



Our country, our future

525/1

S6 CHEMISTRY

Exam 27

PAPER 1

DURATION: 2 HOUR 45 MINUTES

Instructions to candidates:

- Attempt all questions in section A and any six from section B
- All questions are to be answered in the spaces provided
- A periodic table with relevant atomic masses is supplied at the end of the paper.

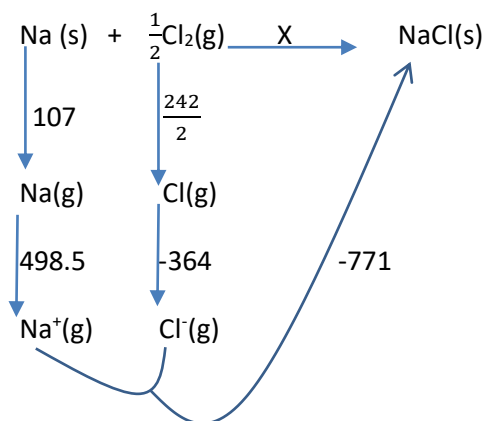
FOR EXAMINER'S USE ONLY																	
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	TOTAL

1. (a) Define the term enthalpy of formation. (1 mark)

Enthalpy of formation is enthalpy change when 1 mole of a compound is formed from its elements at 298K and 1 atmosphere,

- (b) Calculate the enthalpy of formation sodium chloride from the following data. (3 marks)

	ΔH^θ (kJmol ⁻¹)	
$\text{Na(s)} \longrightarrow \text{Na(g)}$	+109	
$\text{Cl}_2(\text{g}) \longrightarrow 2\text{Cl(g)}$	+242	
$\text{Na(g)} \longrightarrow \text{Na}^+(\text{g})$	+498.5	
$\text{Na}^+(\text{g}) + \text{Cl}^-(\text{g}) \longrightarrow \text{NaCl(s)}$	-771	
$\text{Cl(g)} + \text{e}^- \longrightarrow \text{Cl}^-(\text{g})$	-364	

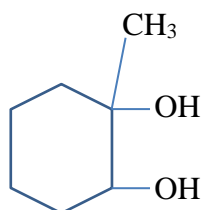
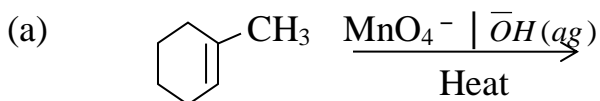


$$X = 107 + 242/2 + 498.5 - 364 - 771 = 408.8 \text{ kJmol}^{-1}$$

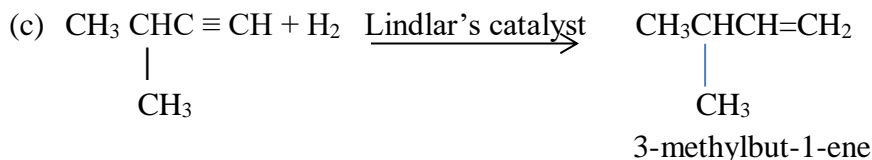
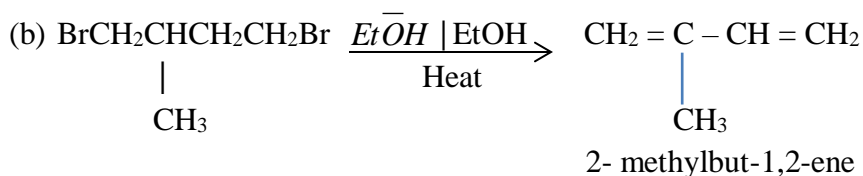
- (c) Comment on the stability of sodium chloride. Give a reason for your answer. (1 mark)

Stable because enthalpy of formation is negative

2. Complete the following reactions and in each case write the IUPAC names of the major organic product. (1 1/2 marks each)



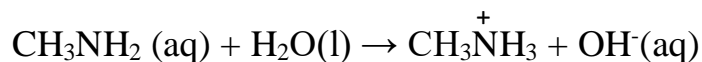
Methylcyclohexan-1,2-diol



3. 0.02M methylamine solution is 4% ionized at 25°C.

(a) Write ;

(i) an equation for the ionization of methylamine in water. (1 mark)



(ii) an expression for the base ionization constant K_b for methylamine. (1 mark)

$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]}$$

(b) Calculate the

(i) pH of the methylamine solution ($K_w = 1.0 \times 10^{-14} \text{ mol}^2 \text{ dm}^{-6}$)

$$[\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] = C\alpha = 0.02 \times \frac{4}{100} = 0.008 \text{ mol dm}^{-3}$$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.008} = 1.25 \times 10^{-12} \text{ mol dm}^{-3}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.25 \times 10^{-12} = 11.9$$

(ii) base ionization constant; K_b for methylamine. (1 ½ marks)

$$[\text{CH}_3\text{NH}_3^+] = [\text{OH}^-] = C\alpha = 0.02 \times \frac{4}{100} = 0.008 \text{ mol dm}^{-3}$$

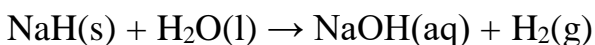
$$[\text{CH}_3\text{NH}_2] = C(1-\alpha) = 0.02 \times \frac{96}{100} = 0.0192 \text{ mol dm}^{-3}$$

$$K_b = \frac{(0.008)^2}{0.0192} = 0.0033 \text{ mol dm}^{-3}$$

4. (a) Write the formula of the hydrides of sodium and sulphur, in each case state the type of bonds present in the compounds. (2 marks)

Elements	Formula of hydride	Type of bond
Sodium	NaH	ionic
Sulphur	H ₂ S	covalent

- (b) Write equations to show how the hydrides react with water. (3 marks)



5. (a) Define the term Osmotic pressure. (1 mark)

Osmotic pressure is the minimum pressure that prevents osmosis through a semipermeable membrane.

- (b) A polysaccharide has the formula (C₁₂H₁₂O₁₁)_n. A solution containing 5.00gdm⁻³ of the sugar has an osmotic pressure of 7.12 x 10² Nm⁻² at 20°C. Find the value of n. (3 ½ marks)

From $PV = nRT$

$$7.12 \times 10^2 \times 10^{-3} = \frac{5}{Mr} \times 8.31 \times (273 + 20)$$

$$Mr = 17100$$

$$(\text{C}_{12}\text{H}_{12}\text{O}_{11})_n = 17100$$

$$n = 52$$

- (c) State any two assumptions made in (b) above. (1 mark)

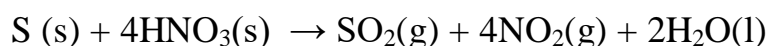
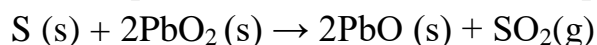
The solution is dilute

6. A powdered element T was investigated as shown in the table below

Experiment	Results
(a) A mixture of T and lead (IV) oxide was heated	A colorless gas with a choking smell and turned acidified potassium dichromate from orange to green was evolved.
(b) Concentrated nitric acid is added to heated T, the products were diluted and barium nitrate solution added.	T dissolved in nitric acid with effervescence of a brown gas. On addition of barium nitrate solution a white precipitate was formed

(i) Identify T (1 mark)
sulphur

(ii) Write equations for the reactions in experiments (a) and (b) (4 marks)



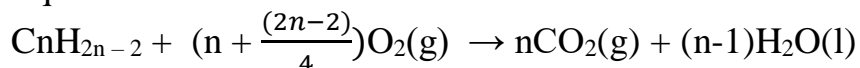
7. (a) 20cm^3 of hydrocarbon Q with general formula $\text{C}_n\text{H}_{2n-2}$ were mixed with 100cm^3 of oxygen. The mixture was ignited and the residual gaseous product at room temperature bubbled through concentrated potassium hydroxide solution. The final volume was found to be 20cm^3 .

(i) Calculate the value of n in Q. (2 marks)

$$\text{Volume of oxygen used} = 100 - 20 = 80\text{cm}^3$$

$$\text{Moles of oxygen used} = 80/20 = 4$$

Equation:



$$\text{Thus } n + \frac{(2n-2)}{4} = 4$$

$$n = 3$$

(ii) Deduce the molecular formula of Q. (½ mark)



(b) Q has two isomers X and Y. X decolorizes bromine water but it does not react with ammoniacal silver nitrate solution. Y forms a white precipitate with ammoniacal silver nitrate solution.

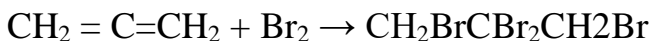
(i) Identify isomers X and Y (1 mark)

$\text{CH}_3\text{C}\equiv\text{CH}$ propyne

$\text{CH}_2 = \text{C}=\text{CH}_2$ prop-1,2-diene

(ii) Write an equation for the reaction between (1 mark)

X and bromine water



Y and ammoniacal silver nitrate solution. (1 mark)



8. Name the reagent(s) that can be used to distinguish between each of the following compounds. State what would be observed in each case.



(a) $\text{KI}(\text{aq})$ and $\text{KCl}(\text{aq})$ (1 ½ marks)



Reagent(s): aqueous $\text{Pb}(\text{NO}_3)_2$

Observations

$\text{KI}(\text{aq})$ – yellow ppt.

$\text{KCl}(\text{aq})$ – white precipitate

(b)  COOH and  OH (1 ½ marks)

Reagents	Observations	
	 COOH	 OH
Sodium hydrogen carbonate solution	Effervescence	No observable change
Neutral iron (III) chloride	Yellow ppt.	Purple solution

(c) $\text{PbCO}_3(\text{s})$ and $\text{BaCO}_3(\text{s})$

(1 ½ marks)

Reagent(s)

HCl

Observations

PbCO_3 – effervescence and white precipitate

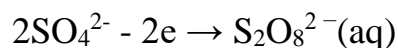
BaCO_3 – effervescence and colorless solution

9. The electrode potentials of $\text{S}_2\text{O}_8^{2-}(\text{aq}) \mid \text{SO}_4^{2-}(\text{aq})$ and $\text{I}_2(\text{aq}) \mid \text{I}^-(\text{aq})$ are +2.01V and +0.54V respectively.

(a) Write an equation for the reaction that occurs at the;

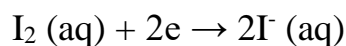
(i) anode

(1 mark)



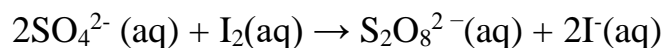
(ii) cathode

(1 mark)



(b) Write the overall cell reaction

(1 mark)



(c) (i) Calculate the e.m.f of the cell generated from the cell reaction in b(ii) above.

$$E_{\text{cell}} = E_{\text{RHE}} - E_{\text{LHE}}$$

$$= 0.54 - 2.01$$

$$= -1.47\text{V}$$

(ii) State whether the above cell reaction is feasible or not. Give a reason for your answer

(1 mark)

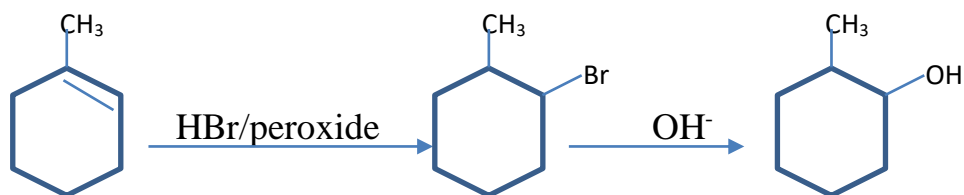
Not feasible, e.m.f is negative

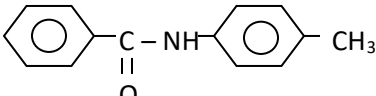
SECTION B: (54 MARKS)

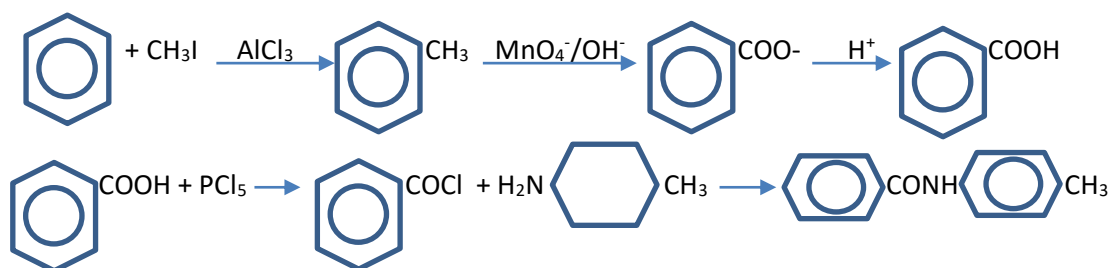
Answer only six questions from this section

10. Write equations to show how the following conversions can be effected. Indicate all reagents and conditions necessary for each reaction.

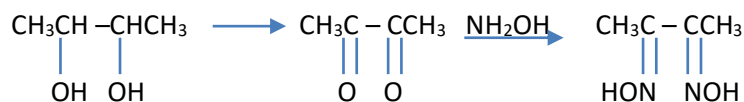
(a) 1 – methylcyclobutene to 2 – methyl cyclobutanol. (3 marks)



(b)  From benzene and bromomethane (4 marks)

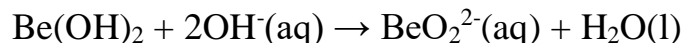


(c) Butane – 2,3 – diol to 2,3 –butane dionedioxime. (2 marks)



11. (a) $\text{Be}(\text{OH})_2$, $\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ are the hydroxides of group II elements. Briefly describe how the hydroxides react with ;

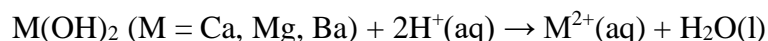
(i) sodium hydroxide solution (2 marks)



$\text{Mg}(\text{OH})_2$, $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ do not react with NaOH

(ii) hydrochloric acid solution (2 marks)

they react with hydrochloric acid to form salts



(b) The solubilities of the hydroxides of group II elements of the periodic table at 25°C are given below

Hydroxide	$\text{Be}(\text{OH})_2$	$\text{Mg}(\text{OH})_2$	$\text{Ca}(\text{OH})_2$	$\text{Sr}(\text{OH})_2$	$\text{Ba}(\text{OH})_2$
Solubility g/100g of water	Insoluble	0.002	0.150	0.900	4.000

(i) State and explain the trend in solubility of the hydroxides.

Solubility increases from $\text{Be}(\text{OH})_2$ down the group to $\text{Ba}(\text{OH})_2$

Down the group both lattice and hydration energies decrease but lattice energy decreases more rapidly than hydration energy.

(ii) Different masses of solid $\text{Ca}(\text{OH})_2$ and $\text{Ba}(\text{OH})_2$ containing the **same number of moles** were separately shaken with the same volume of water at 25°C.

Identify the solution with higher pH value. Give a reason for your answer

(1 ½ marks)

$\text{Ba}(\text{OH})_2$ because it is more soluble than $\text{Ca}(\text{OH})_2$

12. (a) The partition coefficient of ammonia between water and trichloromethane at 25°C is 25.0,
 (i) Define the term partition coefficient. (1 ½ marks)

It is a ratio of solubility of a solute into two immiscible solvent at equilibrium

- (ii) State two conditions under which the partition coefficient ($K_D = 25.0$) is valid other than constant temperature. (1 mark)

- The solute should be in the same molecular conditions in both solvents
- None of the solvent should be saturated

(b) 25cm³ of 0.0056M nickel (II) sulphate solution were added to an **equal** volume of ammonia solution at 25°C. The mixture was shaken with 50cm³ of trichloromethane and allowed to stand until equilibrium was established. The trichloromethane layer required 32cm³ of 0.0025M hydrochloric acid for complete neutralization. 7.060cm³ of the aqueous layer required 20cm³ of 0.02M hydrochloric acid. Nickel (II) ions react with ammonia according to the equation;

$$\text{Ni}^{2+}(\text{aq}) + n\text{NH}_3(\text{aq}) \longrightarrow [\text{Ni}(\text{NH}_3)_n]^{2+}(\text{aq})$$

 (KD of ammonia between water and trichloromethane is 25)

Calculate

- (i) Molar concentration of the free ammonia in the aqueous layer. (2 ½ marks)

Moles of hydrochloric acid that reacted with ammonia in trichloromethane
 1000cm³ contain 0.0025moles

32cm³ contain $\frac{0.0025 \times 32}{1000} = 0.00008\text{moles}$

Let the moles of free ammonia in water be x

$$K_D = \frac{\frac{x}{50}}{\frac{0.00008}{50}} = 25$$

x = 0.002moles

moles of HCl 20cm³ of 0.02M that reacted with moles of ammonia in
 7.060cm³ of aqueous solution
 1000cm³ contain 0.02 moles

$$20\text{cm}^3 \text{ contain } \frac{0.02 \times 20}{1000} = 0.0004\text{moles}$$

Moles of ammonia in 7.060cm^3 of aqueous solution

= moles of HCl

= 0.0004moles

$$\begin{aligned} \text{Moles of ammonia in } 50\text{cm}^3 \text{ of aqueous solution} &= \frac{0.0004 \times 50}{7.060} \\ &= 0.00283\text{moles} \end{aligned}$$

(ii) Molar concentration of ammonia that reacted with nickel (II) ions (2 marks)

$$\begin{aligned} \text{Moles of ammonia that complexed with Ni}^{2+}(\text{aq}) &= 0.00283 - 0.002 \\ &= 0.00083 \text{ moles} \end{aligned}$$

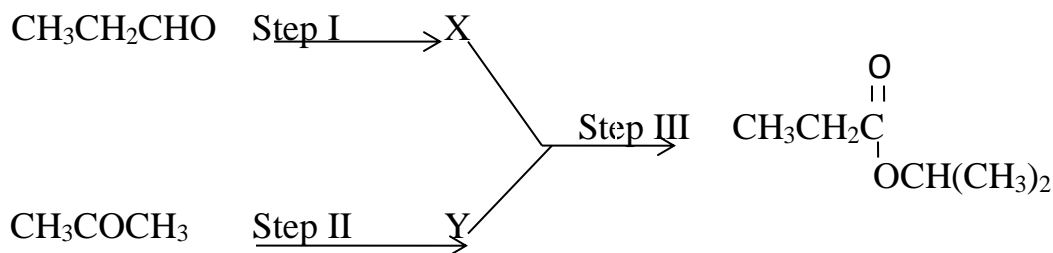
(iii) Use your answer b (II) above to determine the value of n in $[\text{Ni}(\text{NH}_3)_n]^{2+}$

$$\begin{aligned} \text{Moles of Ni}^{2+} &= \frac{0.0056 \times 25}{1000} = 0.00014 \text{ moles} \\ n &= \frac{0.00083}{0.00014} = 6 \end{aligned}$$

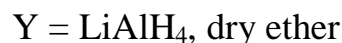
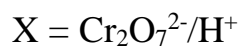
13. (a) Describe a simple chemical test to distinguish between CH_3COCH_3 and $\text{CH}_3\text{CH}_2\text{CHO}$ (2 marks)

Reagent(s)	Observation	
	CH_3COCH_3	$\text{CH}_3\text{CH}_2\text{CHO}$
Hot Fehling's solution	No observable change	Red ppt.
Ammoniacal silver nitrate	No observable change	Silver mirror
I_2/OH^-	Yellow ppt.	No observable change

(b) Compound Z can be synthesized by the reaction between X and Y as shown below



(i) Identify compounds X and Y



(ii) Name the type of reaction that occurs in steps I and II (1 mark)

Step I: oxidation

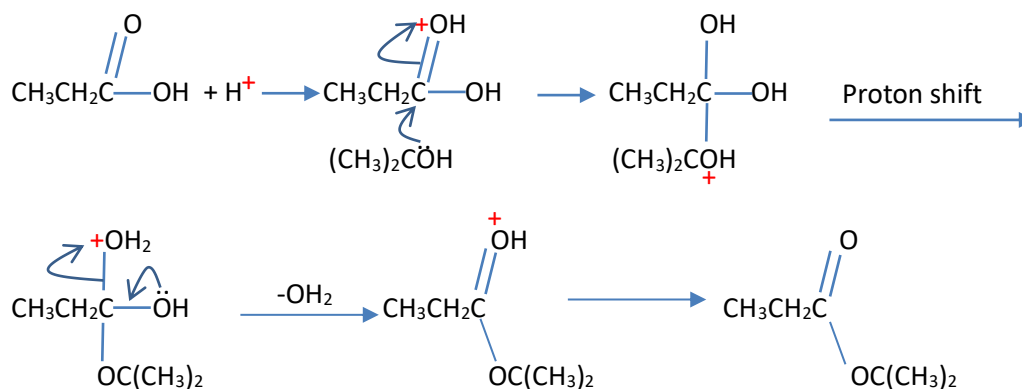
Step II: reduction

(c) Identify the reagents and state the conditions necessary for the reaction in

(i) step I: heat (1 mark)

(ii) step III: mineral acid (2 marks)

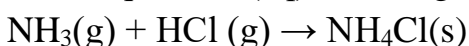
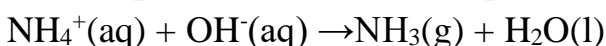
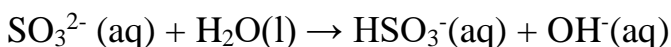
(d) Write the mechanism for the reaction that occurs in step III



14. Explain each of the following observations.

(a) An aqueous solution sodium sulphite when mixed with ammonium chloride produce a colorless gas that forms dense white fumes with concentrated hydrochloric acid on warming. (3 marks)

Sulphite ions hydrolyze in solution to form hydroxide ions that react with ammonium chloride to form ammonia. Ammonia forms a dense white fumes with hydrochloric acid



(b) The acid dissociation constant (K_a) of chloric (I) acid is lower than the K_a for chloric (VII) acid at 25°C, (2 marks)

Oxygen atoms are more electronegative than chloride atoms, oxygen atoms withdraw electrons from hydrogen atom in chloric acids and weaken the bond between hydrogen and oxygen to liberate H^{+} . the more oxygen atoms attached to chlorine atom, the greater the effect. Thus chloric acid (VII) with four oxygen atom is a stronger acid than chloric acid I.

(d) When refluxed with aqueous potassium hydroxide followed by acidified silver nitrate solution. Chloroethane forms a white precipitate which chlorobenzene gives no observable change. (4 mark)

The bond between chloride atom and carbon on chloromethane is weak because it is localized and can easily be substituted by hydroxide ions, the released chloride ions form a white precipitate with silver ions. The bond between chlorine atom and benzene is very strong because the lone pairs on chlorine atoms are delocalized with electrons in the ring thus chlorine ion cannot be easily removed.

15. HF, HCl, HBr and HI are hydrides of group VII elements

(a) Explain the variation in boiling points of the hydrides. (3 marks)

The boiling points increase generally increase from $\text{HCl} < \text{HBr} < \text{HI}$ due to increase in molecular mass. The boiling point of HF is abnormally high

because F has very high electronegativity that HF forms very strong hydrogen bonds that need high temperature to break.

(b) Aqueous solutions of the hydrides of the same concentration at constant temperature have different pH values.

- (i) Identify the hydride whose solution in water has the lowest pH (1 mark)
HF
- (ii) Give a reason for your answer in b (i) above. (2 marks)
H-F bond is very strong that it hardly break to release H^+

(c) Write an equation for the reaction between

- (i) The hydride of fluorine and excess silicon (IV) oxide (1 mark)
 $SiO_2(s) + 6HF(aq) \rightarrow H_2SiF_6(aq) + 2H_2O(l)$
- (ii) Potassium manganate (VII) solution and the hydride of chlorine. (1 mark)
 $2KMnO_4(aq) + 16HCl(aq) \rightarrow 2KCl(aq) + 2MnCl_2(aq) + 5Cl_2(g) + 8H_2O(l)$
- (iii) Concentrated sulphuric acid and the hydride of bromine. (1 mark)
 $H_2SO_4(aq) + 2HBr(aq) \rightarrow Br_2(aq) + SO_2(g) + 2H_2O(l)$

16. Lead (II) iodide is a sparingly soluble salt.

- (a) Write an equation for the solubility of lead (II) iodide in water (1 mark)
 $PbI_2(aq) \leftrightarrow Pb^{2+}(aq) + 2I^-(aq)$
- (b) The concentration of a saturated solution of lead (I) iodide at 40°C is 0.122g per 100cm³ of solution
State whether a mixture of 50cm³ of 0.01M lead (II) nitrate and 50cm³ of 0.001M potassium iodide forms a yellow precipitate of lead (II) iodide or not.
(show your working clearly) (6 marks)

$$\text{Concentration } PbI_2 \text{ in g/l} = \frac{0.122}{100} \times 100 = 1.22g$$

$$\text{Formula mass of } PbI_2 = 207 + 127 \times 2 = 461$$

$$\text{Molarity of } PbI_2 = \frac{1.22}{461} = 0.00264 \text{ mol dm}^{-3}$$

$$K_{sp} = (0.00264)(0.00264 \times 2)^2 = 7.4 \times 10^{-8} \text{ mol}^3 \text{ dm}^{-9}$$

$$\text{Concentration } Pb^{2+} \text{ in resultant solution} = 0.01/2 = 0.005M$$

Concentration of I^- in resultant solution $= 0.001/2 = 0.0005M$

$$\begin{aligned}\text{Ionic equilibrium of resultant solution} &= (0.005)(0.0005)^2 \\ &= 1.25 \times 10^{-9} \text{ mol}^3\text{dm}^{-9}\end{aligned}$$

Precipitation does not occur because ionic product is less than solubility product.

(c) The saturated solution of lead (II) iodide of concentration 0.122g per 100cm³ of solution was heated to 60°C in a closed system

(i) State whether the solution remains saturated at 60°C (½ mark)
It becomes unsaturated

(ii) Give a reason for your answer. (1 ½ marks)
Solubility of lead iodide increases with temperature.

17. A mixture of methanol and water at 50°C is an ideal solution. The partial vapour pressure of methanol in the vapour above the solution varies according to Raoult's law as shown in the table below.

Partial vapour pressure of methanol (mmHg)	40.0	100.0	200.0	260.0	320.0
Mole fraction of methanol in solution	0.10	0.25	0.50	0.65	0.80

(a) (i) Define the term ideal solution. (1 mark)

It is a solution which obeys Raoult's law, it has uniform forces of attraction between like and unlike molecules.

(ii) State Raoult's law (1 mark)

State that the partial pressure of a component in a mixture is a product of mole fraction and its vapor pressure.

(b) Calculate vapor pressure of pure methanol and water at 50°C.

(The composition of methanol in the vapour is 50% when its mole fraction in solution is 0.19)

(i) Saturated vapour pressure of methanol at 50°C. (1 mark)

Let the vapor pressure of methanol be P_m

$$0.1P_m = 40$$

$$P_m = 400\text{mmHg}$$

(ii) Saturated vapour pressure of water at 50°C

Let the vapor pressure of water be P_w

$$\frac{0.19 \times 400}{0.19 \times 400 + (0.81P_w)} = \frac{50}{100}$$

$$P_w = 94\text{mmHG}$$

(c) Compare the volatility of methanol and water at 50°C. Give a reason for your answer. (1 mark)

Methanol is more volatile than water because it has higher vapor pressure at the same temperature.

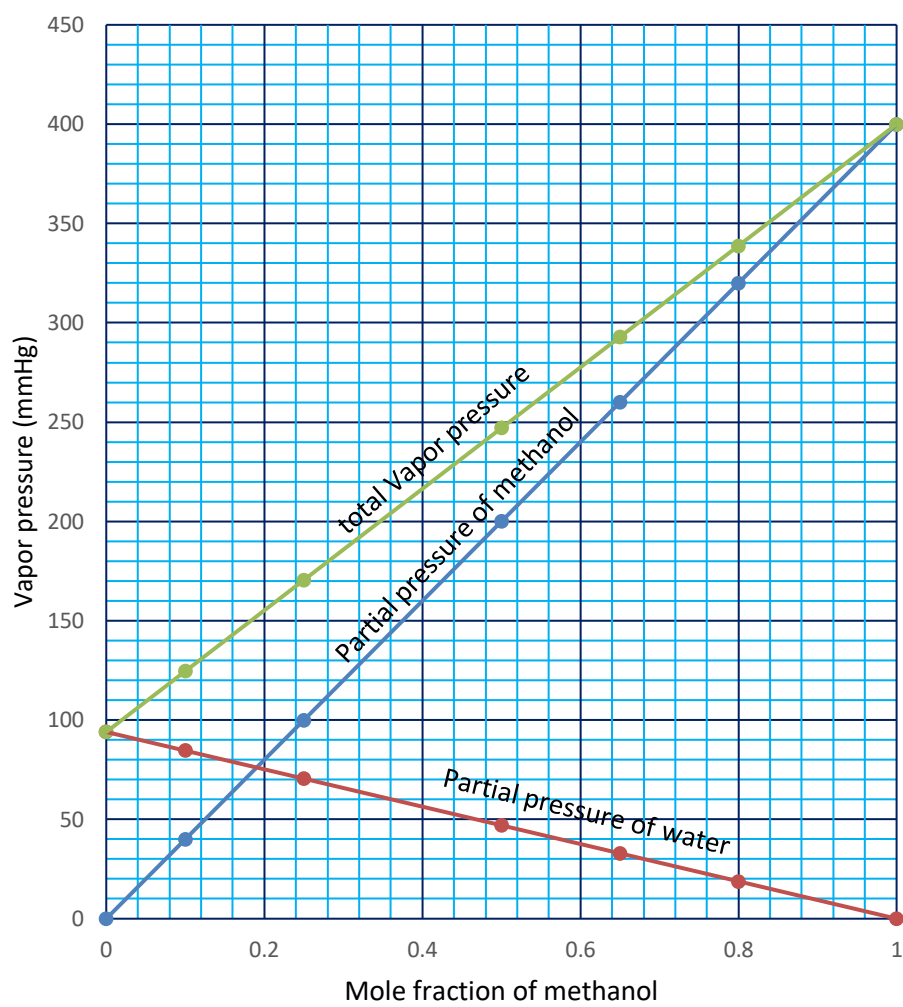
(d) On the same axes, plot a graph of;

(i) Vapour pressure of methanol

(ii) Total vapour pressure above the solution against mole fraction of methanol.

Mole fraction of methanol in solution	0	0.10	0.25	0.50	0.65	0.80	1
Partial vapour pressure of methanol (mmHg)	0	40.0	100.0	200.0	260.0	320.0	400
Partial pressure of water	94	84.6	70.5	47	32.9	18.8	0
Total vapor pressure	94	124.6	170.5	247.0	292.9	338.8	400

Vapor pressure against mole fraction of methanol



THE PERIODIC TABLE

1		2												3	4	5	6	7	8	
1 H 1.0																		1 H 1.0	2 He 4.0	
3 Li 6.9		4 Be 9.0												5 B 10.8		6 C 12.0	7 N 14.0	8 O 16.0	9 F 19.0	10 Ne 20.2
11 Na 23.0		12 Mg 24.3												13 Al 27.0		14 Si 28.1	15 P 31.0	16 S 32.1	17 Cl 35.4	18 Ar 40.0
19 K 39.1	20 Ca 40.1	21 Sc 45.0	22 Ti 47.9	23 V 50.9	24 Cr 52.0	25 Mn 54.9	26 Fe 55.8	27 Co 58.9	28 Ni 58.7	29 Cu 63.5	30 Zn 65.7	31 Ga 69.7	32 Ge 72.6	33 As 74.9	34 Se 79.0	35 Br 79.9	36 Kr 83.8			
37 Rb 85.5	38 Sr 87.6	39 Y 88.9	40 Zr 91.2	41 Nb 92.9	42 Mo 95.9	43 Tc 98.9	44 Ru 101	45 Rh 103	46 Pd 106	47 Ag 108	48 Cd 112	49 In 115	50 Sn 119	51 Sb 122	52 Te 128	53 I 127	54 Xe 131			
55 Cs 133	56 Ba 137	57 La 139	72 Hf 178	73 Ta 181	74 W 184	75 Re 186	76 Os 190	77 Ir 192	78 Pt 195	79 Au 197	80 Hg 201	81 Tl 204	82 Pb 207	83 Bi 209	84 Po (209)	85 At (210)	86 Rn (222)			
87 Fr (223)	88 Ra (226)	89 Ac (227)																		
			57 La 139	58 Ce 140	59 Pr 141	60 Nd 144	61 Pm (145)	62 Sm 152	63 Eu 150	64 Gd 152	65 Tb 159	66 Dy 162	67 Ho 165	68 Er 167	69 Tm 169	70 Yb 173	71 Lu 175			
			89 Ac (227)	90 Th 232	91 Pa 231	92 U 238	93 Np 237	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf 251	99 Es (254)	100 Fm (257)	101 Mv (256)	102 No (254)	103 Lw			

1. $\frac{1}{H}$ - indicates Atomic number.
2. $\frac{H}{1.0}$ - indicates relative Atomic number.

END.