(c) The mass spectrum of an element A contained 4 lines at mass : charge ratio of 54, 56, 57 and 58 with relative abundance of 5.84, 91.68, 2.17 and 0.31

(i) Explain what the term relative intensity means

(ii) Calculate the relative atomic mass of A

(d) Explain why the values of RAM have no units

(e) Thorium decays according to the following equation

$$^{232}_{90}Th \xrightarrow{\alpha} X \xrightarrow{\beta} Y \xrightarrow{\beta} Z$$

Determine the mass numbers and atomic number of X, Y and Z.

20 (a) (i) What is meant the term ionisation energy of an element

(ii) Write equation to show the first ionisation of magnesium

(b) The second and third ionisation energies of magnesium are 1450 and 7730kJmol^{-1} respectively. Explain this trend.

21. (a) Describe the spectrum of a hydrogen atom. Use a diagram to illustrate your answer

(b) Explain how the spectrum of a hydrogen atom

(i) Is formed

(ii) Provide evidence for existence of energy levels in atoms

(c) The frequency of hydrogen at the point of ionisation is $32.8 \times 10^{14} Hz$

Calculate the ionisation energy of hydrogen.

$(Plank's\ constant = 6.63 \times 10^{-34} Js)$

22. (a) The first eight ionisation energies of an element B are shown below.

1^{st}	2^{nd}	3^{rd}	4^{th}	5^{th}	6^{th}	7^{th}	8^{th}
786	1580	3230	4360	16000	20000	23600	29100

(i) Explain what is meant by the term first ionisation energy

(ii) State the factors that determine the value of first ionisation energy

(iii) To which group in the periodic table does element B belong. Give a reason for your answer.

(b) (i) Explain what is meant by electronegativity.

(ii) State the factors that determine the value of electronegativity.

23. The diagram below shows successive ionisation energies for an element X showing removal of all electrons.

(a) Giving reasons, state,

(i) The group and period of element X

(ii) Identify of X

(b) Explain the sudden increase in the energy required to remove electron E

(c) Explain how the size of X will change as electrons are removed.

(d) Explain what would be the sign of energy change if an electron was added to X to form X^{-}. How would you expect it to affect its size?

(e) Explain giving reasons whether you predict X to form compounds in the +1 oxidation state.

24 (a) (i) What is meant by the “Stability of a nucleus”

(ii) Explain the factors that determine the stability of a nucleus

(b) The graph below shows how the number of neutrons vary with that of the protons

(i) What do lines A and B represent

(ii) Describe briefly how nuclei X and Y can gain stability

25. (a) State two methods that they may be used to produce positive ions in a mass spectrometer

(b) What property of the ions does the mass spectrometer measure?

(c) Explain the following observations

(i) When chloroform was analyzed in the mass spectrometer two peaks are observed having an abundance ratio of 3:1.

(ii) When hydrogen chloride was analyzed in the mass spectrometer, four peaks are observed in the molecular ion region.

(iii) When chlorine is analyzed in the mass spectrometer, three peaks are observed in the molecular ion region

26. (a) Uranium – 238, $^{238}_{92}U$, is radioactive and undergoes alpha decay to give isotope of another element

(i) State the mass number and atomic number of the isotope formed.

(ii) Identify the element formed

(iii) The half-life of uranium – 238 is 4.5×10^{9} years. How many years would be required for 1000 atoms of uranium – 238 to decay to 250 atoms?

(iv) After a series of nuclear transformations, uranium – 238 finally ends as lead – 206. Why does the series stop at this?

(b) A sample of carbon from a wooden artifact is found to give 7.00 carbon – 14 counts per gram of carbon. The carbon – 14 from a recently cut wood decays at

a rate of 15.3 disintegrations per minute per gram of carbon. Calculate the age of the artifact.
(Half-life of carbon is 5770 years)

27. Element Y is radioactive, decaying by emission of β – particles with a half-life of 1.3×10^9 years.
    (a) What is a β – particle
    (b) What is meant by "half-life is 1.3×10^9 years?
    (c) How long will element Y take to decay to $^1/_3$ of its original mass (decay constant is $2.3 \times 10^5\ yr^{-1}$)

28. (a) Plutonium – 216 undergoes radioactive decay to give element X according to the equation.

$$^{216}_{84}Po \longrightarrow X + \alpha$$

State the atomic number and mass number of X

(b) X decays further to Z as shown

$$X \longrightarrow Z + \beta$$

State the atomic number and mass number of Z

(c) A sample of X had an initial count of 260 counts per second. After 30 minutes, the activity had declined to 250 counts per second. Calculate the half-life of X

29. (a) The figure below shows the spectrum of magnesium. The heights of the three peaks and the mass number of the isotopes are shown

Calculate the relative atomic mass of magnesium

(b) The mass spectrum of neon shows three peaks corresponding to the isotopes 22, 21, and 20 mass units. The heights of the three are in the ratio of 11.2 : 0.2 : 11.4. Calculate the average atomic mass of neon.

(c) The table below shows the mass number and the percentage abundance of an element Q.

Mass number	Percentage abundance
54	5.84
56	91.68
57	2.17
58	0.31

Determine the RAM of Q

30. (a) Complete the following nuclear equation

(i) ${}^{27}_{13}Al + {}^{1}_{1}H \longrightarrow {}^{24}_{12}Mg +$ … … … …

(ii) ${}^{14}_{7}N + {}^{1}_{0}n \longrightarrow {}^{3}_{1}H +$ … … … …

(iii) ${}^{9}_{4}Be +$ … … … …. $\longrightarrow {}^{12}_{6}C + {}^{1}_{0}n$

(iv) ${}^{14}_{7}N +$ … … … … $\longrightarrow {}^{12}_{6}C + 2{}^{1}_{0}n$

(v) ${}^{226}_{88}Ra \longrightarrow {}^{0}_{-1}e +$ … … … … … ….

(vi) ${}^{7}_{3}Li + {}^{1}_{1}H \longrightarrow$ … … … …

(b) State the applications of radioactivity

31 (a) (i) What is an isotope

(ii) Describe with aid of a diagram how you would determine the RAM of gaseous chlorine having two isotopes, chlorine – 35 and chlorine – 37

(b) (i) An element X gave the following spectrum in a mass spectrometer

Calculate the RAM of X

(ii) When chlorine gas was analyzed in a mass spectrometer peaks were observed at mass number 70, 72 and 74. Explain

32. The diagram below shows parts of the atomic emission spectrum

(a) State

(i) The information obtained from the separate lines about the electronic structure of the hydrogen atom

(ii) How an emission line arises?

(b) Briefly, explain why the emission lines get closer together

(c) State what is meant by the term “principal quantum number”

33. (a) Distinguish between **ionisation** and **excitation** of an electron in atom

(b) Explain how the following provide evidence for the existence of energy levels in atoms

(i) Ionisation

(ii) Hydrogen emission spectrum

34. (a) The half-life of radium is 1620 years. What is the radioactive decay constant of radium

(b) Calculate the time taken for the sample of radium to disintegrate to

  (i) 10% of the original

  (ii) 90% of the original

(c) If a sample of radioactive isotope of half-life 3.11 hours has an activity of 1000 per second at a certain time, what will be the activity one hour later.

(d) The value of the wavelength at the start of the continuum of a sodium emission spectrum is 242nm. Calculate the first ionisation energy of

  (i) Sodium atom

  (ii) Sodium in kJmol^{-1}

(e) The value of the wavelength at the start of the continuum of a potassium emission spectrum is 286nm. Calculate the first ionisation energy of

  (iii) Potassium atom

  (iv) Potassium in kJmol^{-1}

  $(Plank's\ constant, h, = 6.63 \times 10^{-34},\ 1nm = 1 \times 10^{-9}m,$
  $c = 2.998 \times 10^{8}ms^{-1}, Avogadro's\ number = 6.02 \times 10^{23}mol^{-1})$

35. (a) The table below shows the time taken for a radioactive substance M to decay during a given time interval

Time (hours)	0.00	1.80	2.70	3.60	4.50
Activity (s^{-1})	30.35	18.05	13.92	10.73	8.27

  (i) Plot a graph of activity against time

  (ii) The half-life of M

  (iii) Find the decay constant of M

(b) Explain the factors that affect the stability of a nuclide.

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 4: COLLIGATIVE PROPERTIES

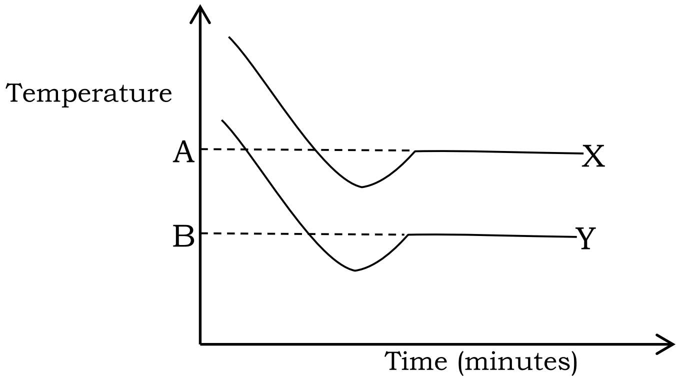
1. (a) One of the limitations of the method of determining the relative molecular mass by freezing point method is that the solute should not associate or dissociate in the solution.
   (i) State three other limitations of determining the molecular mass by freezing point method
   (ii) Explain how association of a solute in solution affects the molecular mass determined by freezing point method
   (b) A solution containing 0.142g of naphthalene in 20.25g of benzene caused a lowering of freezing point of 0.284°C. Calculate the molecular mass of naphthalene. (K_f of benzene is 5.12°Cmol^{-1}kg^{-1})

2. (a) The osmotic pressure of a solution containing 4.00gdm^{-3} of PVC in dioxane is 65Nm^{-2} at 20°C. Calculate the number of PVC monomers
   (b) A solution containing 28.145g of R in 250g of water froze at -3.490°C. determine the molecular mass of R

3. (a) Explain why a solution containing 2.5g of glucose ($C_6H_{12}O_6$), in 100g of ethanol boils at 83°C at 760mmHg yet pure ethanol boils at 78°C at the same pressure.
   (b) Using the data in (a), calculate the molar boiling point constant of ethanol.

4. (a) Define a colligative property.
   (b) A solution contains 1.80g of naphthalene in 3.0g of camphor
   (i) Calculate the melting point of the solution (molecular mass of naphthalene =128, melting point of pure camphor =177°C, K_f for camphor =40°C per mol per 100g.)
   (ii) State whether your answer in (b)(i) significantly affected if the pressure of the system was lowered. Give a reason.

5. The cooling curves of a solution containing 1.2g of sulphur in 20.0g of carbon disulphide and that of pure carbon disulphide are shown



(a) (i) Identify the curves X and Y
(ii) State what points A and B represent
(b) Calculate the relative formula mass of sulphur in carbon disulphide (the freezing point depression constant for carbon disulphide is 6.10°Cmol^{-1}kg^{-1} and the freezing point depression of carbon disulphide is 1.43°C)
(c) (i) Comment on your result in (b) above
(ii) Deduce and draw the molecular structure of sulphur in carbon disulphide.

6. (a) The osmotic pressure of a solution containing 4g per liter of a polymer is 65Nm^{-2} at 298K. calculate the molecular mass of the polymer
(b) The osmotic of pressure of a solution containing 2gdm^{-3} of nylon at 25°C was 0.155mmHg. calculate the molecular mass of nylon (R=0.0821atml^{-1}°Cmol^{-1})

7. (a) (i) Describe how the molecular mass of a substance can be determined using the freezing point depression method.
(ii) Explain why the method you have described above is not suitable for determining the molecular mass of a polymer
(b) Calculate the freezing point of a given solution containing 4.2g of ethane-1,2-diol (molecular 62) in 30g water. (K_f of water is 18.6°Cmol^{-1}per 100g).
(c) The osmotic pressure of various concentrations of solute X in methyl benzene at 25°C are given in the table below

Concentration (gdm^{-3})	1.0	2.0	3.0	4.0	5.0
Osmotic pressure (Nm^{-2})	23	37	53	75	92

(i) Plot a graph of osmotic pressure against concentration
(ii) Use your graph to determine the molecular mass of X

8. (a) Define the term freezing point constant of a substance
(b) A solution contains 1.54g of naphthalene ($C_{10}H_8$) in 18g of camphor freezes at 148.3°C. calculate the freezing point constant of camphor (the freezing point of camphor is 175°C)

9. (a) What is meant by the term boiling constant of a liquid
(b) Describe an experiment that can be used to determine the relative molecular mass of a compound by the method of elevation of boiling point of a liquid. Draw a labelled diagram of apparatus.
(c) Explain why the method you have described is not suitable for determining the relative molecular mass of ethanoic acid in aqueous solution.
(d) A solution of 2.8g of cadmium iodide (CdI_2) in 20g of water boiled at 100.2°C at normal pressure. Calculate the relative molecular mass of cadmium iodide and comment in your result. ($Cd = 112; I = 127$)

10. (a) Explain what is meant by
(i) Osmosis
(ii) Osmotic pressure
(b) State the significance of osmosis
(c) Describe a method which can be used to measure the osmotic pressure of a solution

(d) State the conditions under which solutions do not obey the laws of osmotic pressure

(e) The osmotic pressure of a solution containing 1.24% of a polymer is 3.1×10^{-3} atm at 25°C. Determine the relative molecular mass of the polymer. (take $R = 0.0821 atmol^{-1}{}^{\circ}Cl^{-1}$)

11. The osmotic pressure of a solution containing 1.4g of a polymer X in 100cm^3 of a solution is 1200Nm^{-2} at 25°C.

(a) Calculate the relative molecular mass of X

(b) Determine the number of monomer units in X (the molecular of the monomer is 28)

(c) Determine the freezing point depression for a solution containing 0.025g of sodium chloride in 200g of water (given that the K_f of water is 1.86 °Cmol^{-1}kg^{-1} Na=23, Cl=35.5)

(d) 1.445g of a compound Y was dissolved in 80g of ethanol. The boiling point of the solution was 78.97°C while that of pure ethanol is 78.8°C. calculate the molecular mass of Y in ethanol (K$_b$ of ethanol is 1.15 °Cmol^{-1}kg^{-1})

12. (a) (i) What is a colligative property?

(ii) State four colligative properties of solution

(b) (i) Describe how the molecular mass of a substance can be determined using the method of freezing point depression

(ii) State two limitations of this method

(c) Calculate the boiling point of an aqueous solution of urea ($CO(NH_2)_2$) of concentration 12.0gdm^{-3} at a pressure of 101.325kPa (the boiling point elevation constant of water is 0.52 °Cmol^{-1}kg^{-1})

(d) (i) Explain the term mole fraction

(ii) Calculate the mole fraction of sodium chloride in an aqueous solution of 10g of sodium chloride per 100g of water

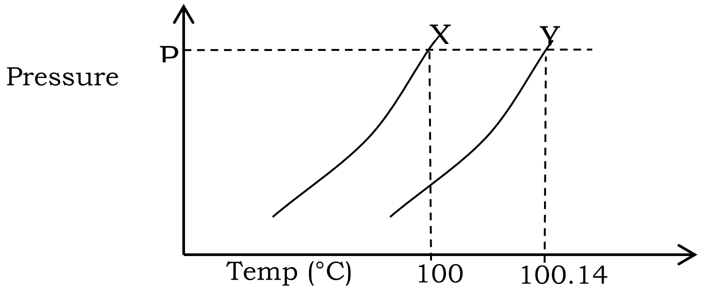
13. (a) An aqueous solution containing 7.2g of a non-cyclic compound Q in 250g of water freezes at -0.744°C. determine the molecular mass of Q. (the K_f of water is 1.86 °Cmol^{-1}kg^{-1})

(b) The boiling point of a solution containing 2.8g of a compound Z in 20g of water is 100.2°C at standard pressure.

(i) Explain how the solute affects the boiling point of water

(ii) Calculate the relative molecular mass of Z

14. 5.5g of a non-volatile substance B was dissolved in 125g of a solute. The vapour pressure curve of the solution and the pure solvent at constant pressure P are shown



(a) Identify the curve for the solution and the solvent

(b) Calculate the molecular mass of B (boiling point elevation constant for the solvent, K_b, is 0.52 °Cmol^{-1}kg^{-1})

(c) State two limitations of your calculations

15. (a) A solution contains 30g of ethane-1,2-diol and 40g of water.

    (i) Calculate the boiling point of the solution (K_b for water is 0.52°Cmol^{-1}kg^{-1})

    (ii) State ay assumption made in the calculations

    (b) (i) A solution containing 4.50g of a solute B dissolved in 125g of water freezes at -0.372°C. Calculate the formula mass of B (the K_f of water is 1.86°Cmol^{-1}kg^{-1})

    (ii) How would you expect the molecular mass of B to change if it ionized in water?

    (c) A solution containing X g of cane sugar (relative formula mass 342) in 105g of water at 101.3kPa boiled at 100.06°C. determine X

16. (a) State Raoult's law.

    (b) The lowering of vapour pressure of a solution of 108.2g of a substance X in 1kg of water at 20°C is 24.790kPa. The vapour pressure of water at 20°C is 2.338kPa. Calculate the relative molecular mass of X

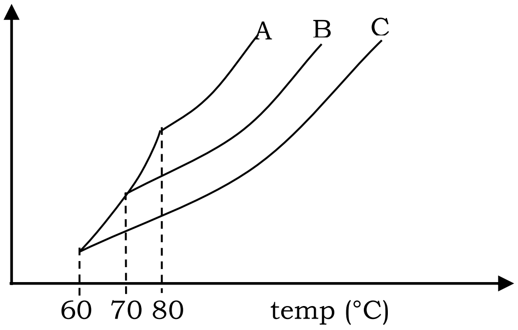
    (c) The boiling point of ethanol is 78°C and its molar elevation constant is 1.15Kmol^{-1}. A solution of 0.56g of camphor in 16g of ethanol had a boiling point of 78.278°C. Calculate the relative molecular mass of camphor

17. (a) A solution of 0.142g of naphthalene in 20.25g of benzene causes a lowering of freezing of 0.284K. The molar depression constant of benzene is 5.12Kmol^{-1}kg^{-1}. Determine the molecular mass of naphthalene.

    (b) The melting point of camphor is 177.5°C while that of a mixture containing 5g of substance Y of molecular mass 128 and 10g of camphor is 147°C. What is the molecular mass of camphor?

    (c) The melting point of a mixture of acetanilide and 10g of camphor is 148.5°C. What is the relative molecular mass of acetanilide?

18. (a) 0.5g of Q was dissolved in 20g of naphthalene to form a solution X. another 0.25g of solute Q was dissolved in 20g of naphthalene to form a solution Y. the graph below shows how the vapour pressure of a solution X, Y and that of pure naphthalene varies with temperature.



(i) State what curves A, B, and C represent

(ii) State the freezing point of naphthalene

(iii) Calculate the relative molecular mass of Q. (K_f of naphthalene is 70°Cmol^{-1}kg^{-1})

19. (a) Define osmotic pressure

(b) The osmotic pressure of solution at 25°C for various concentrations of naphthalene and methylbenzene is given below.

Concentration (gdm^{-3})	0.5	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Osmotic pressure (kPa)	10.0	20.0	28.0	37.0	46.0	56.0	74.0	92.0

Plot a graph of osmotic pressure against concentration and use it calculate the relative formula mass of naphthalene

(c) Explain the following observations

(i) 0.1 mole of sodium chloride depresses the melting point of a given mass of water twice as much as 0.1 mole of glucose

(ii) 0.1 mole of aluminium chloride depressed the freezing point of a given mass of benzene half as much as does 0.1 mole of naphthalene.

20. (a) (i) What is meant by the term colligative property

(ii) State the assumptions made

(b) (i) Describe how the molecular mass of a non-volatile solute can be determined by elevation of boiling point method

(ii) The boiling point of a solvent A is 69.0°C. When 2g of solid X was dissolved in 40g of A the boiling was 71.4°C. calculate the molecular mass of X (boiling point elevation constant for the solvent is 3.2 per 1000g of the solvent)

(c) EXPERIMENT I; a mixture of 2g of camphor and 0.22 g of an organic compound Q of molecular mass 206 was found to have a melting point of 166.2°C

EXPERIMENT II; The following results of melting point were obtained when 1 g of camphor and solid P were mixed

Mass od P(g)	0.00	0.03	0.05	0.07	0.09	0.11
M.P(°C)	189.0	181.8	175.0	168.1	160.1	154.0

(i) Calculate the cryoscopic constant for camphor

(ii) Plot a graph of depression of freezing point against mass of P and use it to determine the RMM of P

21. (a) In order to determine the molecular mass of a compound T, 8.0g of T was dissolved in 250g of water. The solution froze at -0.331°C. if the freezing point of water is 0°C. Determine the molecular mass of the compound. (K_f of water s 1.86°Cmol^{-1}kg^{-1})

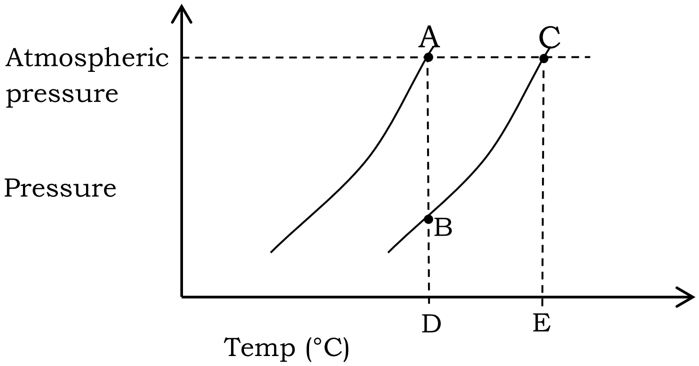
(b) When 15g of glucose ($C_6H_{12}O_6$) was dissolved in 50g of a solvent of molecular mass 200, the freezing point was depressed by 8.0°C. Determine the freezing point constant for the solvent

(c) When 5g of sulphur were dissolved in 63cm^3 of carbon disulphide, the vapour pressure recorded was 52340Pa. (the vapour pressure f carbon disulphide at this temperature is 53330Pa and its density is 1.27gcm^3)

(i) Determine the molecular mass of sulphur

(ii) What is molecular formula of sulphur in carbon disulphide

22\. (a) A substance was dissolved in a solvent Z. the graph below shows how the vapour pressure of the solution and that of pure Z vary with temperature



State what points A to E and lines AB and AC represent

(b) A solution was prepared by dissolving 7.5g of propane-1,2,3-triol ($C_3H_8O_3$) in 200g of water at 25°C. Calculate the boiling point of the solution at atmospheric pressure. (K_f of water is 0.52°Cmol^{-1}kg^{-1})

23\. A solution containing 20g of a polymer X in 1litre of a solvent exerts an osmotic pressure of 1.4mmHg at 25°C.

(a) Explain the term osmotic pressure

(b) Determine the molecular mass of X

(c) The formula of the monomer of X is $CH_2 = CHCN$. Determine the number of monomers units in X

(d) Explain why freezing point depression method is not suitable for determining the molecular mass of a polymer

24\. (a) The osmotic pressure of a solution containing 1.40g of Y per 100cm^3 of solution is 1200Nm^{-2} at 25°C.

(i) Calculate the relative molecular mass of Y

(ii) Determine the number of monomer units in Y (RFM of the monomer is 28)

(b) (i) The vapour pressure of a solvent at 25°C is 3.15×10^3Nm^{-2}. Calculate the vapour pressure of a solution containing 6.0g of urea ($CO(NH_2)_2$) in 100g of water at the same temperature.

(ii) The vapour pressure of a solution containing 29.0g of a substance X in 100g of water at 50°C is 1.12×10^4Pa. if at the same temperature, the vapour pressure of water alone is 1.22×10^4Pa, calculate the molecular mass of X

25\. (a) A solution of 3.1g of sucrose, $C_{12}H_{22}O_{11}$, in 100g of water froze at a temperature of -0.2.4°C. If a solution containing 27.3gdm^{-3} of W freezes at -0.282°C. Calculate the molecular mass of W.

(b) Calculate the freezing point of a solution of 28.0g of ethanamide CH_3CONH_2 in 500g water. (the cryoscopic constant for 100g of water is 18.6°C)

26. (a) The vapour pressure of water at 94200Nm^{-2}. The vapour pressure of a 1% solution of sucrose is 94150Nm^{-2}. Calculate the molecular mass f sucrose
(b) The vapour pressure of water at 20°C is 3.14Nm^{-2}. Determine the vapour pressure of a solution of 2.5g of a solute of molecular mass 180 in 50g of water at this temperature.
(c) The vapour pressure of water at 50°C is 12333Pa. at this temperature, a solution of 9.14g of urea in 150g of water has a vapour pressure of 12108Pa. determine the RFM of urea.

27. (a) Find the lowering in vapour pressure if 2.8g of naphthalene, $C_{10}H_8$ dissolves in 250g of butyric acid, $C_4H_8O_2$, at 20°C. The vapour pressure of butyric acid at this temperature is 0.112kPa.
(b) When 3.4g of naphthalene was dissolved in 200g of butyric acid at 50°C, the vapour pressure lowering caused was 8.649Pa. Determine the molecular mass of naphthalene. The vapour pressure of butyric acid at 50°C.

28. (a) When 7.6g of camphor, $C_{10}H_{16}O$, was dissolved in 400g of propanone at 0°C, and its vapour pressure was lowered by 68.08Nm^{-2}. Determine the vapour pressure of pure propanone at this temperature.
(b) Determine the lowering of vapour pressure at 0°C when 20.8g of camphor dissolve in 500g of propanone whose vapour pressure at ths temperature is 9.39kNm^{-2}.
(c) Calculate the vapour pressure of a solution made by dissolving 15.2g of camphor in 480g of propanone at 0°C. the vapour pressure of pure propanone at this temperature is 9390Pa.

29. (a) 10.5g of a compound R was dissolved in 500g of propanone at 25°C and the vapour pressure of the resulting solution was 30354.8Nm^{-2}. Determine the molecular mass of R. (the vapour pressure of pure propanone at this temperature is 30.6kPa).
(b) At 25°C, the vapour pressure of propanone is 30600Nm^{-2}. If 3.8g of a compound Y in 250g of propanone decrease the vapour pressure of propanone by 88.74Pa, calculate the molecular mass of Y.

30. (a) When 4.5g of urea, $CO(NH_2)_2$, were dissolved in 250g of water, the boiling point of the resultant solution was 100.154°C. Determine the boiling point elevation constant for water.
(b) Determine the boiling point of a solution made by dissolving 6.0g of urea in 400g of water. (the boiling point elevation for water is 0.512°Cmol^{-1}kg^{-1})
(c) What is the elevation in boiling point when 10.2g of urea are dissolved in 500g of water? (boiling point elevation for water is 5.12°Cmol^{-1}per 100g)
(d) Determine the relative molecular mass of a compound X if a solution containing 5.8g of X in 480g of water boils at 100.103°C. (the boiling point elevation for water is 0.512°Cmol^{-1}kg^{-1})

(e) Calculate the mass of urea that should be dissolved in 200g of water so that the boiling point of the solution is 100.128°C. (the boiling point elevation for water is 0.512°Cmol^{-1}kg^{-1})

31. (a) When 4.2g of urea was dissolved in 200g of ethanol, the boiling point of the resultant solution was 79.017°C. if the boiling point of pure ethanol is 78.6°C. Determine the boiling point elevation constant for ethanol.

(b) Determine the boiling point of a solution made by dissolving 3.8g of urea in 250g of water. (the boiling point of pure ethanol and its boiling point elevation constant are 78.6° and 1.19°Cmol^{-1}kg^{-1})

(c) What is the elevation in boiling point when 5.4g of urea is dissolved 400g of ethanol? (the boiling point elevation constant for ethanol is 1.19°Cmol^{-1}kg^{-1})

(d) Determine the relative molecular mass of compound K if a solution containing 6.8g of K in 450g of ethanol boils at 79°C. (the boiling point elevation for ethanol 1.19°Cmol^{-1}kg^{-1})

(e) What mass of urea should be dissolved in 480g of ethanol to increase its boiling point to 78.89°C? (the boiling point elevation constant for ethanol is 1.19°Cmol^{-1}kg^{-1})

32. The table below shows how the elevation of the boiling point of benzene, ΔT, varies with concentration of a substance M at 25°

Concentration (gl^{-1})	6.4	9.0	12.8	16.0	20.0	24.0
ΔT, (°C)	0.133	0.186	0.265	0.331	0.414	0.497

(a) Plot a graph of elevation in boiling point, ΔT, against concentration.

(b) Use your graph to find the relative molecular mass of M. (the boiling point elevation constant for benzene is 2.65°Cmol^{-1}kg^{-1})

33. The table below shows the boiling point of different solution of naphthalene in ethanol at different concentrations at 25°C.

Concentration (gl^{-1})	5.4	8.6	10.8	12.8	20.6	30.2
Boiling point (°C)	78.85	78.88	78.90	78.92	78.99	79.08

(a) Plot a graph of boiling point elevation against concentration

(b) Use your graph to determine the boiling point elevation for ethanol (the boiling point of pure ethanol is 78.8°C)

34. The table below shows how the boiling point of butanone varies with the amount of substance Q dissolved in it at 25°C.

Concentration (gl^{-1})	0.0	4.0	8.0	10.0	14.0	16.0
Boiling point (°C)	80	80.06	80.15	80.18	80.21	80.24

(a) Plot a graph of boiling elevation against concentration

(b) Determine the molecular mass of Q. (boiling point elevation for butanone is 2.28°Cmol^{-1}kg^{-1})

35. The table below shows how the boiling point elevation of cyclohexane changes with increase in the amount of camphor dissolved in it.

Concentration (gl^{-1})	7.0	10.0	15.0	18.0	20.0	28.0
ΔT, (°C)	0.13	0.18	0.27	0.33	0.36	0.51

(a) Plot a graph of boiling point elevation against concentration

(b) Using your graph, determine the boiling point elevation constant for cyclohexane (molecular mass of camphor is 152)

36. When a substance W was dissolved in acetone, the boiling points of the different solutions of different concentrations were noted as shown.

Concentration (gl^{-1})	6.4	9.1	11.9	14.6	18.2	22.8
Boiling point (°C)	56.17	56.20	56.23	56.26	56.30	56.35

(a) Plot a graph of boiling point elevation against concentration

(b) Using your graph, determine the molecular mass of W. (the boiling point of acetone is 56.1 and its boiling point elevation constant is 1.67°$Cmol^{-1}$ per 1000g)

37. The table below shows the freezing points of a solution of glucose ($C_6H_{12}O_6$) in water at different concentrations.

Concentration (gl^{-1})	5.9	9.7	15.0	19.4	24.2	30.0
Freezing point (°C)	-0.061	-0.100	-0.155	-0.200	-0.250	-0.310

(a) Plot a graph of freezing point depression against concentration.

(b) Using your graph, determine the freezing point depression constant (K_f) for water. (C=12, H=1, O=16)

38. The table below shows the freezing point of water when different amounts of substance P are added.

Concentration (gl^{-1})	10.30	15.80	20.31	25.80	31.40	34.94
Freezing point (°C)	-0.056	-0.086	-0.110	-0.140	-0.170	-0.190

(a) Plot a graph of freezing point depression against concentration

(b) Use your K_f value above (in number 37) and your graph above to determine the molecular mass of P.

39. The table below shows how the osmotic pressure of a solution varies with the amount of polymer R

Concentration (gl^{-1})	1.40	4.20	8.40	12.60	15.40	17.50
Osmotic pressure (Nm^{-2})	49.6	148.7	297.3	446.0	545.1	619.4

(a) Plot a graph of osmotic pressure against concentration

(b) Using your graph, determine the molecular mass of the polymer

(c) The molecular mass of the monomer of R is 28. Determine the number of monomer units

40. The table below shows how the osmotic pressure of a solution varies with the amount of polymer Y

Concentration (gl^{-1})	1.25	4.40	6.25	10.65	12.50	15.65
Osmotic pressure (Nm^{-2})	48.7	171.3	243.7	414.2	487.4	609.2

(a) Plot a graph of osmotic pressure against concentration

(b) Using your graph, determine the molecular mass of the polymer

(c) Given that the number of monomer units in Y are 2235, determine the molecular mass of the monomer of Y

41. Vinyl chloride polymerises according to the equation

$$nCH_2 = CHCl \longrightarrow -(CH_2CHCl)_n-$$

Use the table to determine the value of n

Concentration (gl^{-1})	1.25	4.40	6.25	10.65	12.50	15.65
Osmotic pressure (Nm^{-2})	48.7	171.3	243.7	414.2	487.4	609.2

(a) Plot a graph of osmotic pressure against concentration

(b) Using your graph, determine the value of n

43. (a). 2.0g of phosphorus raises the boiling point of 37.4g of carbon disulphide by 1.003°C whereas 4.65g of sulphur raises the boiling point of 100g of carbon disulphide by 0.42°C. Calculate the

(i). Boiling point constant of carbon disulphide

(ii). Molar mass of phosphorus in carbon disulphide

(b) Determine the molecular formula of phosphorus.

44. (a). State one colligative property other than depression of freezing point or elevation of boiling point of a solvent.

(b) Ethane-1,2-diol is used as an antifreeze for water in car radiators. Calculate the mass of ethane-1,2-diol that should be added to 1 kg of water to prevent it from freezing at -10°C. (freezing point depression constant for water is1.86°Ckgmol^{-1})

45. (a). Describe an experiment that can be carried out to determine the relative molecular mass of benzoic acid in benzene by depression of freezing point method.

(b) State four limitations of the depression of freezing point as a method for determination of molecular mass of a substance

(c) A solution containing 0.368g of methanoic acid in 50g of benzene froze at 5.093°C. Calculate the molecular mass of methanoic acid. (the freezing point f benzene is 5.533°C; the freezing point constant of benzene is 5.5°Cmol^{-1}kg^{-1})

(d) Comment on your answer in (c). (the molecular mass of methanoic acid is 46)

46. (a).

42.

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 9: CHEMICAL KINETICS

1. Substance A undergoes the following reaction in aqueous solution.

$$A(aq) + H^+(aq) + H_2O(l) \longrightarrow B(aq)$$

The reaction is acid catalysed and is first order with respect to each of the reacting species.

(a). (i). Write an expression for the rate of reaction
 (ii). What would be the effect of doubling the catalyst concentration on the rate of the reaction?
(b). Under certain conditions, the reaction is overall first order
 (i). State the conditions
 (ii). Write the corresponding rate equation
 (iii). If the rate constant. K is $2.0 \times 10^{-5}s^{-1}$, calculate the time reqauored for the concentration of A decreases to a third of its original value.
(c). (i). Explain what is meant by the term activation complex
 (ii). Draw a potential energy diagram for a chemical reaction and label it fully
 (iii). What is the effect of a catalyst on the rate of the chemical reaction?

2. (a). For a reversible reaction;

$$\mathrm{A(g)} + B(g) \leftrightharpoons C(g) + D(g)\ ; \Delta H = +45kJmol^{-1}$$

The activation energy for the forward reaction is 195kJmol^{-1}. The following data was experimentally obtained on the rates of reaction under different conditions at 298K

Experiment number	[A]/ moll^{-1}	[B]/ moll^{-1}	Rate /moll^{-1}s^{-1}
1	2.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}
2	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{2}
3	4.0×10^{-2}	1.0×10^{-2}	4.0×10^{2}

Write the expression for the rate equation using the data given in the above table.

(b). Calculate the rate constant ad state its units
(c). Calculate the activation energy for the backward reaction

3. The following kinetic data was obtained for the reaction

$$\mathrm{A(g)} + 2B(g) + C(g) \leftrightharpoons D(g) + 2E$$

Experiment number	[A]/ moll^{-1}	[B]/ moll^{-1}	[C]/ moll^{-1}	Rate /moll^{-1}s^{-1}
1	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{-2}	2.0×10^{2}
2	2.0×10^{-2}	1.0×10^{-2}	2.0×10^{-2}	2.0×10^{2}
3	4.0×10^{-2}	4.0×10^{-2}	2.0×10^{-2}	8.0×10^{2}
4	2.0×10^{-2}	4.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}

(a). Write the rate equation

(b). Determine the rate of formation of E in experiment 2 given that, that in the table was of D.

(c). Hence find the rate of consumption of B in experiment 3

4. The kinetic data for the reaction is shown below.

$$A(g) + 2B(g) + C(g) \longrightarrow products$$

Experiment number	[A]/ moll^{-1}	[B]/ moll^{-1}	[C]/ moll^{-1}	Rate /moll^{-1}s^{-1}
1	0.2	0.3	0.1	2.0×10^{2}
2	0.4	0.3	0.1	4.0×10^{2}
3	0.2	0.6	0.1	8.0×10^{2}
4	0.2	0.3	0.2	2.0×10^{2}

(a). Determine the rate equation

(b). What is the overall order of reaction?

5. Substance B reacts with potassium iodide to form iodine. The iodine is titrated with standard sodium thiosulphate solution. The volume of sodium thiosulphate is the measure of the concentration of B remaining at a given time, t.

$Volume\ (cm^3)$	24.70	17.80	12.90	9.25	5.50	3.60
$Time\ (minutes)$	0	60	120	180	240	300

(a). Plot a graph of volume against time

(b). From the graph in (a), deduce the time taken for the concentration of B to
  (i). Reduce to half of the original value
  (ii). Reduce to a quarter of the original value.

(c). What is the order of reaction with respect of B

(d). Write the rate equation for the reaction.

(e). Determine the rate constant.

6. (a). Draw a fully labelled potential energy versus reaction coordinate diagram for an endothermic reaction

(b). Explain the effect of temperature on the rate of a chemical reaction.

(c). Distinguish between order of reaction and molecularity

(d). Discuss the role of a catalyst in speeding up the rate of a reaction.

7. The data below was obtained for the reaction

$$A(g) + B(g) \longrightarrow products$$

Experiment number	[A]/ moldm^{-3}	[B]/ moldm^{-3}	Rate /moldm^{-3}s^{-1}
1	0.1	0.1	1.6×10^{-3}
2	0.1	0.2	3.2×10^{-3}
3	0.1	0.3	4.8×10^{-3}
4	0.2	0.1	6.4×10^{-3}
5	0.3	0.1	y

(a). Determine the
   (i). Order of reaction with respect to B
   (ii). Value of y in the table
(b). Write the rate equation for the reaction
(c). Calculate the value of the rate constant and state its units

8. The following data was obtained for the reaction

$$A + B \longrightarrow C$$

Experiment	Initial [A]/ moldm^{-3}	Initial [B]/ moldm^{-3}	Initial rate /moldm^{-3}min^{-1}
1	0.1	0.1	1.0×10^{-4}
2	0.1	0.3	9.0×10^{-4}
3	0.1	0.3	2.7×10^{-3}

(a). Determine the order of reaction with respect to
   (i). A
   (ii). B
(b). Write the rate equation for the reaction.
(c). If the initial concentration of both A and B are 0.4M, calculate the initial rate of formation of C.

9. Compound B is converted to C and D according to the equation.

$$B \longrightarrow C + D$$

The data below was obtained for the reaction

$time\ (minutes)$	0.0	7.2	18.0	36.0	72.0	108.0
$[B]/\ moldm^{-3}$	100	91	79	63	40	25

(a). Plot a graph of concentration of B against time
(b). Using your graph, determine the
   (i). Half-life of the reaction
   (ii). Order of reaction
   (iii). Rate constant of the reaction and state its units.

10. For a reversible reaction indicated below, the activation energy, E_a, and the enthalpy change, ΔH, for the forward reaction are +180 and +40kJmol^{-1} respectively.

$$\mathrm{A(g)} + B(g) \leftrightharpoons C(g) + D(g)$$

(a). The following data was obtained experimentally on the rates of reaction under different conditions at 298K

Experiment	[A]/ moldm^{-3}	[B]/ moldm^{-3}	Rate /moldm^{-3}s^{-1}
1	2.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}
2	2.0×10^{-2}	2.0×10^{-2}	4.0×10^{2}
3	6.0×10^{-2}	1.0×10^{-2}	3.0×10^{2}

(i). Write an expression for the rate equation using the data in the table above

(ii). Calculate the rate constant and give its units

(b). (i). Sketch a fully labelled diagram showing the energy versus reaction coordinate for this reaction.

(ii). Determine the activation energy for the backward reaction

(c). How do you expect the

(i). Equilibrium constant for the reaction to change if temperature was raised

(ii). Rate of the reaction to change if temperature was raised

(d). Sketch on the same diagram the variation of the concentration of D with time during the reaction after A and B are mixed for two temperatures T_1 and T_2 where $T_1 > T_2$

11. (a). State what is meant by the term order of reaction.

(b). Methyl ethanoate is hydrolysed in water in the presence of an acid according to the equation

$$CH_3COOCH_3(aq) + H_2O(l) \xrightarrow{H^+} CH_3COOH(aq) + CH_3OH(aq)$$

(i). State the molecularity of the reaction

(ii). Determine the order of the reaction

(iii). Sate the conditions under which the reaction can be overall first order

(c). The table below shows some kinetic data for the reaction

$$3A + B \longrightarrow 2P$$

Experiment	[A]/ moldm^{-3}	[B]/ moldm^{-3}	Rate /moldm^{-3}s^{-1}
1	0.2	0.2	1.2×10^{-8}
2	0.2	0.6	1.2×10^{-8}
3	0.4	0.6	4.8×10^{-8}

(i). Write the overall rate equation

(ii). Calculate the rate constant for the reaction and state its units

12. (a). Differentiate between order of reaction and molecularity of a reaction.

(b). The table below shows some data for the reaction

$$A + 2B \longrightarrow C;\ \Delta H = +Q\ kJmol^{-1}$$

Experiment	[A]/ moldm^{-3}	[B]/ moldm^{-3}	Rate /moldm^{-3}s^{-1}
1	1.00×10^{-2}	2.80×10^{-3}	2.1
2	1.00×10^{-2}	5.60×10^{-3}	4.3
3	5.00×10^{-3}	2.80×10^{-3}	1.1

(i). Determine the order of reaction with respect to A and B

(ii). Write the rate equation for the reaction (iii). Calculate the rate constant for the reaction and give its units

(iv). Calculate the rate of reaction when the concentration of A and B are 8.5×10^{-3} and 3.83×10^{-3} moldm^{-3} respectively.

(c). State what would happen to the order of the reaction in above if B was in large excess. Explain your answer.

(d). Draw a fully labelled potential energy diagram for the reaction

13. (a). Derive an expression for the half-life of a first order reaction. $2.303 \log\left(\frac{a_o}{a_o - x}\right) = kt$. Where a_o is the initial concentration and $(a_o - x)$ is the concentration after time, t.

(b). The half-life of a first order reaction is 100s.

(i). Calculate the rate constant

(ii). Determine the percentage of the reactants that reacted in 250 seconds.

14. (a). Briefly describe how you would determine the rate of the following reactions

(i). Decomposition of hydrogen peroxide

(ii). Reaction of sodium thiosulphate and dilute hydrochloric acid

(iii). Iodination of propanone catalysed by sulphuric acid

(b). For each of the following reactions describe experiments to show that

(i). The decomposition of hydrogen peroxide is a first order reaction

(ii). The reaction of hydrochloric acid with sodium thiosulphate is a first order reaction with respect to hydrochloric acid

(iii). The acid catalysed reaction of iodine and propanone is zero order with respect to iodine.

15. (a). Explain what is meant by

(i). Rate equation

(ii). Order of reaction

(iii). Rate constant

(b). The following results were obtained for two compounds A and B reacting to form product C.

Initial [A]/ moldm^{-3}	Initial [B]/ moldm^{-3}	Initial rate /moldm^{-3}s^{-1}
2.0×10^{-1}	2.4×10^{-1}	2.0×10^{-4}
4.0×10^{-1}	2.4×10^{-1}	8.0×10^{-4}
4.0×10^{-1}	4.8×10^{-1}	16.0×10^{-4}

(i). Deduce the rate equation

(ii). Calculate the rate constant and indicate it units

16. (a). A gas decomposes according to the following equation

$$X_2(g) \longrightarrow 2X(g); \quad \Delta H = -ve$$

Sketch a graph to show how the concentration of X_2 and X vary with time

(b). Using the same scale, sketch another graph to show how the concentration of X_2varies with time, showing what happens under similar conditions in which the

(i). Temperature is raised

(ii). Pressure is lowered.

Comment on the results in each case.

(c). The following results were obtained for the decomposition of dinitrogen tetraoxide.

$Time\ (s)$	0	250	300	750	1000	1500	2000	2500
$Concentration\ (moldm^{-3})$	2.33	1.95	1.68	1,42	1.25	0.95	0.70	0.50

(i). Plot a graph of concentration against time

(ii). Use your graph to determine the order of reaction

(iii). Calculate the rate constant and state its units

17. (a). Distinguish between order of reaction and molecularity

(b). (i). Define a catalyst

(ii). Explain the effect of a catalyst on the rate of reaction

(c). For a reaction with between P. Q and R, the rate equation is given as $Rate = [P]^2[Q][R]$. State how the rate of reaction would be altered if;

(i). [P] and [Q] are kept constant but [R] doubled

(ii). [P] and [R] are kept constant but [Q] halved

(iii). [Q] and [R] are kept constant but [P] doubled.

(iv). Concentration of all species are doubled.

(d). Ammonia decomposes on a hot tungsten surface into nitrogen and hydrogen. The following data was obtained

$Initial\ pressure\ of\ NH_3\ (kPa)$	38.0	19.0	9.5
$Half-life\ (s)$	490	250	130

(i). Write the equation for the decomposition of ammonia

(ii). Using the above table, explain the term **half-life**.

(iii). Plot a suitable graph and use the graph to determine the order and rate constant of the reaction.

18. (a). Distinguish between

(i). Reaction rate and rate constant.

(ii). Homogeneous and heterogeneous catalyst

(b). The table below was obtained during the hydrolysis of sucrose. The initial concentration was 1.00M.

$Time\ (minutes)$	0	60	90	130	180
$Sucrose\ reacted\ (moldm^{-3})$	0.00	0.195	0.277	0.373	0.478

The hydrolysis of sucrose is as shown in the equation below

$$\underset{(sucrose)}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \longrightarrow \underset{(Glucose)}{C_6H_{12}O_6(aq)} + \underset{(Fructose)}{C_6H_{12}O_6(aq)}$$

(i). Plot a suitable graph to show that the order of reaction with respect to sucrose is one

(ii). Determine the half-life and rate constant for the reaction.

(iii). State the effect of halving the initial concentration of sucrose on the value of the half-life and rate constant

(iv). Explain why the reaction is first order yet water us a reactant in the stoichiometric equation

(c). The following data was obtained during the hydrolysis of 2-chloro-2-methylpropane by sodium hydroxide

$Experiment$	1	2	3	4	5
$[2-chloro-2-methylpropane]\ (Moldm^{-3})$	0.1	0.1	0.075	0.050	0.025
$[\bar{O}H]\ (Moldm^{-3})$	0.5	0.25	0.25	0.25	0.25
$Initial\ rate\ (Moldm^{-3}s^{-1})$	0.0020	0.0020	0.0015	0.0010	0.0005

(i). Determine the order of the reaction with respect 2-chloro-2-methylpropane and sodium hydroxide

(ii). Calculate the value of the rate constant and state its units

(iii). Suggest a mechanism for the reaction

(d). The following results were obtained for the decomposition of dinitrogen pentaoxide

$Temperaure$ (℃)	25	35	45	55	65
$Rate\ constant; K\ (s^{-1})$	1.74×10^{-5}	6.6×10^{-5}	2.51×10^{-4}	7.59×10^{-4}	2.0×10^{-3}

(i). Plot a graph of log K against $\frac{1}{Temp}$

(ii). Use you graph to determine the activation energy of the reaction. $\left(take\ slope\ = \frac{-E_a}{2.303R}\right)$ where R= 8.314 and E_a is activation energy.

19. (a). The data below was obtained from the following reaction

$$2NO(g)\ +\ 2H_2(g) \longrightarrow 2H_2O(g)\ +\ N_2$$

$Experiment$	1	2	3	4
$[NO]\ (Moldm^{-3})$	0.5	0.5	0.1	0.1
$[H_2]\ (Moldm^{-3})$	0.1	0.2	0.5	0.5
$Rate\ of\ formation$ of $N_2\ (Moldm^{-3}s^{-1})$	0.045	0.09	0.09	0,36

(i). Determine the rate equation

(ii). Calculate the rate constant and state its units

(iii). State the effect on the reaction if the concentration of nitrogen monoxide is halved while that of hydrogen remains constant

(iv). What is the effect on the rate of the reaction by doubling the concentration of nitrogen monoxide and increasing the concentration of hydrogen by three times?

20. (a). Propanone and iodine react in the presence of an acid according to the equation

$$CH_3COCH_3(aq)\ +\ I_2(aq) \xrightarrow{H^+} CH_3COCH_2I(aq)\ +\ HI(aq)$$

The reaction is first order with respect to propanone and is independent of the concentration of iodine

(i). Write the expression for the rate law

(ii). Describe briefly how the order with respect to iodine can be determined

(b). The following data was obtained for the reaction

$$A + B + C \longrightarrow D$$

Experiment	Initial [A] (moldm^{-3})	Initial [B] (moldm^{-3})	Initial [C] (moldm^{-3})	Initial rate (moldm^{-3}min^{-1})
1	0.1	0.1	0.1	1.0×10^{-4}
2	0.1	0.3	0.1	9.0×10^{-4}
3	0.3	0.3	0.1	2.7×10^{-3}
4	0,1	0.1	0.3	1.0×10^{-4}

(i). Determine the order of reaction with respect to A, B and C. explain how you arrive at your answer.

(ii). Write the rate equation for the reaction

(iii). If the initial concentration of A, B, and C are each 0.4moldm^{-3}. Calculate the initial rate of reaction.

21. (a). Hydrogen peroxide decomposes in the presence of iron(III) chloride according to the equation.

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

The decomposition is first order reaction with respect to hydrogen

(i). Write the rate law

(ii). Describe briefly how the order with respect to hydrogen peroxide can be determined

(b). The following data show the hydrolysis of ethyl ethanoate catalysed by sodium hydroxide

$$CH_3COOCH_2CH_3(l) + H_2O(l) \xrightarrow{\bar{O}H} CH_3COOH(aq) + CH_3CH_2OH(aq)$$

The initial concentration of the ethyl ethanoate being 0.05M

Time (seconds)	100	200	300	400	600
Percentage of ester hydrolysed	29.5	44.2	55.5	62.2	70.3

(i). Plot a suitable graph and from it determine the order of reaction

(ii). Hence determine the rate constant K

22. The following kinetic data was obtained for a reaction in which a certain compound W was converted to Y at 25°C.

Time (minutes)	0	9	18	27	40	54	72	105	118
[W] (moldm^{-3})	0.106	0.096	0.086	0.077	0.065	0.054	0.043	0.030	0.025

(a). Plot a graph of concentration against time

(b). From the graph, deduce the time taken for the concentration of W to reduce to

  (i). Half of the original value

  (ii). Quarter of the original value

  What is the order of reaction with respect to W.

(c). Write the rate equation for the reaction in which W is changed to Y.

(d). Determine the rate constant and state its units.

23. In the presence of an acid, sucrose is converted to a mixture of glucose and fructose according to the equation.

$$\underset{(sucrose)}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H^+} \underset{(Glucose)}{C_6H_{12}O_6(aq)} + \underset{(Fructose)}{C_6H_{12}O_6(aq)}$$

The following data was obtained at 25°C.

[sucrose] (moldm^{-3})	0.08	0.06	0.04	0.02
Rate (moldm^{-3}s^{-1})	0.004	0.003	0.002	0.001

Draw a suitable graph and use it to determine the

(i). Order of reaction

(ii). Rate constant

(iii). Rate of reaction when the concentration of sucrose is 01.12 moldm^{-3}.

24. The following data refers to the reaction at 6°C.

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + 5O_2(g)$$

Time (seconds)	0	20	45	73	105	140	185	243	325
Partial pressure of N_2O_5(Pa)	100	90	80	70	60	50	40	30	20

Plot a graph of partial pressure against time and use it to determine the

(a). Order of reaction with respect to N_2O_5

(b). Rate constant.

25. Compound A is converted to compounds B and C according to the equation.

$$A \longrightarrow B + C$$

Time (minutes)	0.0	7.2	18.0	36.0	71.0	108.0
[A] (moll^{-1})	100	91	79	63	40	25

(a). Plot a graph of concentration of A against time

(b). Use your graph to determine the time taken for the concentration of A to decrease from

  (i). 80 to 40 moll^{-1}

(ii). 60 to 30 $moll^{-1}$

(c). Determine the

(i). Half-life of the reaction

(ii). Order of the reaction

(iii). Rate constant and state its units.

26. Bromoethane reacts with sodium hydroxide according to the equation.

$$CH_3CH_2Br(l) + \bar{O}H(aq) \longrightarrow CH_3CH_2OH(aq) + Br^-(aq)$$

The overall reaction is bimolecular.

(a). Draw a fully labelled diagram of energy versus reaction path for the reaction

(b). Explain what is meant by the terms

(i). Bimolecular reaction

(ii). Activated complex

(c). Write the rate equation for the reaction.

(d). Outline the mechanism for the reaction.

27. (a). Write an equation to show how benzene diazonium chloride can be prepared in the laboratory.

(b). Benzene diazonium chloride decomposes according to the equation when heated.

$$C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$$

The reaction is first order with respect to benzene diazonium chloride

(i). Write an expression for the rate equation for the decomposition of benzene diazonium chloride

(ii). Sketch a graph to show the variation in concentration of benzene diazonium chloride with time

(iii). Use the graph to show how the order of reaction can be determined by half-life method

28. (a). For a reversible reaction indicated below; the enthalpy of reaction; ΔH is $+50kJmol^{-1}$ and the activation energy; E_a; is $+200kJmol^{-1}$ both for the forward reaction.

$$A(g) + B(g) \leftrightharpoons C(g) + D(g)$$

The following data were obtained experimentally on the rates of reaction under different conditions at 300K

[A] ($moll^{-1}$)	[B] ($moll^{-1}$)	Rate ($moll^{-1}s^{-1}$)
2.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}
2.0×10^{-2}	2.0×10^{-2}	2.0×10^{2}
4.0×10^{-2}	2.0×10^{-2}	4.0×10^{2}

(i). Write down an expression for the experimental rate equation using the data above.

(ii). Calculate the rate constant at 300K and give its units

(b). (i). Sketch a diagram showing the energy versus the reaction path for this reaction. Label the diagram carefully and indicate the ΔH and E_a.

(ii). What is the activation energy for the backward reaction?

(c). Explain how you would expect the

(i). Equilibrium constant for the reaction to change if the temperature was raised

(ii). Rate of reaction to change if the temperature was raised

(d). Sketch on the same diagram, the variation of the concentration, C, with time during the reaction at two temperatures T_1 and T_2 where $T_2 > T_1$

29. 2-bromo-2-methylpropane reacts with aqueous sodium hydroxide to form 2-methylpropan-2-ol.

(a). Write down an equation for the reaction

(b). Draw an energy diagram for the reaction

(c). Write a mechanism for the reaction

(d). State the

(i). Rate determining step of the reaction

(ii). Technique used to study the reaction

30. The table below shows how the initial rate of reaction between reactants X and Y varies with different starting concentrations of X and Y

$$X + Y \longrightarrow Z$$

[X] (moll^{-1})	[Y] (moll^{-1})	Initial rate (moll^{-1}s^{-1})
0.2	0.2	4.0×10^{-3}
0.2	0.4	4.0×10^{-3}
0.4	0.2	16.0×10^{-3}

(a). Determine the order of the reaction with respect to X and Y

(b). Write the rate equation for the reaction

(c). Calculate the

(i). Rate constant

(ii). Rate of reaction when the concentration of X and Y are 0.1 and 0.2 respectively.

31. The results of hydrolysis of 2-bromo-2-methylpropane by aqueous sodium hydroxide at 25°C is shown below.

$[(CH_3)_3C-Br]$ (moll^{-1})	$[\bar{O}H]$ (moll^{-1})	Initial rate of hydrolysis (moll^{-1}s^{-1})
0.100	0.500	0.0020
0.100	0.250	0.0020
0.050	0.250	0.0010
0.025	0.250	0.0005

(a). Deduce the order of reaction with respect to

(i). 2-bromo-2-methylpropane

(ii). Sodium hydroxide

(b). Write the rate equation for the reaction

(c). Calculate the rate constant, K, for the reaction and state its units

32. (a). State what is meant by the term order of reaction

(b). Methyl ethanoate is hydrolysed by water in the presence of an acid according to the following equation

$$CH_3CO_2CH_3(l) + H_2O(l) \xrightarrow{H^+} CH_3CO_2H(aq) + CH_3OH(aq)$$

(i). State the molecularity of the reaction

(ii). Determine the order of the reaction

(iii). Under which conditions can the overall order be the first order.

(c). The table below shows some kinetic data for the reaction

$$3A + B \longrightarrow 2P$$

[A] (moll^{-1})	[B] (moll^{-1})	Initial rate (moll^{-1}s^{-1})
0.2	0.2	1.2×10^{-8}
0.2	0.6	1.2×10^{-8}
0.4	0.6	4.8×10^{-8}

(i). Write the overall rate equation

(ii). Calculate the rate constant and give its units

32. The kinetics data for the reaction between P and sodium hydroxide is shown below

[P] (moldm^{-3})	0.105	0.088	0.074	0.051	0.037	0.026	0.016	0.010
Time (hour)	0.0	3.5	7.0	14.5	20.0	27.0	35.5	45.0

(a). Plot a graph of concentration of P against time

(b). Determine

(i). The half-life of P.

(ii). The order of the reaction.

(iii). The rate constant for the reaction.

33. Nitrogen(II) oxide combines with oxygen at 80°C and 200atm.

$$2NO(g) + O_2(g) \leftrightharpoons 2NO_2(g)$$

(a). The kinetic data for the reaction is shown below

Initial rate (Nm^{-2}s^{-1})	6.8	27.2	61.2	108
P_{NO}^2 (N^2m^{-4})	0.04	0.16	0.36	0.64

P_{NO} = the partial pressure of NO

(i). Plot a graph of initial rate against P_{NO}^2

(ii). Using your graph, determine the order of the reaction with respect to nitrogen(II) oxide

(iii). Give a reason for your answer in (a) (ii) above

(b). When the partial pressure of oxygen was doubled to a new constant value, the value of the gradient of the graph in a (i) above doubled.

(i). Determine the order of the reaction with respect to oxygen. Explain your answer.
(ii). Write the rate equation for the reaction in (b)
(iii). Calculate the rate constant when the initial $rate = 170\ Nm^{-2}s^{-1}$; $P_{NO} = 0.1\ Nm^{-2}$ and $P_{O_2} = 1.36\ Nm^{-2}$ and state its units.

(c). State the effect of the following on the rate of this reaction.
(i). Having P_{NO} and O_2 that of is kept constant.
(ii). Doubling the P_{O_2} and that of P_{NO}.

34. The rate equation for a certain reaction is; Rate = K[P][Q]^2[R]

(a). State what would happen to the rate of the reaction if
(i). [P] and [Q] are kept constant but [R] doubled
(ii). [P], [Q] and [R] all halved
(iii). [P], [Q] and [R] all doubled

(b). The following results were obtained in a study of a reaction between peroxodisulphate and iodide ions

$[S_2O_8^{2-}]$ (moll^{-1})	$[I^-]$ (moll^{-1})	Initial rate (moll^{-1}s^{-1})
0.024	0.024	9.6×10^{-6}
0.048	0.024	1.92×10^{-5}
0.048	0.012	9.6×10^{-6}

(i). Write the rate equation
(ii). Calculate the rate constant and state its units.

35. The kinetic data for a reaction between X and Y are given below

[X] (moll^{-1})	[Y] (moll^{-1})	Initial rate (moll^{-1}s^{-1})
0.30	0.15	1.5×10^{-2}
0.30	0.30	3.0×10^{-2}
0.60	0.30	6.0×10^{-2}
0.60	0.60	1.2×10^{-1}

(a). Determine the order of the reaction with respect to
(i). X
(ii). Y

(b). Determine the overall order of the reaction
(c). Calculate the rate constant for the reaction and indicate its units

36. (a). Differentiate between order of reaction and molecularity
(b). The table below shows kinetics data for the following reaction

$$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \longrightarrow 3Br_2(aq) + 3H_2O(l)$$

Volume of BrO_3^- (cm^3)	3.0	4.0	5.0	6.0	8.0	10.0
Time; t (s)	69.0	45.0	35.0	31.0	24.0	18.5

(i). Plot a graph of $\frac{1}{t}$ against volume of bromate(V); BrO_3^-

(ii). Determine the order of reaction with reaction with respect to bromate(V) and give a reason for your answer

(iii). Determine the rate constant for the reaction and state its units

(iv). Write equation for the rate of reaction in terms of concentration of bromate(V)

(c). The kinetic data for the reaction between substances X and Y are shown below

[X] (moll-1)	[Y] (moll-1)	Initial rate (moll-1s-1)
5.0×10^{-3}	5.0×10^{-3}	3.0×10^{-3}
1.0×10^{-2}	1.0×10^{-2}	2.4×10^{-2}
5.0×10^{-3}	1.0×10^{-2}	6.0×10^{-3}

Determine the

(i). Rate equation for the reaction

(ii). Value of rate constant and state its units

(iii). Initial rate of the reaction when the concentration of X and Y are 1.5×10^{-2} and 7.5×10^{-3} moldm-3 respectively.

(d). Explain how the following factors that affect the rate of a reaction

(i). Temperature

(ii). Concentration

(iii). Surface area

37. (a). State what is meant by the following terms order of a reaction and half-life of a reaction.

(b). A compound B decomposes according to the following equation

$$2B \longrightarrow Products$$

The table below shows the concentration of B at variation time

Time (minutes)	2.0	4.0	7.0	10.0	14.0	20.0
[B] (moldm-3)	0.820	0.670	0.490	0.372	0.240	0.141

Draw a graph of a $\log_{10}[B]$ against time

(c). Using your graph, determine the

(i). Original concentration of B

(ii). Order of the reaction

(iii). Rate constant for the reaction

(iv). Half-life for the reaction

(d). (i). Using the same axes, draw a labelled diagram for energy-reaction coordinate for a catalysed and uncatalysed reaction

(ii). State the difference in your diagrams

(iii). State how a catalyst increases the rate of a reaction.

38. Sucrose is hydrolysed in dilute acid to give a mixture of glucose and fructose

$$\underset{(sucrose)}{C_{12}H_{22}O_{11}(aq)} + H_2O(l) \xrightarrow{H^+} \underset{(Glucose)}{C_6H_{12}O_6(aq)} + \underset{(Fructose)}{C_6H_{12}O_6(aq)}$$

The table below shows the concentration of sucrose; [S] remaining at different time intervals

Time (minutes)	10	20	30	40	50	60
[S] (moldm^{-3})	1.25	1.04	0.87	0.73	0.60	0.50

(a). Plot a graph of In[S] against time

(b). Using your graph, determine the

- (i). Original concentration of sucrose
- (ii). Order of reaction
- (iii). Rate constant for the reaction
- (iv). Half-life for the reaction

(c). State the conditions under which the reaction in (a) can be overall first order

39. (a). Sodium thiosulphate solution reacts with dilute hydrochloric acid according to the following equation

$$Na_2S_2O_3(aq) + 2HCl(aq) \longrightarrow 2NaCl(aq) + S(s) + SO_2(g) + H_2O(l)$$

The rate equation for the reaction is given by $Rate = K[HCl]^2[Na_2S_2O_3]$

State and explain how the rate of reaction would be affected if

- (i). $[HCl]$ is doubled while $[Na_2S_2O_3]$ is kept constant
- (ii). $[Na_2S_2O_3]$ is halved while the $[HCl]$ is kept constant
- (iii). $[HCl]$ is halved while the $[Na_2S_2O_3]$
- (iv). $[HCl]$ and $[Na_2S_2O_3]$ are both halved

(b). Describe an experiment to show that the order of reaction in in (a) is first order reaction with respect to sodium thiosulphate

(c). The table below shows how the rate constant; K varies with temperature for a reaction between hydrogen and iodine to form hydrogen iodide

$Temperaure$ (K)	500	550	600	650	700
$Rate\ constant; K\ (mol^{-1}l^3s^{-1})$	6.81×10^{-4}	2.64×10^{-2}	0.56	7.31	66.67

- (i). Plot a graph of $\log_{10} K$ against $\frac{1}{Temp}$
- (ii). Use your graph to determine the activation energy, E_a, for the reaction

(d). State how a catalyst increases the rate of a chemical reaction

40. The information in the table below gives the time taken for a substance S to form with different concentration of the reactant R

$Time; t(s)$	0.96	0.64	0.48	0.39	0.32
$[R](moll^{-1})$	0.447	0.548	0.632	0.707	0.775

(a). Plot a graph of $\frac{1}{t}$ against $[R]^2$

(b). Use your graph to determine the

- (i). Order of reaction with respect to R. Give a reason for your answer
- (ii). Rate constant and state its units
- (iii). Write the rate equation for the reaction

41. The table below shows the amount of the reactant, A, remaining at different time intervals in a reaction in which A is converted into a product B.

$$A \longrightarrow B$$

$Time; t(minuts)$	0.5	1.0	1.5	2.0	2.5
$[A](moll^{-1})$	0.067	0.045	0.030	0.020	0.014

(a). Plot a graph of In[A] against time

(b). Use your graph to determine the
  (i). Original concentration of A
  (ii). Rate constant for the reaction
  (iii). Order of the reaction with respect to A
  (iv). Half-life of A

(c). Write the rate equation for the reaction

42. The table below shows how the concentration of a given reactant, K, varies with time.

$Time$(minutes)	0.0	2.0	4.0	6.0	8.0	10.0
$[K](moll^{-1})$	1.20	0.72	0.46	0.26	0.14	0.06

(a). Draw a graph of
  (i). Concentration of K against time
  (ii). $\log_{10}\left(\frac{[K]_t}{[K]_0}\right)$ against time

(b). Using each graph; determine the
  (i). Rate constant for the reaction
  (ii). The order of reaction with respect to K
  (iii). The half-life for the reaction

43. X and Y react to form W according to the equation

$$X(g) \quad + \quad Y(g) \quad \leftrightharpoons \quad W(g);\ \Delta H = +50kJmol^{-1}$$

The table below shows the rates of reaction when various concentrations of X and Y were used at 298K

[X] ($moll^{-1}$)	[Y] ($moll^{-1}$)	Initial rate ($moll^{-1}s^{-1}$)
2.0×10^{-2}	1.0×10^{-2}	1.0×10^{2}
2.0×10^{-2}	2.0×10^{-2}	2.0×10^{2}
4.0×10^{-2}	2.0×10^{-2}	4.0×10^{2}

(a). (i). Differentiate between 'order of reaction' and 'rate constant'
  (ii). Determine the order of reaction with respect to X and Y
  (iii). Write the expression for the rate equation
  (iv). Calculate the rate constant for the reaction at 298K and state its units

(b). (i). Distinguish between activation energy and enthalpy of reaction
  (ii). Draw a fully labelled potential energy versus reaction coordinate for the reaction between X and Y
  (iii). Calculate the activation energy for the backward reaction (the activation energy for the forward reaction is +200kJmol^{-1})

(c). State how you would expect the

  (i). Activation energy for the reaction to change if a catalyst is used. Give a reason for your answer

  (ii). Rate of reaction to change if the reaction was carried out at a temperature above 298K. give a reason for your answer.

(d). The react was carried out at temperatures T_1 and T_2 where T_2 is greater than T_1. Sketch on the same axes graphs to show how the concentration of W varies with time during the reactions at T_1 and T_2

44. Various concentrations of X and Y were reacted at a constant temperature. The table below shows the initial concentration of X and Y and their initial rates for the reaction.

[X] (moldm^{-3})	[Y] (moldm^{-3})	Initial rate (moldm^{-3}s^{-1})
0.2	0.2	3.5×10^{-4}
0.4	0.4	1.4×10^{-3}
0.8	0.4	5.6×10^{-3}

(a). State the order of reaction with respect to

  (i). X

  (ii). Y

(b). Give reasons for your answer in (a)

(c). Determine the overall order of the reaction

(d). Calculate the value for the rate constant

45. (a). The rate of a chemical reaction can be affected by the concentration of the reactants. State two other factors that can affect the rate of a chemical reaction.

(b). Describe an experiment to determine the rate of decomposition of hydrogen peroxide.

(c). The table below shows variation in the concentration of sodium thiosulphate with time when a fixed volume of hydrochloric acid was added to sodium thiosulphate of various concentrations

Concentration of sodium thiosulphate (moldm^{-3})	0.2	0.16	0.12	0.08	0.04
Time; t (s)	24	29	39	60	138
$\frac{1}{t}$ (s^{-1})					

  (i). Copy the table and fill in the values of $^1/t$

  (ii). Plot a graph of $^1/t$ against concentration of sodium thiosulphate.

  (iii). What is the order of the reaction? Give a reason for your answer.

  (iv). Calculate the rate constant of the reaction and indicate its units.

  (v). Determine the time taken for the concentration of sodium thiosulphate to decrease from 0.2 moldm^3 to 0.1 moldm^3

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 8: CHEMICAL EQUILIBRIA

1. (a). During the manufacture of sulphuric acid by contact process, sulphur dioxide is oxidised to sulphur(VI) oxide according to the following equation.

$$2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)\,;\ \Delta H = -188kJmol^{-1}$$

State the effect on the yield of sulphur(VI) oxide if
   - (i). Temperature was increased
   - (ii). Pressure was decreased
   - (iii). Concentration of sulphur dioxide was increased

   (b). Write equation to show how sulphuric acid can be obtained from sulphur(VI) oxide

2. Nitrogen monoxide combines with oxygen according to the following equation

$$2NO(g) + O_2(g) \leftrightharpoons 2NO_2(g)$$

   (a). Write an expression for the equilibrium constant K_c
   (b). 3.0 moles of nitrogen monoxide and 1.5 moles of oxygen were put in a 1 litre vessel. When equilibrium was attained, the vessel was found to contain 0.5 mole of oxygen. Calculate the equilibrium constant Kc at this temperature.
   (c). When temperature was raised to 500 °C, the mixture in (b) was found to contain 25% of the initial nitrogen monoxide. Calculate the equilibrium constant K_c at this temperature.
   (d). From your answers in (b) and (c), deduce whether the process is endothermic or exothermic.

3. Consider the reaction between sulphur dioxide and oxygen to produce sulphur trioxide at 700°C.

$$2SO_2(g) + O_2(g) \leftrightharpoons 2SO_3(g)\ \ \Delta H = -ve$$

   (a). Write the expression for the equilibrium constant, K_c, an state its units
   (b). What happens to the sulphur trioxide in the equilibrium mixture if,
   - (i). Temperature was raised from 700 to 800°C.
   - (ii). More oxygen is added
   - (iii). More nitrogen is added
   - (iv). Volume of the reaction vessel is increased.

   (c). The equilibrium mixture above at 700°C contains 0.4 mol of sulphur dioxide and 0.03 mol of oxygen and 1.00 mol of sulphur trioxide in 20 dm^3 container. Calculate the value of equilibrium constant K_c.

4. The reaction between nitrogen and hydrogen takes place as follows.

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)\ \ \Delta H = -ve$$

(a). Write the expression for the equilibrium constant, K_c, for the forward reaction

(b). At 500°c, the equilibrium concentration of hydrogen is 0.25 moldm^{-3} and that of nitrogen is 0.27 moldm^{-3}. Calculate the equilibrium concentration of ammonia at the same temperature given that the equilibrium constant, K_c is 6.0×10^{-2} mol^{-2}dm^{6}

(c). What would happen to the ammonia at equilibrium if

(i). Helium was added

(ii). Temperature was increased

5. (a). The degree of dissociation of 3.4 mole of hydrogen iodide at 460°C was found to be 20%. Calculate the

(i). Number of moles of hydrogen iodide, hydrogen and iodine formed at equilibrium

(ii). Equilibrium constant, K_c, for the dissociation reaction.

(b). A mixture containing 28 moles of hydrogen and 22 moles of iodine was heated in a sealed tube at 460 °C until equilibrium was attained when 36 moles of hydrogen iodide was obtained. Calculate the degree of dissociation of hydrogen iodide at 460°C.

6. (a). In the Haber process, ammonia is synthesised from nitrogen and hydrogen.

(i). Write the equation for the reaction leading to the formation of ammonia

(ii). Write an expression for the equilibrium constant, K_c.

(b). When nitrogen was reacted with hydrogen at 690K, the total pressure of the system at equilibrium was 32 atmospheres and the partial pressure of hydrogen and nitrogen were 8 and 3 atmospheres respectively. Calculate the

(i). Partial pressure of ammonia in equilibrium mixture

(ii). Equilibrium constant for the reaction

7. Phosphorus(V) chloride decomposes at high temperature according to the following equation

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

When 40.2 g of phosphorus(V) chloride was placed in 4.5 litre vessel and heated at a certain pressure, 4.2g of chlorine was formed at equilibrium.

(a). Calculate the

(i). Amount of phosphorus(V) chloride and phosphorus(III) chloride at equilibrium in moles per litre.

(ii). Equilibrium constant, K_c, for the reaction and state its units

(b). State how the value of equilibrium constant would be affected and in each case, give a reason for your answer if

(i). The pressure was increased.

(ii). Some chlorine was removed.

8. Hydrogen and iodine react to form hydrogen iodide according to the equation

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$$

(a). (i). Write an expression for the equilibrium constant, K_c, for the reaction (ii). 1 mole of hydrogen and $\frac{1}{3}$ mole of iodine were heated together at 450°C until equilibrium was attained. Calculate the number of moles of hydrogen iodide present in the equilibrium mixture at 450°C. (K_c for the reaction between hydrogen and iodine is 50)

(b). Briefly describe how the concentration of iodine in the equilibrium mixture can be determined.

(c). Describe an experiment to determine the equilibrium constant, K_c, for the decomposition of phosphorus(V) chloride.

9. (a). Ethanol reacts with ethanoic acid to form ethylethanoate according to the equation

$$CH_3COOH(l) + CH_3CH_2OH(l) \leftrightharpoons CH_3COOCH_2CH_3(l) + H_2O(l)\,; \quad \Delta H = -ve$$

(i). State the conditions for the reaction

(ii). Describe how the equilibrium constant, K_c, for the reaction can be determined by a titrimetric method.

(b). Explain what would happen to the equilibrium constant if

(i). A catalyst was added

(ii). Temperature was increased

(c). A mixture of 0.69g of ethanol and 0.9g of ethanoic acid were allowed to react at 90°C until equilibrium was reached. Calculate the mass of ethylethanoate formed. (equilibrium constant, K_c, for the reaction is 3.6)

10. (a). At a certain temperature, the equilibrium constant for the reaction between nitrogen and hydrogen, K_p, is $4.82 \times 10^{-2}\ atm^{-2}$ and the partial pressures of nitrogen and hydrogen are 30 and 120 atm respectively

(i). Write the expression for the equilibrium constant. K_p, for the reaction

(ii). Calculate the partial pressure of ammonia at equilibrium

(b). 1 mole of sulphur trioxide was introduced into a 1dm^3 vessel. The vessel was heated to 1000K until equilibrium was attained. At equilibrium, 0.35 mol of sulphur trioxide was present.

(i). Write equation for the decomposition of sulphur trioxide

(ii). Write an expression for the equilibrium constant, Kc.

(iii). Calculate the value of K_c.

11. Nitrogen(II) oxide combines with oxygen at 80°C and 200 atm to form nitrogen(IV) oxide according to the equation.

$$2NO(g) + O_2(g) \leftrightharpoons 2NO_2(g)\,; \Delta H = -ve$$

(a). (i). Write an expression for the equilibrium constant, K_p, for the reaction.

(ii). Calculate the value of K_p if the mixture contained 67% nitrogen(IV) oxide at equilibrium

(b). State how the value of K_p will be affected if

(i). Temperature was increased

(ii). A catalyst was added

12. Ethanol decomposes according to the following equation

$$CH_3CH_2OH(g) \leftrightharpoons CH_4(g) + CO(g)\,;\ \Delta H = -ve$$

(a). Write an expression for the equilibrium constant, K_p, for the reaction
(b). Explain how the value of K_p would be affected if
  (i). Temperature was increased
  (ii). Pressure is increased

13. (a). Write an
  (i). Equation for the reaction between hydrogen and nitrogen
  (ii). Expression for the equilibrium constant of the reaction in (i)
(b). When hydrogen was reacted with nitrogen at 895K, the total pressure of the system was 30 atm at equilibrium and the total pressure of nitrogen and hydrogen were 2 and 6 respectively. Calculate the equilibrium constant for the reaction

14. (a). Manganese(IV) sulphide reacts with acids according to the equation

$$MnS(s) + 2H_3O^+(aq) \leftrightharpoons Mn^{2+}(aq) + 2H_2O(l) + H_2S(aq)$$

State giving a reason in each case, what would happen to the equilibrium if
  (i). Hydrogen chloride is bubbled in the equilibrium mixture
  (ii). pH of the mixture is increased
  (iii). The mixture was diluted with water.
(b). Hydrogen reacts with iodine according to the following equation

$$H_2(g) + I_2(g) \leftrightharpoons 2HI(g)$$

A mixture of 0.8 mole of hydrogen and 0.6 mole of iodine was allowed to react in a sealed tube at 450°C. at equilibrium, 0.2 mole of iodine had reacted.
  (i). Write an expression for the equilibrium constant, K_c, for the reaction
  (ii). Calculate the value of Kc at 450°C.

15. (a). State three characteristics of a chemical equilibrium.
(b). Phosphorus pentachloride decomposes when heated at 190°C according to the following equation

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

Describe an experiment that can be carried out to determine the equilibrium constant, K_c, for the reaction
(c). Sulphur dioxide dichloride (sulphoryl dichloride) decomposes when heated according to the following equation.

$$SO_2Cl_2(g) \leftrightharpoons SO_2(g) + Cl_2(g)$$

When 67.5g of sulphur dioxide dichloride was heated in a 1 dm^3 vessel at 120°C and 3.6 atmospheres, it was found that at equilibrium, 45% of it had decomposed.
  (i). Write the expression for the equilibrium constant, K_p.
  (ii). Calculate the number of moles of each substance present at equilibrium.

(iii). Determine the value of the equilibrium constant, K_c.

16. Nitrogen reacts with hydrogen according to the equation

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

(a). Write an expression for the equilibrium constant, K_p, for the reaction and state its units

(b). Stoichiometric amounts of nitrogen and hydrogen were reacted at 40 atm and at equilibrium, 0.8 mole of ammonia was formed. Calculate the
  (i). Amount of hydrogen at equilibrium
  (ii). Value of the equilibrium constant, K_p

17. (a). In the industrial production of sulphuric acid by contact process, sulphur dioxide is oxidised to sulphur trioxide in the presence of a catalyst according to the equation.

$$SO_2(g) + \frac{1}{2}O_2(g) \leftrightharpoons 2SO_3(g); \Delta H = -96Kjmol^{-1}$$

  (i). Name the catalyst used in the process
  (ii). Explain why the reaction is carried out at 500°C
  (iii). Sulphuric acid is used in the manufacture of superphosphate fertiliser. Write the equation for the reaction
  (iv). Give one other large scale of sulphuric acid.

(b). Concentrated sulphuric acid contains 98% of the acid. Calculate the mass of concentrated sulphuric acid required to make 2.0M solution of sulphuric acid.

(c). Name one reagent that can be used to identify the anion in sulphuric acid. State what would be observed and write the equation for the reaction that takes place when the reagent you have named is used

18. Hydrogen reacts with nitrogen to produce ammonia according to the following equation

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

(a). Write the expression for the equilibrium constant, K_c.

(b). State giving reasons, what would happen to the value of equilibrium constant when
  (i). Pressure is added to the equilibrium mixture
  (ii). Argon is added to the reaction mixture at constant pressure
  (iii). Argon is added to the reaction mixture at constant volume

19. Hydrogen iodide decomposes when heated according to the equation

$$2HI(g) \leftrightharpoons H_2(g) + I_2(g)$$

(a). Write an expression for the equilibrium constant, Kc, for the reaction

(b). 1.54g of hydrogen iodide was heated in a 600cm^3 bulb at 530°C. When equilibrium was established, the bulb was broken under potassium iodide solution. The iodine formed from the decomposition required 67.0cm^3 of 0.1M sodium thiosulphate solution for complete reaction. Calculate the

(i). Number of moles of hydrogen iodide in 1.54g
(ii). Number of moles of iodine formed
(iii). Value of equilibrium constant K_c.

(c). State what would be the effect on the value of Kc if
(i). Temperature was increased from 530 to 800°C.
(ii). The volume of the bulb was decreased to 120cm^3

20. (a). Discuss the effect of the following on the position of equilibrium of a reversible reaction, the rate of attainment of equilibrium and the value of equilibrium constant.
(i). Temperature
(ii). Pressure
(iii). Catalyst

(b). Write an expression for the equilibrium constant K_c or K_p as appropriate for the following reactions at equilibrium and indicate the units in each case.

$$2A + B \leftrightharpoons C + 3D$$

(i). A, B, C and D are all gases
(ii). A, B, C, and D are all liquids
(iii). A, B, C are solids and D is a gas

21. Phosphorus(V) chloride when heated decomposes according to the equation

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

(a). A sample of pure phosphorus(V) chloride was heated in a 1 litre vessel to 250°C. When equilibrium was attained, the vessel was found to contain 40.7% chlorine. Calculate the
(i). Molar concentration of phosphorus(V) chloride at equilibrium
(ii). Equilibrium constant, K_c, for the reaction at 250°C.

(b). Explain what would happen to the concentration of chlorine if the pressure in the vessel was decreased at constant temperature.

22. Dinitrogen tetraoxide dissociates according to the equation

$$N_2O_4(g) \leftrightharpoons 2NO_2(g)\,;\,\Delta H = +54kJmol^{-1}$$

(a). State and explain the effect of each of the following on the position and rate of attainment of equilibrium for the above reaction
(i). Increase in pressure
(ii). Increase in temperature
(iii). Increase in the volume of the vessel

(b). One litre of a gases mixture above at equilibrium was found to contain 57% of the original 2.8g of dinitrogen tetraoxide. Calculate the equilibrium constant K_c for the reaction.

23. (a). Distinguish between position of equilibrium and rate of attainment of equilibrium

(b). Sulphur dioxide dichloride, SO_2Cl_2, decomposes according to the equation

$$SO_2Cl_2(g) \leftrightharpoons SO_2(g) + Cl_2(g)$$

(i). Write the expression for the equilibrium constant, K_p.

(ii). Explain the effect on the equilibrium above when a catalyst is added.

(iii). At pressure of 1 atm and temperature of 100°C, a sample of sulphur dioxide dichloride was found to contain 34% of chlorine. Calculate the value of K_p.

(c). Phosphorus(V) chloride decomposes according to the equation.

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

Deduce that the total pressure, $P_T = 3K_p$ when 50% of phosphorus(V) chloride has dissociated.

24. (a). Explain what is meant by the term **equilibrium constant**

(b). Discuss the effect of each of the following on the position of equilibrium, the rate of attainment and value of equilibrium constant

(i). Concentration

(ii). Temperature

(c). Carbon monoxide and steam react according to the equation,

$$CO(g) + H_2O(g) \leftrightharpoons CO_2(g) + H_2(g); \quad \Delta H = -40kJmol^{-1}$$

Equal moles of carbon monoxide and steam were made to react in a 1 litre vessel. When equilibrium was attained, the vessel was found to contain 16.7% carbon dioxide. Calculate the

(i). Molar concentration of carbon monoxide at equilibrium

(ii). Equilibrium constant, K_c, for the reaction

(d). If the percentage yield of ammonia from nitrogen and hydrogen at 700K and 200 atm is 15%. Calculate the equilibrium constant, K_p.

25. (a). Write an expression for the equilibrium constant, K_p or K_c as appropriate for the following at equilibrium and indicate units in each case.

$$P + Q \leftrightharpoons 2R + S$$

(i). P, Q, R and S are all gases

(ii). P, Q, R and S are all liquids

(b). Ammonium hydrogen sulphide dissociates according to the equation

$$NH_4HS(s) \leftrightharpoons NH_3(g) + H_2S(g)$$

At 298K, in a closed vessel, equilibrium was established when the partial pressure of the system is 0.88 atm.

(i). Write the expression for the equilibrium constant, K_p.

(ii). Calculate the value of K_p and give its units (iii). Calculate the partial pressure of ammonia in the mixture if 0.1 atm of ammonia gas was added to the system.

26. (a). When 60g of ethanoic acid and 46g of ethanol were made to react to equilibrium at 100°C, the percentage of esterification was 54%
    (i). Write equation for the esterification reaction
    (ii). Calculate the value of K_c
    (iii). Write the mechanism for the reaction between ethanoic acid and ethanol
    (b). The degree of dissociation of 2.0 moles of phosphorus(V) chloride in a 1dm^3 vessel was founds to be 22%. Calculate the equilibrium constant, K_c, for the reaction.
    (c). The degree of dissociation of 0.5 moles of hydrogen iodide was found to be 25% at a certain temperature in a 1.5dm^3 vessel. Calculate the equilibrium constant, K_p.

27. (a). Carbon monoxide reacts with steam according to the following equation

$$CO(g) \ + \ H_2O(g) \ \leftrightharpoons \ CO_2(g) \ + \ H_2(g); \quad \Delta H = -40kJmol^{-1}$$

    (i). Write the expression for the equilibrium constant, K_c.
    (ii). Equal moles of carbon monoxide and steam were made to react in a 1 litre vessel. When equilibrium was established at 750°C, the vessel was found to contain 26.7% carbon dioxide. Calculate the equilibrium constant, K_c, for the reaction.
    (b). State, giving reasons, how the concentration of carbon dioxide would be affected if at equilibrium
    (i). Temperature was increased
    (ii). Pressure was increased
    (iii). Helium was added at constant volume.

28. Find the equilibrium constant, K_c, for the following
    (a). 2.0 moles of phosphorus(V) chloride that is 22% dissociated in a 1 litre vessel
    (b). 3.6 moles of phosphorus(V) chloride that is 38% dissociated in a 2 litre vessel
    (c). 1.8 moles of phosphorus(V) chloride whose degree of dissociation is 15% in a 1 litre vessel
    (d). 2.4 moles of phosphorus(V) chloride whose degree of dissociation is 35%,

29. (a). At a given temperature, 3.2 moles of phosphorus pentachloride dissociated so that at equilibrium, it was found to contain 20% chlorine. Calculate the value of K_c.
    (b). When 2.4 moles of phosphorus pentachloride were heated in a 1.5 dm^3 vessel and at equilibrium, it was found to contain 23.53% phosphorus trichloride
    (i). Write equation for the decomposition of phosphorus pentachloride
    (ii). Write the expression for the equilibrium constant K_p and K_c for the reaction
    (iii). Determine the value of equilibrium constant, K_c.

30. Find the equilibrium constant, K_c, for the following
    (a). 3.2 moles of phosphorus pentachloride were heated in a 2 litre vessel and at equilibrium, it was found to contain 53.85% phosphorus pentachloride

(b). 2.0 mole of phosphorus pentachloride were heated in a 1 litre vessel and at equilibrium, it was found to contain 1.48 mole of phosphorus pentachloride.

31. (a). When 2.6 mole of phosphorus(V) chloride was heated in a 1.5dm^3 vessel, equilibrium was established when 1.04 mole of phosphorus(III) chloride was formed. Calculate the value of equilibrium constant, K_c.
    (b). 3.0 mole of phosphorus pentachloride was heated in a 1 litre vessel and when equilibrium was attained, it was found to contain 1.14 mole of chlorine gas. Determine the value of equilibrium constant K_c.

32. (a). 2.6 mole of phosphorus pentachloride was heated in a 500cm^3 closed vessel. At equilibrium, it was found to contain 1.04 mole of phosphorus trichloride. Determine the value of equilibrium constant, K_c.
    (b). 2.0 mole of phosphorus(V) chloride was heated in a 800cm^3 closed vessel and at equilibrium, it was found to contain 1.48 moles of phosphorus trichloride. Calculate the value of equilibrium constant, K_c.
    (c). 3.0 mole of phosphorus pentachloride was heated in a 750cm^3 vessel until equilibrium was established. The vessel contained 1.14 moles of chlorine. Determine the value of equilibrium constant, K_c.

33. (a). 2.085g of phosphorus pentachloride was heated in a 1 dm^3 vessel until equilibrium was attained. The vessel was then broken under excess potassium iodide solution. The iodine liberated required 40cm^3 of 0.1M sodium thiosulphate solution. Determine the equilibrium constant, K_c, for the reaction.
    (b). 2.085g of phosphorus pentachloride was heated in a 400cm^3 vessel until was attained. The chlorine liberated was bubbled through a solution of potassium iodide. The iodine liberated required 20cm^3 of 0.2M sodium thiosulphate for complete reaction. Calculate the value of equilibrium constant, K_c for the reaction

$$PCl_5(g) \leftrightharpoons PCl_3(g) + Cl_2(g)$$

34. (a). Determine the composition of the equilibrium mixture if 83.4g of phosphorus pentachloride is heated in a 5 dm^3 vessel whose degree of dissociation is 20%, hence find the equilibrium constant K_c.
    (b). Ammonia decomposes according to the following equation

$$2NH_3(g) \leftrightharpoons N_2(g) + 3H_2(g)$$

Determine the equilibrium constant K_c for the reaction given 3.0 moles of ammonia were found to be 15% dissociated.

35. Find the equilibrium constant K_c for the following
    (a). 2.4 mole of ammonia heated in a 1 litre vessel and at equilibrium, it is found to contain 19.41% nitrogen.
    (b). 1.8 mole of ammonia was heated in a 1 litre vessel and at equilibrium it was found to contain 42.86% hydrogen.

(c). 2.5 mole of sulphur trioxide heated in a 2 litre vessel, and found to be 20% dissociated at equilibrium.

(d). 1.5 moles of sulphur trioxide heated in a 1 litre vessel whose degree of dissociation is 15% at a given temperature.

36. Nitrogen combines with hydrogen according to the equation

$$N_2(g) + 3H_2(g) \leftrightharpoons 2NH_3(g)$$

(a). Find the equilibrium constant, K_p, for the reaction given that the equilibrium mixture contains

(i). 20% ammonia at 110 atm of pressure

(ii). 50% ammonia at 700 atm of pressure

(iii). 45% ammonia at 600 atm of pressure

(b). Find the equilibrium constant, K_c, for the above reaction when

(i). 0.007 moles of nitrogen and 0.073 moles of hydrogen are heated and at equilibrium 0.01 moles of ammonia were formed

(ii). 0.2 moles and 0.47 moles of nitrogen and hydrogen respectively when heated to equilibrium in a 1 litre vessel and 0.18 moles of ammonia were formed

(iii). 0.03 moles of nitrogen and 0.05 moles of hydrogen are heated at equilibrium to from 0.015 moles of ammonia

37. (a). Find the equilibrium composition when 0.2 mole of phosphorus(V) chloride is heated in a 1 litre vessel until equilibrium is established ($K_c = 5.294 \times 10^{-3} moldm^{-3}$).

(b). Calculate the percentage of chlorine is the equilibrium mixture if 0.4 moles of phosphorus(V) chloride were heated in a 1 dm^3 vessel and the equilibrium constant is $0.02 moldm^{-3}$.

(c). Determine the mass of each of the substance at equilibrium when 0.52 moles of phosphorus(V) chloride is heated at equilibrium. ($K_c = 0.043 moldm^{-3}$)

38. (a). Hydrogen chloride decomposes according to the equation

$$2HI(g) \leftrightharpoons H_2(g) + I_2(g)$$

Given that the equilibrium constant for the reaction is 0.02. Calculate the equilibrium composition of the following if they are heated.

(i). 0.2 mole of hydrogen iodide.

(ii). 0.15 mole of hydrogen iodide.

(iii). 0.05 mole of hydrogen iodide.

(b). When 0.4 mole of hydrogen iodide was heated to equilibrium, it dissociated.

(i). Write equation for the dissociation of hydrogen iodide

(ii). Write the expression for the equilibrium constant, K_c.

(iii). Determine the degree of dissociation of hydrogen iodide, given that the equilibrium constant is 0.025

39. Hydrogen reacts with iodine according to the equation

$$H_2(g) \ + \ I_2(g) \ \leftrightharpoons \ 2HI(g)$$

(a). Find the equilibrium concentration of each of the following
  (i). 0.2 mole of iodine and 0.3 moles of hydrogen are reacted in a 1dm^3 vessel
  (ii). 0.25 mole of iodine and 0.4 mole of hydrogen are reacted in a 2 litre vessel
  (iii). 0.42 moles of iodine and 0.26 moles of hydrogen are reacted in a 1.5 dm^3 vessel. Give that the equilibrium constant, K_c, for the reaction is 50

(b). Equimolar quantities of iodine and hydrogen were heated in a 1 litre vessel until equilibrium was attained and it was found to contain
  (i). 25.2% hydrogen iodide
  (ii). 13.5% hydrogen iodide
  (iii). 20.5% hydrogen iodide

Determine the equilibrium constant, K_c, in each case.

40. (a). 0.03 moles of nitrogen and 0.09 moles of hydrogen were heated in a 1 dm^3 vessel until equilibrium was attained at 299K. If at equilibrium, the vessel contained 0.056 moles of ammonia
  (i). Write the equation for the reaction
  (ii). Write the expression for the equilibrium constant, K_p.
  (iii). Determine the equilibrium constant, K_p.

(b). Nitrogen dioxide decomposes when heated according to the equation.

$$2NO_2(g) \ \leftrightharpoons \ 2NO(g) \ + \ O_2(g)$$

  (i). Write the equilibrium expression, K_c for the reaction
  (ii). Determine the value of K_c.

41. (a). Sulphur dioxide decomposes according to the equation when heated

$$2SO_3(g) \ \leftrightharpoons \ 2SO_2(g) \ + \ O_2(g) \ ; \ \Delta H = +ve$$

  (i). State the conditions for the reaction
  (ii). Write an expression for the equilibrium constant for the reaction, K_p

(b). When sulphur trioxide was heated in a closed vessel, at 270°C and 0.25 atmospheres, 46% of sulphur trioxide was decomposed at equilibrium. Calculate the value of K_p

(c). Calculate the heat of decomposition of sulphur trioxide (the heat of formation of sulphur dioxide and trioxide are -279 and $-392 \ kJmol^{-1}$)

(d). Explain how the position of the equilibrium, value of equilibrium constant and the rate of attainment of equilibrium would be affected if
  (i). The temperature of the reaction was increased
  (ii). The pressure of the reaction was decreased
  (iii). A catalyst was added to the reaction mixture

42. (a). Hydrogen reacts with iodine according to the equation

$$H_2(g) \quad + \quad I_2(g) \quad \leftrightharpoons \quad 2HI(g)$$

0.2 moles of iodine and 0.3 moles of hydrogen were enclosed in a 1liter vessel and heated. When equilibrium was attained, 0.36 moles of hydrogen iodide had formed. Calculate the equilibrium constant for the reaction K_c.

(b). Hydrogen reacts with nitrogen according to the equation.

$$3H_2(g) \quad + \quad N_2(g) \quad \leftrightharpoons \quad 2NH_3(g)$$

When 1.65 moles of hydrogen and 0.6 moles of nitrogen were heated to 150°C in a 1.5dm^3 closed vessel, equilibrium was attained when 0.9 moles of ammonia were formed. Calculate the value of equilibrium constant, K_c for the reaction.

(c). Ethanol reacts with ethanoic acid at 50°C according to the following equation

$$CH_3COOH(l) + \quad CH_3CH_2OH(l) \quad \leftrightharpoons \quad CH_3COOCH_2CH_3(l) \quad + \quad H_2O(l)$$

3.12g of ethanoic acid and 2.07g of ethanol were reacted in a 1 liter closed vessel at 50°C. at equilibrium, 0.36g of water were formed. Calculate the value of equilibrium constant for the reaction, K_c.

(d). Methane reacts with steam according to the equation

$$CH_4(g) \quad + \quad 2H_2O(g) \quad \leftrightharpoons \quad CO_2(g) \quad + \quad 4H_2(g)$$

When 0.18 moles of methane and 0.22 moles of steam were heated in a 5 dm^3 vessel, 0.1 mole of carbon dioxide was found to be present at equilibrium. Calculate the value of Kc.

(e). Phosphorus(V) chloride decomposes when heated according to the equation

$$PCl_5\ (g) \quad \leftrightharpoons \quad PCl_3\ (g) \quad + \quad Cl_2\ (g)$$

When 33.36g of phosphorus(V) chloride was heated in a 2.5litre vessel, 8.34g of phosphorus(V) chloride remained at equilibrium. Find then value of Kc.

(f). Nitrogen monoxide combines with oxygen according to the equation

$$2NO(g) \quad + \quad O_2(g) \quad \leftrightharpoons \quad NO_2(g)$$

A closed vessel of 500cm^3 containing 0.33 moles of nitrogen monoxide and 0.355 moles of oxygen was heated. Equilibrium was established when 0.105 moles of oxygen had reacted. Calculate the value of Kc.

(g). Hydrogen reacts with nitrogen according to the equation.

$$3H_2(g) \quad + \quad N_2(g) \quad \leftrightharpoons \quad 2NH_3(g)$$

When 0.58 moles of nitrogen and 1.03 moles of hydrogen were reacted in a 1liter vessel, equilibrium was established when 21.36% of hydrogen had remained. Calculate the value of Kc.

(h). Sulphur dioxide reacts with oxygen according to the equation

$$SO_2(g) \quad + \quad O_2(g) \quad \leftrightharpoons \quad 2SO_3(g)$$

0.425 moles and 0.294 moles of oxygen were heated in a 1.6liter vessel and at equilibrium, it was found that 52.02% of oxygen had reacted. Calculate the value of equilibrium constant Kc.

(i). Sulphur dioxide reacts with oxygen according to the following equation

$$2SO_2(g) \quad + \quad O_2(g) \quad \leftrightharpoons \quad SO_3(g)$$

When 0.6 and 0.425 moles of sulphur dioxide and oxygen respectively were reacted in a 1liter vessel to equilibrium, the equilibrium mixture contained 18.75% sulphur dioxide. Calculate the equilibrium constant value; K_c

(j). Nitrogen reacts with hydrogen to form ammonia according to the equation

$$3H_2(g) \quad + \quad N_2(g) \quad \leftrightharpoons \quad 2NH_3(g)$$

0.8 moles of nitrogen and 0.9 moles of hydrogen were heated in a 1500cm^3 closed vessel. At equilibrium, the mixture contained 20% hydrogen. Find the value of equilibrium constant Kc

(k). Sulphur dioxide dichloride decomposes when heated decomposes according to the equation

$$SO_2Cl_2(g) \quad \leftrightharpoons \quad SO_3(g) \quad + \quad Cl_2(g)$$

When 1.325 moles of sulphur dioxide dichloride were heated in a 2.0l vessel, equilibrium mixture contained 6% sulphur dioxide dichloride. Calculate the value of equilibrium constant, K_c.

(l). Phosphorus(V) chloride decomposes when heated according to the equation

$$PCl_5\,(g) \quad \leftrightharpoons \quad PCl_3\,(g) \quad + \quad Cl_2\,(g)$$

When 266.88g of phosphorus(V) chloride was heated strongly in a 2.5 dm^3 vessel, the equilibrium mixture contained 50% chlorine. Calculate the value of equilibrium constant, K_c.

43. (a). At 1 atmosphere and 48°C, dinitrogen tetraoxide is 30% dissociated.
   - (i). Calculate the equilibrium constant for the reaction, K_p
   - (ii). Determine the degree of dissociation of dinitrogen tetraoxide at 48°C and 6 atmospheres

(b). 75.06g of phosphorus(V) chloride were heated to 200°C in 1 dm^3 vessel at a pressure of 170kPa. Calculate the
   - (i). Degree of dissociation of phosphorus(V) chloride
   - (ii). Value of equilibrium constant, K_p, at 200°C

44. (a). At 26.7°C, and 25 atmospheres, 20% of phosphorus(V) chloride is dissociated. Calculate
   - (i). The partial pressure of each component in the equilibrium mixture
   - (ii). The equilibrium constant, K_p, for the reaction
   - (iii). The pressure that would be required to increase the dissociation to 30% at the same temperature.

(b). When 0.2 mole of nitrogen and 0.4 mole of hydrogen were introduced in a 1 litre vessel at 300°C and 500 atm equilibrium was attained when 0.18 mole of ammonia was formed. Calculate the equilibrium constant, K_p, for the reaction at this temperature.

(c). When stoichiometric amounts of nitrogen and hydrogen were introduced into a vessel and heated to 250°C and 210 atm, the equilibrium mixture contained 7.5% nitrogen. Calculate the equilibrium constant K_p for the reaction.

(d). When 0.58 moles of nitrogen and 1.03 moles of hydrogen were reacted in a 1liter vessel at 200°C and 350 atm, equilibrium was established when 21.36% of hydrogen had remained. Calculate the value of Kc.

45. (a). Describe an experiment that can be carried out to determine the equilibrium constant values for the reaction between nitrogen and hydrogen.
Nitrogen reacts with hydrogen according to the equation

$$3H_2(g) \quad + \quad N_2(g) \quad \leftrightharpoons \quad 2NH_3(g)$$

(b). 0.2 mole of phosphorus(V) chloride was heated in 1 dm^3 vessel at 160°C and a pressure of $8.0 \times 10^5 Nm^{-2}$. Calculate the
   - (i). Degree of dissociation of phosphorus(V) chloride
   - (ii). Value of equilibrium constant; K_p, for the reaction at 160°C.

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 12: IONIC EQUILIBRIA

1. (a). Write the equation for the ionisation of aqueous hydrogen fluoride in a
   - (i). Dilute solution
   - (ii). Concentrated solution

   (b). In which of the two solutions in (a) above would you expect hydrogen fluoride to be more acidic? Explain.

   (c). Calculate the ionisation constant, K_a, for ethanoic acid at 25°C given the degree of ionisation of the acid in a 0.1M aqueous solution is 0.00133

2. (a). What is meant by the term pH

   (b). A solution of magnesium hydroxide contains 0.0002 moles per litre of magnesium ions. Calculate the
   - (i). Number of moles of hydroxide ions present in the solution
   - (ii). The pH of the solution. ($K_w = 1.0 \times 10^{-14}$mol^{2}dm^{-6})

3. (a). Silver chromate is a sparingly soluble salt in water.
   - (i). Write the equation for the dissolution of silver chromate in water
   - (ii). Write the expression for the solubility product of silver chromate.

   (b). Calculate the mass of silver chromate required to saturate 0.5 litre of water given the solubility product constant, K_{sp}, of silver chromate is 1.15×10^{-12} at 25°C

4. Sodium sulphide is salt that undergoes hydrolysis when dissolved in water

   (a). Explain what is meant by the term salt hydrolysis

   (b). Write the equation for the hydrolysis of sodium sulphide in water

   (c). State whether the pH of and aqueous solution of sodium sulphide will be greater, less than or equal to 7. Explain your answer.

5. Sodium benzoate undergoes hydrolysis when dissolved in water.

   (a). Write an equation for the hydrolysis of sodium benzoate in water

   (b). Write an expression for the hydrolysis constant, K_h, for sodium benzoate

   (c). The hydrolysis constant of sodium benzoate is 1.6×10^{-10}moll^{-1}.
   - (i). Calculate the concentration of hydroxide ions in a 0.1M solution of sodium benzoate ($K_w = 1.0 \times 10^{-14}$mol^{2}dm^{-6})
   - (ii). State the assumptions made in the calculation in (c) (i)
   - (iii). From your result in c (i), calculate the hydrogen ion concentration of the solution

6. (a). 20cm^3 of 0.1M sodium hydroxide solution was added to 100cm^3 of 0.1M solution of ethanoic acid. Calculate the pH of the resulting solution. ($K_a = 1.75 \times 10^{-5}\ moldm^{-3}$)

   (b). Barium sulphate is sparingly soluble in water.
   - (i). Write equation for solubility of barium sulphate in water
   - (ii). Write the expression for the solubility product of barium sulphate

(iii). A saturated solution of barium sulphate contains 1.1×10^{-5} moles per litre pf the salt. Calculate the solubility of barium sulphate in gl^{-1}

(iv). Calculate the solubility of barium sulphate in a litre of 0.1M barium chloride solution

7. (a). Phenylamine hydrochloride undergoes hydrolysis when dissolved in water. Write an equation for the reaction.
   (b). A 0,2M solution of phenylamine hydrochloride has a pH of 3.5. Calculate
      (i). The molar concentration of hydrogen ions in the solution
      (ii). The hydrolysis constant, K_h, of phenylamine hydrochloride

8. (a). Explain what is meant by
      (i). Salt hydrolysis
      (ii). Common ion effect
      (iii). Solubility product
   (b). When sodium hydroxide solution is added to aqueous calcium hydroxide, a white precipitate is formed, but when ammonia solution is used instead, no precipitation occurs. Explain
   (c). Mercury(I) iodide was dissolved in 0.3M sodium iodide solution. Calculate the concentration of mercury(I) iodide in solution in gdm^{-3}. The solubility of mercury(I) iodide in water is 3.0×10^{-7}gdm^{-3}. Mercury(I) iodide dissolves in water according to the following equation

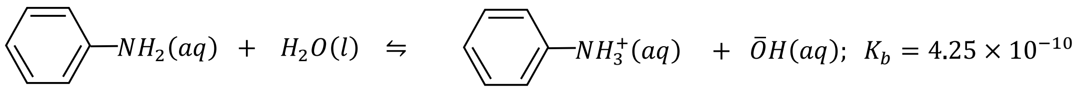
$$Hg_2I_2(s) \quad \leftrightharpoons \quad Hg_2^{2+}(aq) \quad + \quad 2I^-(aq)$$

9. (a). A solution contains 0.05 moles of nitric acid in 1 litre. Calculate the pH of the solution
   (b). A 0.1M ethanoic acid solution was titrated with 0.1M sodium hydroxide solution until the acid was exactly half neutralised. Calculate the pH of the resultant solution. $K_a = 1.8 \times 10^{-5}\ moldm^{-3}$.
   (c). Two drops of aqueous sodium hydroxide solution were added to the resultant solution in (b). State and explain what happened to the pH of the solution.

10. (a). Phenylamine hydrochloride undergoes hydrolysis in water. Write
      (i). Equation for the reaction.
      (ii). An expression for the hydrolysis constant, K_h.
   (b). A solution containing 15.0g of phenylamine hydrochloride in 100 cm^3 of water was shaken with 100cm^3 of benzene. At equilibrium, the benzene layer contained 0.12g of phenylamine. Calculate the
      (i). Molar concentration of phenylamine in the benzene layer
      (ii). Hydrolysis constant, K_h, of phenylamine hydrochloride.

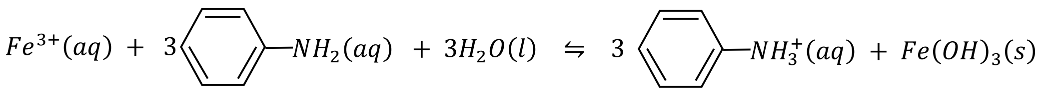
11. Iron(III) hydroxide and phenylamine react with water according to the following equations

$$Fe(OH)_3(s) \quad \leftrightharpoons \quad Fe^{3+}(aq) \quad + \quad 3\bar{O}H(aq);\ K_{sp} = 1.0 \times 10^{-38}$$



(a). Write the expression for the solubility product. K_{sp}, for iron(III) hydroxide and the base dissociation constant, K_b, for phenylamine. In each case, state the assumptions made

(b). The equation for the reaction between phenylamine and iron(III) ions is given below



(i). Write the expression for the equilibrium constant, K_c, for the reaction

(ii). Express the equilibrium constant in terms of K_{sp} and K_b

(iii). Calculate the value of equilibrium constant, K_c.

12. (a). Describe how the solubility product of magnesium hydroxide in water can be determined

(b). (i). A saturated solution of magnesium hydroxide in water contains 1.44×10^{-4} mol of magnesium hydroxide per litre of solution. Calculate the value of solubility product, K_{sp}, of magnesium hydroxide

(ii). Solid magnesium hydroxide was shaken with a 0.1M solution of magnesium nitrates until equilibrium was attained. Calculate the amount of magnesium hydroxide in grams per litre that dissolved.

(c). Equations of some reactions are given below

$$AgCl(s) \leftrightharpoons Ag^+(aq) + Cl^-(aq)\ ;\ K_1 = 1.7 \times 10^{-10}$$

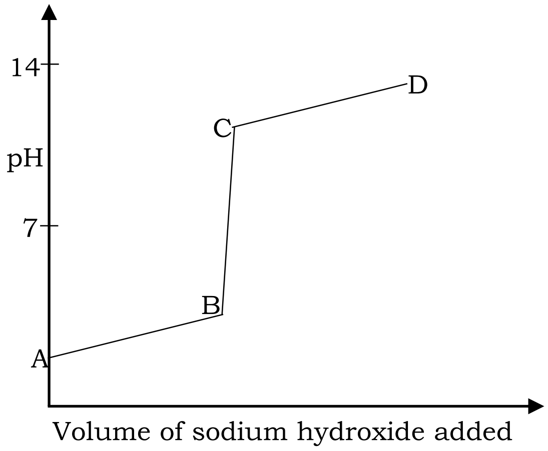
$$Ag^+(aq) + 2NH_3(aq) \leftrightharpoons Ag(NH_3)_2^+(aq)\ ;\ K_2 = 1.7 \times 10^{-7}$$

(i). Derive an expression for the equilibrium constant for the following reaction.

$$AgCl(s) + 2NH_3(aq) \leftrightharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$

(ii). Calculate the value of the equilibrium constant in (i)

13. The curve below was obtained for when hydrochloric acid was titrated with sodium hydroxide



(a). Explain what happens to the pH in the region

(i). AB

(ii). BC
(iii). CD

(b). Name one indicator that can be used in the titration in (a)

(c). (i). Sketch a graph that would be obtained if hydrochloric acid is titrated with ammonia solution
(ii). Explain the shape of the graph in c (i) above

14. A 0.01M solution of ammonia is 4.0% ionised.
    (a). Calculate the pH of the solution $K_w = 1.0 \times 10^{-14}\ mol^2dm^{-6}$
    (b). Determine the base dissociation constant, K_b, for ammonia

15. (a). Write an expression to show the relationship between acid dissociation constant, K_a, and the degree of dissociation, ∝, for a weak acid
    (b). Calculate the value of the acid dissociation constant, K_a, for a 0.1M ethanoic acid and state its units. (the molar conductivity of a 0.1M ethanoic acid is $5.2 \times 10^{-4}\Omega^{-1}cm^2mol^{-1}$ while the molar conductivity of ethanoic acid at infinite dilution is $3.9 \times 10^{-2}\Omega^{-1}cm^2mol^{-1}$)

16. (a). Ethanoic acid is a weak acid.
    (i). Explain what is meant by the term a weak acid
    (ii). Calculate the pH of a 0.05M ethanoic acid solution (K_a for ethanoic acid is $1.8 \times 10^{-5}\ moldm^{-3}$)
    (b). (i). Explain what is meant by the term “buffer solution”.
    (ii). Discuss the action of the buffer solution.
    (c). a solution was made by dissolving 7.2g of ethanoic acid and 12.0g of sodium ethanoate to make 1 litre of solution. Calculate the pH of the solution. State any assumption made

17. Ammonium chloride undergoes hydrolysis when dissolved in water
    (a). Write the equation for the hydrolysis of ammonium chloride in water
    (b). Calculate the
    (i). pH of a 0.1M solution of ammonium chloride, $K_h = 5.6 \times 10^{-10}$
    (ii). Percentage hydrolysis of a 0.1M ammonium chloride solution.

18. (a). A solution contains a mixture of sodium hydroxide and sodium carbonate in 1 litre. Briefly describe how the percentage of sodium hydroxide in the mixture can be determined using standard hydrochloric acid
    (b). Sketch a graph to show the variation of pH during the titration of hydrochloric acid with
    (i). Sodium hydroxide
    (ii). Ammonia solution
    (c). Explain the shape of each graph in (b) above
    (d). Calculate the pH of the resultant solution when 10cm^3 of 0.1M sodium hydroxide solution is added to 25cm^3 of 0.1M ethanoic acid (K_a for ethanoic acid is $1.8 \times 10^{-5}\ moldm^{-3}$)

19. (a). The pH of a 0.1M solution of a weak acid HX is 3.65. calculate the acid dissociation constant, K_a.

(b). When 50cm^3 of 0.1M solution of aqueous ammonia was added to 50cm^3 of 0.1M hydrochloric acid solution, the pH of the resultant solution was less than 7. Explain this observation

20. (a). At 25°C, ammonia has a base dissociation constant, K_b, of $1.8 \times 10^{-5}\ moldm^{-3}$
    (b). Write an expression for the K_b, of ammonia
    (c). Calculate the concentration of hydroxide ion concentration which occurs when 0.01M ammonium chloride is added to 1 dm^3 of the solution in (b). State the assumptions made.
    (d). Explain the change in the hydroxide ion concentration in (c).

21. (a). Write an equation for the hydrolysis of sodium ethanoate in water
    (b). Write an expression for the hydrolysis constant, K_h, of sodium ethanoate.
    (c). Calculate
        (i). The value of hydrolysis constant, K_h,for sodium ethanoate and indicate its units. (K_a for ethanoic acid is $1.8 \times 10^{-5}\ moldm^{-3}$, $K_w = 10 \times 10^{-14}\ moldm^{-3}$)
        (ii). The pH of a 0.1M sodium ethanoate solution
    (d). State what would be the effect on the pH of the solution in c (ii) if 1 cm^3 of 0.1M ethanoic acid was added to it.

22. Lead(II) sulphate is sparingly soluble in water
    (a). Write an expression for the solubility product of lead(II) sulphate
    (b). 5g of lead(II) sulphate was shaken with 1dm^3 of water. Determine the percentage of lead(II) sulphate that dissolved in water. (the solubility product K_{sp}, of lead(II) sulphate is 1.6×10^{-8}; $Pb = 207; S = 32; O = 16$)
    (c). If 0.05M sulphuric acid was used instead of water in (b), calculate the percentage of lead(II) sulphate that dissolved and state assumption made.

23. (a). Explain
        (i). What is meant by a buffer solution
        (ii). How a buffer solution works
    (b). Calculate the pH of a buffer solution made by mixing 15cm^3 with 25cm^3 of 0.1M sodium ethanoate solution.
    (c). (i). Draw a graph to show pH changes when a strong acid is titrated with a weak base
        (ii). Explain the shape of the graph in c(i)

24. The solubility of lead(II) sulphate is $1.5 \times 10^{-4} moll^{-1}$ at 25°C
    (a). (i). Write the equation for the solubility of lead(II) sulphate in water
        (ii). Write an expression for the solubility product constant, K_{sp}, of lead(II) sulphate
    (b). Calculate the solubility product constant, K_{sp}, for lead(II) sulphate at 25°C.
    (c). When a solution of sodium sulphate was added to a saturated solution of lead(II) sulphate, a precipitate was formed. Explain this observation
    (d). The solubility product of calcium sulphate is $2.0 \times 10^{-5} mol^2 l^{-2}$. A solution Q contains calcium ions and lead(II) ions. Using your results from part (b), which ion will be precipitated first on addition of sulphate ions to Q. Explain your answer.

25. The solubility product of zinc hydroxide is $1.5 \times 10^{-4}\ mol^3dm^{-9}$.
    (a). Write the
        (i). Equation for the solubility of zinc hydroxide in water
        (ii). Expression for the solubility product constant, K_{sp} of zinc hydroxide
    (b). Determine the concentration in moles per litre of zinc and hydroxide ions in a saturated solution of zinc hydroxide
    (c). State how the solubility of zinc hydroxide would change if its saturated solution is treated separately treated with
        (i). Aqueous zinc sulphate
        (ii). Ammonia solution
    (d). Briefly explain your answer in (c) above.

26. (a). Write an expression for the
        (i). Acid dissociation constant, K_a, for ethanoic acid
        (ii). Relationship between acid dissociation constant, K_a, and the degree of dissociation.
    (b). The electrolytic conductivity of ethanoic acid at 20°C of a $1.6 \times 10^{-2}M$ ethanoic acid is $1.9 \times 10^{-2}\ Sm^2mol^{-1}$. Calculate the
        (i). Degree of ionisation of the acid at 20°C.
        (ii). pH of the acid
    (c). state any other factor that can affect the pH of an acid

27. (a). Write the equation for the solubility of silver bromide in water.
    (b). The solubility product of silver bromide is $5.1 \times 10^{-13}\ mol^2l^{-2}$. Calculate the solubility of silver bromide in gdm^{-3} in
        (i). Water
        (ii). 0.1M potassium bromide solution. State any assumptions made.
    (c). State two methods that can be used to determine the solubility product of a sparingly soluble salt.

28. (a). Define the term **buffer solution**.
    (b). Calculate the mass of sodium ethanoate that should be added to 1 litre of 0.1M ethanoic acid solution in order to produce a solution of pH 4.0
    (K_a *for ethanoic acid is* $1.8 \times 10^{-5}\ moldm^{-3}$)
    (c). State what would happen to the pH of the solution in (b) id a small amount of the following are added
        (i). Sodium hydroxide solution
        (ii). Hydrochloric acid solution
    (d). State one biological use of buffer solutions

29. (a). Write
        (i). The equation for the solubility of silver sulphate in water
        (ii). The expression for the solubility product, , K_{sp}, of silver sulphate
    (b). Determine the molar concentration of silver and sulphate ions in a saturated solution of silver sulphate (, K_{sp} of silver sulphate is $1.7 \times 10^{-5}mol^3dm^{-9}$)
    (c). State how the solubility of silver sulphate would be affected if the following substances were added

(i). Sodium sulphate
(ii). Ammonia solution
(d). Explain your answer in (c) above.

30. (a). Draw diagrams to show the change in pH when a 0.1M sodium hydroxide solution is added in portions to
    (i). 20cm^3 of a 0.1M hydrochloric acid
    (ii). 20cm^3 of a 0.1M ethanoic acid
(b). Explain the shape if the curves in (a)
(c). 20cm^3 of 0.1M sodium hydroxide was added to 100cm^3 of a 0.1M ethanoic acid. Calculate the pH of the resulting solution (K_a $for\ ethanoic\ acid\ is$ $1.8 \times 10^{-5}\ moldm^{-3}$)
(d). The solubility of calcium phosphate is 0.0011g per 100g of water at 25°C. calculate the solubility product of calcium sulphate.

31. (a). Write the equation for the
    (i). Solubility of silver chromate in water
    (ii). Solubility constant, K_{sp}, for silver chromate.
(b). The solubility of silver chromate at 25°C is $3.207 \times 10^{-2}\ gdm^{-3}$. Calculate the solubility constant for silver chromate.
(c). Determine the molar concentration of silver ions required to precipitate silver chromate from an aqueous solution containing 0.005M chromate ions
(d). A solution containing silver ions was added to a solution containing 0.005M chromate ions and 0.005M chloride ions. State which of the salts, silver chromate or silver chloride was precipitated first. Give a reason for your answer. (K_{sp} of silver chloride is $1.96 \times 10^{-10}\ mol^2dm^{-6}$).

32. (a). Write the
    (i). Equation for the ionisation of methylamine in water
    (ii). Expression for the base dissociation constant, K_b, for methylamine
(b). The hydrogen ion concentration of a 1M methylamine solution is $2.5 \times 10^{-13}\ M$. Calculate the base dissociation constant, K_b, for methylamine.

33. The solubility product of lead(II) chloride is $1.6 \times 10^{-6}\ mol^3l^{-3}$.
(a). Write the
    (i). Equation for the solubility of lead(II) chloride in water
    (ii). Expression for the solubility product, K_{sp}, of lead(II) chloride
(b). Calculate the
    (i). Concentration of the chloride ions in moll^{-1} in a saturated solution of lead(II) chloride
    (ii). The solubility of lead(II) chloride in gl^{-1}
(c). State what would be observed if a saturated solution of lead(II) ethanoate was added to a solution of lead(II) chloride. Give a reason for your answer.

34. (a). State how
    (i). The solubility product of a sparingly soluble salt may be determined
    (ii). The solubility product of a sparingly soluble salt can be affected by addition of a common ion.

(b). Calcium fluoride is sparingly soluble in water. Write
  (i). An equation for the solubility of calcium fluoride in water
  (ii). An expression for the solubility product, K_{sp}, fir calcium fluoride
(c). Calculate the solubility of calcium fluoride in a solution containing 0.35M of sodium fluoride
(d). State one application of solubility product

35. (a). A solution containing 0.001M of methanoic acid is 1% ionised. Calculate the
  (i). pH of methanoic acid solution
  (ii). Acid dissociation constant, K_a, for methanoic acid

36. (a). What is meant by the term common ion effect
(b). Calcium iodate is sparingly soluble in water. Write the
  (i). Equation for the solubility of calcium iodate in water
  (ii). Expression for the solubility product, K_{sp}, of calcium iodate
(c). The solubility product of calcium iodate is $1.72 \times 10^{-9} mol^3 dm^{-9}$. Calculate the solubility of calcium iodate in gl^{-1} in
  (i). Water
  (ii). 0.1M sodium iodate solution
(d). Comment on your answers in (c) above.

37. (a). 25cm^3 of 0.3M sodium hydroxide was added to 225cm^3 of water. Calculate the pH of the resultant solution.
(b). Calculate the mass of sodium ethanoate that should be added to 1dm^3 of 0.1M ethanoic acid at 25°C to give a solution whose pH is 5.5. state any assumptions made. (K_a for ethanoic acid is $1.8 \times 10^{-5} moldm^{-3}$)
(c). A few drops of dilute hydrochloric acid were added to the solution in (b) above.
  (i). State what was happen to the pH of the solution
  (ii). Give a reason for your answer.

38. (a). Describe an experiment to determine the solubility product of calcium iodate
(b). The solubility product of calcium iodate is $1.70 \times 10^{-9} mol^3 dm^{-9}$. Calculate the concentration of iodate ions in a saturated solution of calcium iodate
(c). State three factors that can affect the value of solubility product.
(d). 0.1M of calcium nitrate was added to a litre of saturated solution of calcium iodate and the mixture stirred. Calculate the mass of calcium iodate which was precipitated. State any assumptions made.
(e). Triphosphate ions form a soluble complex with calcium ions. State what would happen when triphosphate ions are added to a saturated solution of calcium iodate. Give a reason for your answer.
(f). State two applications of solubility product.

39. (a). Write the equation for the hydrolysis of sodium ethanoate in water
(b). Write an expression for the hydrolysis constant, K_h, of sodium ethanoate
(c). The pH of 0.1M aqueous sodium ethanoate solution is 8.9. calculate the

40. (a). Write

(i). Equation for the hydrolysis of sodium benzoate in water

(ii). The expression for the hydrolysis constant, K_h, of sodium benzoate

(b). A solution of 0.2M sodium benzoate was made

(i). Calculate the pH of the solution ($K_h = 1.6 \times 10^{-10}\ moldm^{-3}$; $K_w = 1.0 \times 10^{-14}\ moldm^{-3}$)

(ii). State any assumptions made in (b)

41. (a). Strontium hydroxide is sparingly soluble in water.

(i). Write the equation for the solubility of strontium hydroxide in water

(ii). Write the expression for solubility product, K_{sp}, for strontium hydroxide

(b). The solubility product of strontium hydroxide is 0.524g per 100cm^3 of water at 20°C. calculate the

(i). Solubility product of strontium hydroxide and state its units

(ii). Volume of 0.01M potassium chromate(VI) solution that must be added to 1dm^3 of a saturated solution of strontium hydroxide to precipitate strontium chromate(VI). (K_{sp} of strontium chromate(VI) is $3.6 \times 10^{-5}\ mol^2dm^{-6}$ ($Sr = 87.6$)

(c). Sodium hydroxide was added to a saturated solution of strontium hydroxide

(i). State what happened to the solubility of strontium hydroxide

(ii). Give a reason for your answer in c (i) above

42. Dimethylammonium chloride undergoes hydrolysis in water according to the equation

$$(CH_3)_2NH_2^+(aq) \quad + \quad H_2O(l) \quad \leftrightharpoons \quad (CH_3)_2NH(aq) \quad + \quad H_3O^+(aq)$$

(a). Write the expression for the hydrolysis constant, K_h, for dimethylammonium chloride

(b). When 4.0M of dimethylammonium chloride was hydrolysed. 25.0cm^3 of the resulting solution required 7.5cm^3 of 0.01M sodium hydroxide for complete neutralisation. Calculate the

(i). pH of the solution

(ii). Hydrolysis constant, K_h, and state any assumptions made

43. (a). Silver ethanedioate is sparingly soluble in water. Write the

(i). Equation for the solubility of silver ethanedioate in water.

(ii). The expression for the solubility constant, K_{sp}, for silver ethanedioate.

(b). The solubility product, K_{sp}, of silver ethanedioate is $5.3 \times 10^{-2}\ mol^3dm^{-9}$ at 25°C. calculate the concentration of the following ions in a saturated solution of silver ethanedioate

(i). Silver ions

(ii). Ethanedioate

(c). Calculate the mass of silver nitrate that should be added to the saturated solution in (b) in order to reduce the concentration of the ethanedioate ions to a fifth of its original concentration.

(d). Sodium ethanedioate solution was added to the solution in (b). state how the concentration of the silver ions was affected and give a reason for your answer.

44. (a). Write the equation for the ionisation of phenol in water

(b). If the pH of a 0.01M solution of a phenol is 5.95. calculate the dissociation constant, K_a, of phenol (c). 10 litres of aqueous solution of trichloroethanoic acid were completely neutralised by 10cm^3 of 0.01M sodium hydroxide. Calculate the pH of the solution of trichloroethanoic acid.

(d). The solution of trichloroethanoic acid in (b) was added to a 0.1M sodium trichloroethanoate. Calculate the pH of the mixtures

45. (a). Define the following terms
    - (i). Solubility product
    - (ii). Common ion effect

(b). The solubility product expression of silver oxalate, $Ag_2C_2O_4$, is given by $K_{sp} = [Ag^+]^2[C_2O_4]$ describe an experiment that can be carried out to determine the solubility product of silver oxalate

(c). A saturated solution of silver oxalate contains 1.1×10^{-4} moles of silver oxalate per litre. Calculate the solubility product of silver oxalate and indicate its units

(d). Determine the solubility of silver oxalate in 0.01M silver nitrate solution. State any assumption made.

(e). Explain how the solubility of silver oxalate would be affected if few drops of the following were added
    - (i). Concentrated ammonia solution
    - (ii). Sodium oxalate solution.

46. (a). Ammonium chloride solution gives effervescence with magnesium ribbon while sodium ethanoate gives a blue precipitate with aqueous copper(II) chloride. Explain these observations.

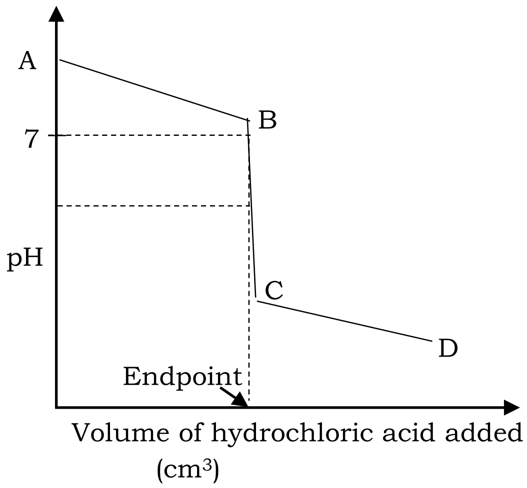
(b). The hydrolysis constant of sodium methanoate is $6.25 \times 10^{-11}\ moldm^3$ at 25°C.
    - (i). Calculate the pH of a 0.1M aqueous solution of sodium methanoate at 25°C ($K_w = 1 \times 10^{-14} mol^2dm^{-6}$)
    - (ii). To 1 dm^3 of 0.1M sodium methanoate solution was added to 10cm^3 of 1M hydrochloric acid. Calculate the pH of the resultant solution (K_a for methanoic acid is $1.6 \times 10^{-4}\ moldm^3$)

(c). Explain what would happen to the pH of a solution containing sodium methanoate and methanoic acid, if to it was added a small amount of s
    - (i). Hydrochloric acid
    - (ii). Sodium hydroxides

47. (a). Explain why the pH of a solution containing ammonia and ammonium chloride would remain almost constant when mixed with a small amount of
    - (i). Sodium hydroxide
    - (ii). Dilute hydrochloric acid

(b). 1.07g of ammonium chloride was dissolved in 1dm^3 of 0.01M ammonia solution. Calculate the pH of the solution and state the assumptions made in the calculations. (K_b for ammonium is $1.75 \times 10^{-5}\ moldm^3$; $K_w = 1 \times 10^{-14} mol^2dm^{-6}$)

(c). The graph below shows the variation in pH of ammonia solution when it was titrated with dilute hydrochloric acid



Explain the shape of the graph

48. (a). Hydrochloric acid was added to 25cm^3 of 0.1M ammonia solution and the pH of the solution was measured at intervals. The data below was obtained

Volume of hydrochloric acid (cm^3)	10.0	15.0	16.5	17.0	20.0	25.0
pH of the mixture	9.08	8.30	6.70	2.97	1.96	1.60

(i). Plot a graph of pH against volume of hydrochloric acid
(ii). Explain the shape of the graph
(iii). Calculate the molarity of the hydrochloric acid

(b). The pH ranges of some indicators are given below

Indicator	pH range
Thymol blue	1.2 – 2.8
Methyl red	4.8 – 6.0
Phenolphthalein	6.6 – 8.0

Which one of the above indicators is most suitable for use in the above titration? Give a reason for your answer.

(c). Calculate
(i). The molarity of ammonium chloride at end point
(ii). The hydrolysis constant for ammonium chloride

49. Methanoic acid is a weak acid
(a). Explain what is meant by the term weak acid
(b). Write an equation for the ionisation of methanoic acid in water
(c). Calculate the pH of a 0.04M methanoic acid whose acid dissociation constant, K_a, is $1.5 \times 10^{-5}\ moldm^3$. State any assumptions made.

50. (a). Aminoethane is a weak base. What is meant by a weak base.
(b). The pH of a 0.0024M solution of aminoethane is 9.6. Calculate
(i). The base dissociation constant, K_b.
(ii). Degree of ionisation of aminoethane

(c). 25cm^3 of a 0.01M aminoethane required 25cm^3 of 0.01M hydrochloric acid for neutralisation. Calculate the
  (i). pH of the resultant solution
  (ii). Degree of hydrolysis of the salt formed
(d). Explain why the pH of water decreases with increase in temperature.

51. (a). A solution of 0.01M methanoic acid is 4% ionised. Calculate the
  (i). Dissociation constant of the acid
  (ii). pH of the solution
(b). the hydrolysis constant for sodium benzoate is $1.6 \times 10^{-10}\ moldm^3$.
  (i). Calculate the pH of a solution of sodium benzoate
  (ii). State any assumptions made
(c). Explain the following observations
  (i). A solution of sodium methanoate has a pH greater than 7
  (ii). A solution of ammonium chloride has a pH less than 7

52. Ammonium chloride undergoes hydrolysis in water
(a). Write the
  (i). Equation for hydrolysis of ammonium chloride in water
  (ii). Expression for the hydrolysis constant, K_h, for ammonium chloride
  (iii). Expression for the hydrolysis constant, K_h, fo ammonium chloride in terms of K_w and K_b.
(b). Calculate the
  (i). Hydrolysis constant K_h for ammonium chloride
  (ii). The hydrogen ion concentration in solution
  (iii). The pH of 0.01M ammonium chloride.
  ($K_b = 1.8 \times 10^{-5}\ moldm^3$; $K_w = 1 \times 10^{-14} mol^2dm^{-6}$

53. (a). What is meant by a **buffer solution**.
(b). Describe how the following act as buffers
  (i). A solution of ethanoic acid and sodium ethanoate
  (ii). A solution of ammonium chloride and ammonia solution
(c). A solution is made by dissolving 7.2g of ethanoic acid and 12.0g of sodium ethanoate to make 1 dm^3. To this solution was added 14cm^3 of 1M hydrochloric acid calculate the pH of the solution. Stating any assumptions made. ($K_a = 1.8 \times 10^{-5}\ moldm^3$)
(d). Calculate the pH
  (i). Of a solution made by mixing 40cm^3 of 0.1M aminoethane and 16cm^3 of 0.1M hydrochloric acid
  (ii). Change if 6cm^3 of 0.1M potassium hydroxide is added to the solution in (d) (i) above ($K_b = 1.8 \times 10^{-5}\ moldm^3$)

54. (a). Silver chloride is a sparingly soluble salt in water
  (i). Write an equation for the solubility of silver chloride in water
  (ii). Write an expression for the solubility product, K_{sp}, for silver chloride
(b). Explain how the solubility of silver chloride is affected by addition of
  (i). Ammonia solution
  (ii). Sodium chloride solution

(c). The solubility of anhydrous calcium iodate in water is 3.07gdm^{-3}. Calculate its
  (i). Solubility product
  (ii). Solubility in gdm^{-3} in a solution of 0.1M sodium iodate solution
  (iii). Mass grams precipitated in a 0,1M sodium iodate solution

(d). 25.0cm^3 of a saturated solution of lead(II) chloride required 17.8cm^3 of 0.1M silver nitrate solution for complete removal of chloride ions from the solution. Calculate the
  (i). The molar concentration of lead(II) ions in the solution
  (ii). Solubility product of lead(II) chloride at 25°C.

55. (a). Briefly describe an experiment by which the solubility of lead(II) hydroxide in water can be determined

(b). A saturated solution of lead(II) hydroxide in water contains 2.38×10^{-5} mol per litre of solution.
  (i). Calculate the value of solubility product, K_{sp}, of lead(II) hydroxide
  (ii). Solid lead(II) hydroxide was shaken with 0.1M solution of lead(II) nitrate unitl equilibrium was attained. Calculate the amount of lead(II) hydroxide in grams per litre that dissolved

(c). Explain the following observations
  (i). Addition of aqueous ammonia to a solution of aluminium hydroxide is precipitated but in the presence of ammonium chloride, no precipitate is formed
  (ii). Silver chloride is more soluble in aqueous ammonia than in sodium chloride solution
  (iii). Copper(II) sulphide is precipitated in the presence of an acid, while nickel(II) sulphide in an alkaline medium using hydrogen sulphide.

56. (a). What is an acid – base indicator

(b). Give an example of an acid – base indicator and describe how it functions

(c). Sketch a graph each to show the variation of the pH of the resultant solution when
  (i). Dilute hydrochloric acid is added to sodium hydroxide solution
  (ii). Aqueous ammonia is added to dilute hydrochloric acid
  (iii). Sodium hydroxide solution is added to ethanoic acid
  (iv). Ethanoic acid is added to sodium hydroxide solution
  (v). Dilute hydrochloric acid is added to aqueous ammonia solution
  (vi). Sodium hydroxide solution is added to dilute hydrochloric acid

(d). Explain the shape of each graph above and suggest the suitable indicator to be used in the titration, giving a reason for your answer.

57. (a). Explain the meaning of
  (i). Salt hydrolysis
  (ii). Buffer solution

(b). Give three applications of buffer solutions

(c). Calculate the pH of the solution obtained by adding
  (i). 20 cm^3 of 0.1M sodium hydroxide to 40cm^3 of 0,1M hydrochloric acid
  (ii). 55cm^3 of 0,2M sodium hydroxide to 35cm^3 of 0.2M hydrochloric acid

58. (a). Sodium hydroxide was added in portions to 25cm^3 of 0.1M ethanoic acid and the pH of the resultant solution was measured at intervals and the results are as shown in the table below

Volume of sodium hydroxide (cm^3)	0.0	8.0	16.0	20.0	22.0	23.0	28
pH of the solution	2.8	4.0	5.1	5.8	7.0	10.5	12.5

Plot a graph for the pH against volume of sodium hydroxide added

(b). Use your graph above to determine the
  (i). pH at end point and account for this value
  (ii). Molarity of sodium hydroxide solution
  (iii). Dissociation constant, K_a, of ethanoic acid.

(c). To 20cm^3 of 0.02M aqueous ammonia was added an equal volume of 0.02M hydrochloric acid. Calculate the pH of the resultant solution and explain your answer.
($K_b = 1.8 \times 10^{-5}\ moldm^3$, $K_w = 1 \times 10^{-14} mol^2dm^{-6}$)

59. (a). (i). Define the term **buffer solution**
  (ii). Describe how an acidic buffer of pH 3.5 can be prepared using methanoic acid of pKa value of 3.75
  (iii). Explain how an acidic buffer solution works

(b). State two applications of buffer solutions

(c). Benzoic acid ionises in water according to the following equation

$$C_6H_5CO_2H(aq) \quad + \quad H_2O(l) \quad \leftrightharpoons \quad C_6H_5CO_2^-(aq) \quad + \quad H_3O^+(aq)$$

  (i). Write an expression for the ionisation constant, K_a, for benzoic acid
  (ii). Using the expression in c(i) above, calculate the ration of the concentration of benzoate ions to the concentration of benzoic acid in a solution of pH 4 and that in a solution of pH 6 (K_a for benzoic acid is $6.3 \times 10^{-5}\ moldm^{-3}$)
  (iii). At which of the two pH values would better buffering occur. Give a reason for your answer.

60. (a). Describe how the solubility product of silver chromate(VI) can be determined by titrimetric method.

(b). The solubility of silver chromate at 25°C is $2.0 \times 10^{-5} mol^3dm^{-9}$. Calculate the
  (i). Solubility product for silver chromate
  (ii). Solubility of silver chromate(VI) in 0.1M silver nitrate solution

(c). (i). Explain the term buffer solution
  (ii). Calculate the pH when 1.0cm^3 of 1M hydrochloric acid is added to a solution on 1.07gl^{-1} ammonium chloride in 0.01M ammonia solution

61. (a). What is meant by the following terms
  (i). Solubility product
  (ii). Saturated solution
  (iii). Solubility of a salt

(b). The solubility product of silver phosphate at 25°C is $1{,}4 \times 10^{-21} mol^4l^{-4}$. Calculate the
  (i). Solubility of silver phosphate in gdm^{-3} at 25°C.

(ii). Molar concentration of silver ions in a saturated solution of silver phosphate at 25°C. $(Ag = 108; P = 31; O = 16)$

(c). Describe how the solubility product of silver phosphate can be determined

(d). Calculate the

(i). The volume of 0.1M sodium phosphate solution required to precipitate half of the silver ions in a saturated solution of silver phosphate at 25°C.

(ii). The concentration of silver nitrate solution in gl^{-1} required to precipitate a fifth of the phosphate ions in a saturated solution of silver phosphate at 25°C.

62. (a). What is meant by the terms

(i). Solubility product

(ii). Common ion effect

(b). Describe an experiment that can be used to determine the solubility product of silver sulphate

(c). The solubility of silver sulphate in 0.1M sodium sulphate at 25°C is $2.034\ gdm^{-3}$. Calculate the solubility product of silver sulphate at this temperature. $(Ag = 108; S = 32; O = 16)$

(d). State and explain the effect on the solubility of silver sulphate when the following were added to its saturated solution

(i). Silver nitrate solution

(ii). Ammonia solution

(e). State two application of solubility product.

63. (a). Define the tem **buffer solution**

(b). Explain the action of an acid buffer

(c). 50cm^3 of a 0.05M ethanoic acid was added to 50cm^3 of 0.02M sodium hydroxide solution

(i). Write an equation for the reaction that took place

(ii). Calculate the pH of the resultant solution at 25°C

$(K_a$ for ethanoic acid is $1.8 \times 10^{-5}\ moldm^{-3}$

(d). To 50cm^3 of a 0.02M ethanoic acid was added an equal volume of 0.02M potassium hydroxide solution

(i). Calculate the pH of the resultant solution

(ii). Explain your answer in d (i)$(K_w = 1 \times 10^{-14} mol^2dm^{-6})$

64. (a). What do you understand by the term **weak base?**

(b). Write the

(i). Equation for the ionisation of methylamine in water

(ii). An expression for the base dissociation constant, K_b, for methylamine

(c). The pK_b of 0.02M methylamine is 3.45 at 25°C

(i). Calculate the pH of the solution $(K_w of\ water = 1.0 \times 10^{-14} mol^2dm^{-6})$

(ii). 650cm^3 of 0.02M methylamine was mixed with 350cm^3 of 0.02M hydrochloric acid at 25°C. Calculate the pH of the resultant solution.

(d). State and explain how the pH of the resultant solution in c(ii) above would be affected if portions of sodium hydroxide and hydrochloric acid were added.

(e). Explain the following observations

(i). Ethanoic acid is a weaker acid than benzoic acid

(ii). An aqueous solution of methylammonium chloride has a pH less than 7.

65. Lead(II) chloride is a sparingly soluble salt

(a). Write an

(i). Equation for the solubility of lead(II) chloride in water

(ii). Expression for the solubility product of lead(II) chloride

(b). Describe an experiment that can be carried out to determine the solubility product of lead(II) chloride at 25°C

(c). The solubility of lead(II) chloride in water at 25°C is 0.623g per 100g of water. Calculate the

(i). The solubility product of lead(II) chloride at 25°C

(ii). The solubility of lead(II) chloride in a 0.5M potassium chloride solution

(d). State and explain the effect of adding the following solutions to the above solution in (c)

(i). Dilute hydrochloric acid

(ii). Concentrated hydrochloric acid

(e). Calculate the mass of lead(II) chloride that would precipitate when 1dm^3 of 0.1M sodium chloride at 25°C.

(f). Calculate the mass of lead(II) nitrate that should be added to the saturated solution in (c) in order to reduce the concentration of chloride ions by a quarter of its original value

(g). Calculate the volume of 0.5M hydrochloric acid that should be added to 1dm^3 of 0.02M lead(II) nitrate to cause precipitation

(h). Calculate the volume of 0.03M sodium chloride that should be added to 30cm^3 of 0.05M lead(II) nitrate solution to precipitate lead(II) chloride at 25°C.

$(Pb = 207; Cl = 35.5; N = 14; O = 16)$

END

ADVANCED LEVEL PHYSICAL CHEMISTRY PROBLEMS

CHAPTER 6: PHYSICAL EQUILIBRIA

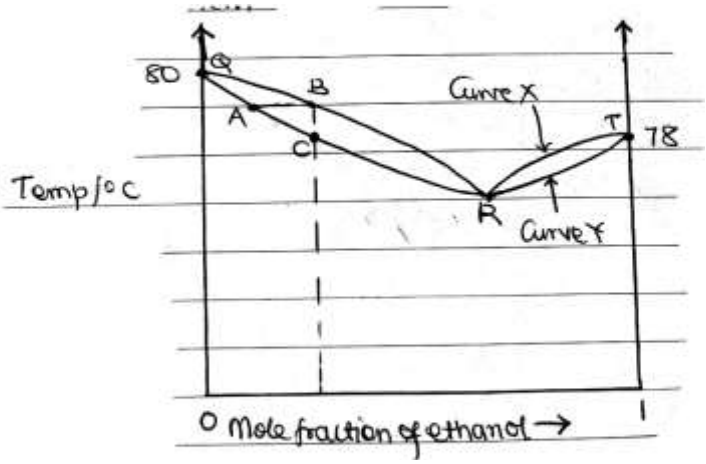
PART I: RAOULT'S LAW AND DEVIATIONS

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

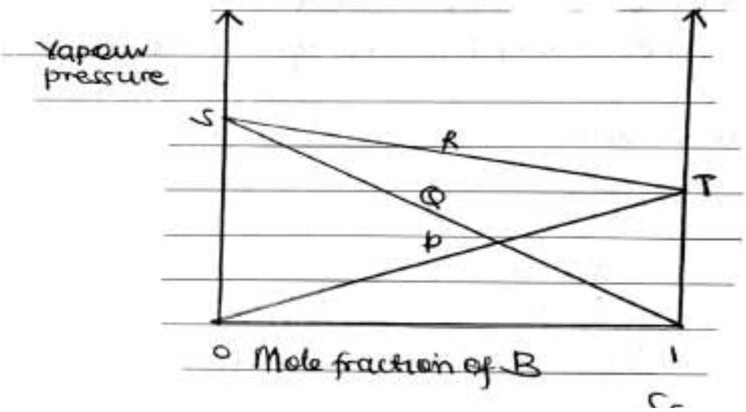
   (i) Plot a graph of total vapour pressure of the mixture against the mole fraction of trichloromethane
   (ii) Using your graph, deduce how the mixture deviates from Raoult's law. Give a reason for your answer
   (iii) Explain the causes of the deviation you have stated in b (ii)
   (iv) Determine the 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 I 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

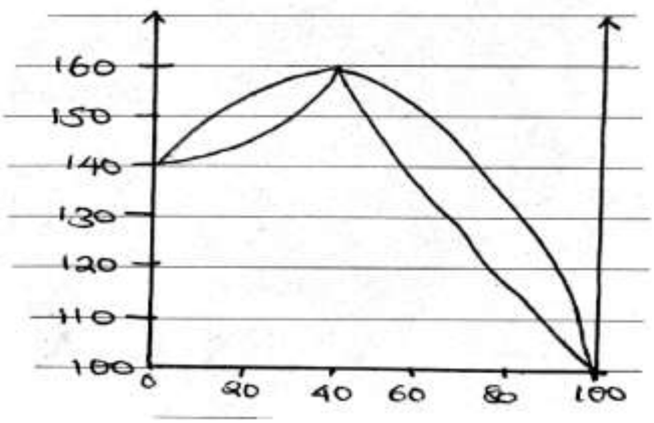
  (i) Explain why mixtures may deviate positively from Raoult's law

  (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

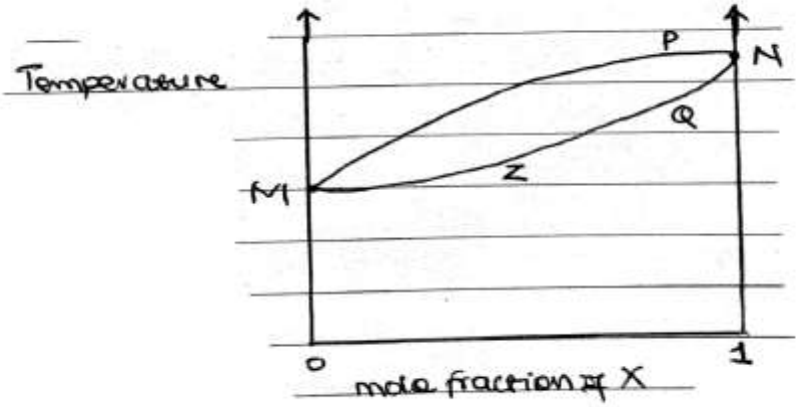
12. (a) State Raoult's law

(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 20°C.

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

  (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

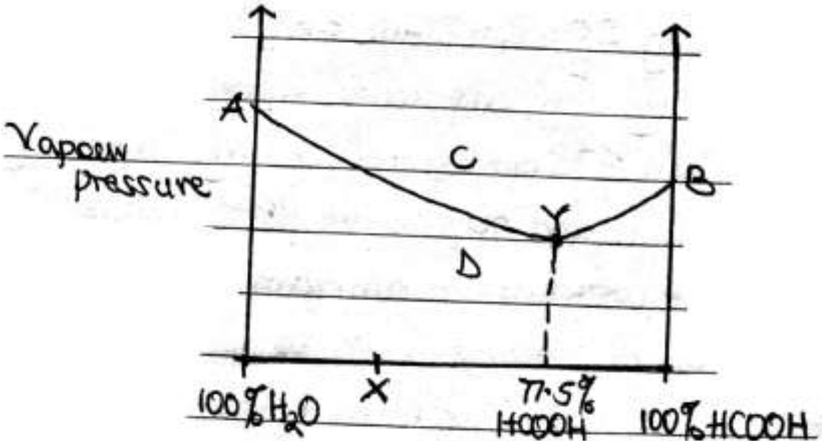
(iii) Explain how the principle in c (ii) can be used to separate liquid mixtures by fractional distillation

13. (a) The vapour pressures of methanol and water are 125.9 and 23.8mmHg respectively at 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

  (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 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

  (i) The variation of the vapour pressure with composition

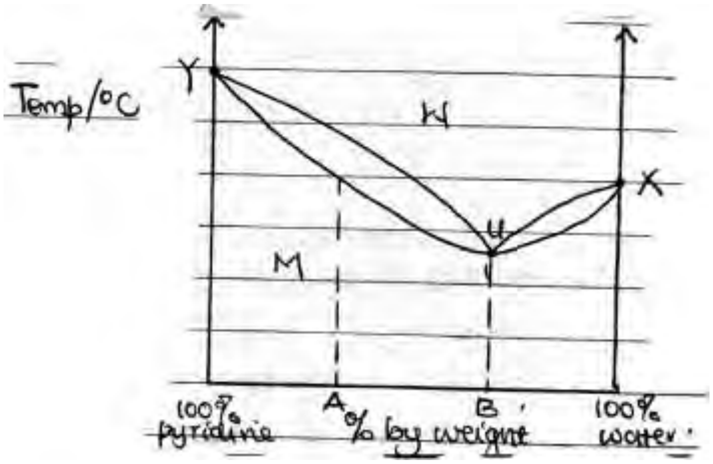
  (ii) The variation of boiling points of the mixture with composition

(e) (i) Calculate the composition of the vapour at 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 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 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 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 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 $4.8 \times 10^4\ Nm^{-2}$ 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	091	1.0

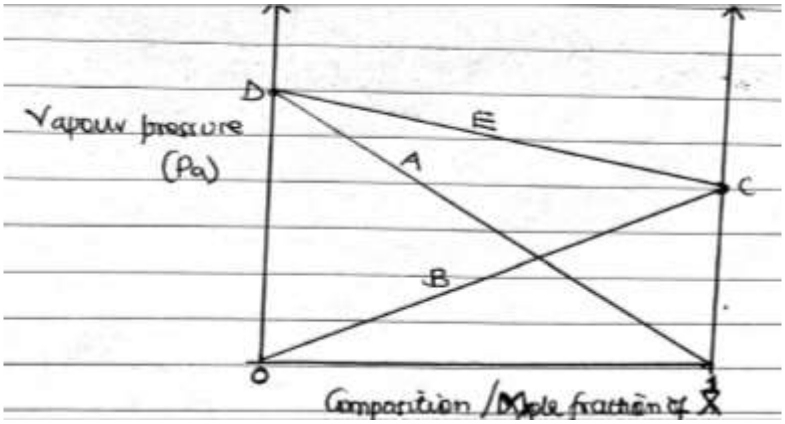
(i) Plot an accurate boiling point–composition diagram for the system
(ii) Calculate the ratio of saturated vapour pressure of pure benzene to the total vapour pressure of the system at 100°C
(iii) Explain how this mixture deviates from Raoult's law

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 x 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-nitrolphenol 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 cm^3 of a solution containing 0.966g of iodine in tetrachloromethane was shaken with 50 cm^3 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 moll^{-1} and 0.725 moll^{-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 cm^3 of a solution contains 30g of substance Z. calculate the mass of Z extracted by shaking with
      (i). 100 cm^3 of ethoxyethane
      (ii). Two 50 cm^3 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 cm^3 of an aqueous solution containing 20g of W was shaken once with 50cm^3 of ether. Calculate
   (i). The mass extracted by ether
   (ii). The mass of W the would be extracted by shaking the solution twice with 25 cm^3 of ether

   (b). 50.0g of substance Y was dissolved in water to make 100 cm^3 of solution. The partition ratio of Y between water and ether is 0.2. Calculate the mass of Y extracted by shaking the 100 cm^3 of solution with
   (i). 500 cm^3 of ether
   (ii). Two successive portions of 250 cm^3

5. (a). State the **distribution law**
   (b). Under which conditions is the law in (a) valid
   (c). 100 cm^3 of a solution containing 10g of compound Q was shaken with 100 cm^3 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.

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

   (a). (i). Plot a graph of $[NH_3](0.1M\,CuSO_4)$ against $[NH_3](CHCl_3)$
   (ii). Determine the distribution constant, K$_D$, of ammonia between aqueous copper(II) ions and chloroform
   (iii). State what value of K$_D$, you have determined indicates about the distribution of ammonia

   (b). (i). Determined the number of moles of ammonia that react with copper(II) ions
   (ii). Write the equation for the reaction between ammonia and copper(II) ions

7. 1.00dm^3 of an aqueous solution contains 5.00g of butanoic acid. Calculate the mass butanoic acid extracted when the solution was shaken with
   (a). 50 cm^3 of solvent Q
   (b). Twice with 25cm^3 of solvent Q (the Kd 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 1dm^3. The resultant solution was shaken with trichloromethane and left to settle. 50cm^3 of the organic layer needed 25.0cm^3 of 0.05M hydrochloric acid for complete neutralisation. 25cm^3 of the aqueous layer was neutralised with by 40cm^3 of 0.5M hydrochloric acid.
   (i). Write equation for the reaction between copper(II) ions and ammonia
   (ii). 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 500cm^3 of water was shaken with 200cm^3 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 100cm^3 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 cm^3 of a solution containing 0.171g of ammonia in trichloromethane was shaken with 100cm^3 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 100cm^3 of an aqueous solution containing 30g of ethanoic acid were shaken with 50cm^3 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 25cm^3 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 stat its units
    (b). Briefly describe how the partition ratio for the distribution of iodine between water and trichloromethane can be determined
    (c). (i). 60cm^3 of an aqueous solution containing 0.3g of a compound Y was shaken with 30cm^3 of ethoxyethane and the mixture allowed to stand. Calculate the mass of Y that was extracted in to 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 15cm^3 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.

$[CH_3NH_2](0.1M\ NiSO_4)$/ moll^{-1}	0.87	1.10	1.33	1.57	1.8
$[CH_3NH_2](CHCl_3)$/ moll^{-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 cm^3 of 0.1M iodine solution in aqueous potassium iodide was vigorously shaken with in a separating funnel with 20cm^3 of tetrachloromethane. The colour of tetrachloromethane gradually changed to purple and finally dark purple.
    - (a). (i). Explain the role of potassium iodide solution in this experiment.
        - (ii). Explain the observed colour changes in the tetrachloromethane layer.
    - (b). 10cm^3 of the tetrachloromethane layer reacted with 18cm^3 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 500cm^3 contains 5.0g. Calculate the mass of A that will be extracted by using
        - (i). 100cm^3 of ethoxyethane
        - (ii). Two successive portions of 50.0cm^3 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 50cm^3 of 0.5M sulphuric acid. The excess acid remaining after absorption required 20.0cm^3 of 0.01M sodium hydroxide for neutralisation
    - (d). The table below shows the partition of ammonia between 0.1M copper(II) sulphate and tetrachloromethane.

$[NH_3](0.1M\ CuSO_4)$/ $moll^{-1}$	0.86	1.10	1.57	1.80	2.40
$[NH_3](CCl_4)$/ $moll^{-1}$	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.

$[Benzoic\ acid]_{water}$ ($moll^{-1}$)	0.86	1.10	1.57	1.80	2.40
$[Benzoic\ acid]_{water}$ ($moll^{-1}$)	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 100cm^3 of water containing 2g of aniline by using 20cm^3 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). 50cm^3 of an aqueous solution containing 5.08gl^{-1} of iodine was shaken with 50cm^3 of chloroform. The mixture was left to stand for some time. 25cm^3 of the organic layer required 12.5cm^3 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 0.01dm^3 of molten zinc and 0.2dm^3 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 100cm^3 of aqueous solution containing 40g of X by extracting with

(i). 100cm^3 of ether

(ii). Two successive portions of 50cm^3 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

$$I_2(aq) + I^-(aq) \leftrightharpoons I_3^-(aq)$$

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.

$[NH_3](0.1M\ CuSO_4)$/ moll^{-1}	0.86	1.10	1.57	1.80	2.40
$[NH_3](CHCl_3)$/ 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. 10cm^3 of the aqueous layer required 21.6cm^{3}of 0.5M hydrochloric acid while the organic layer required 18.8cm^3 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 100cm^3 of this solution is shaken with 20cm^3 of ethoxyethane, the ethoxyethane layer extracts 0.8g of phenol. Calculate mass of phenol extracted when 500cm^3 of the aqueous layer was shaken with

(i). 50cm^3 of the ethoxyethane.

(ii). two successive 25cm^3 portions of the ethoxyethane.

21. (a). To 1 dm^3 of a solution of 0.045M copper(II) sulphate solution was added excess ammonia, tetrachloromethane and the mixture was allowed to settle. 25.0cm^3 of the tetrachloromethane layer required 12.5cm^3 of 0.05M hydrochloric acid for complete reaction. 25.0cm^3 of aqueous layer required 20.0cm^3 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

$$M^+(aq) + nNH_3(aq) \leftrightharpoons [M(NH_3)_n]^+(aq)$$

25cm^3 of ammonia solution was added to 25cm^3 of 0.1M aqueous solution of metal M ions, followed by 50cm^3 of trichloromethane. The mixture was shaken and allowed to reach equilibrium. The aqueous layer required 27.5cm^3 of 1.0M nitric acid while the trichloromethane layer required 18.0cm^3 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)