G.C.E. (A/L) Examination
2000 August
Chemistry II / Three hours

Important : This question paper consists of four sheets. Put the sheets together in the correct order of pages before answering

Use of calculators is not allowed.

This question paper consists of three parts A, B and C. The time allotted for all three parts is three hours.

PART A - STRUCTURED ESSAY

Answer all the questions.
Write your answer in the space provided below each question. Please note that the space provided is sufficient for the answer and that extensive answers are not expected.

PART B AND PART C - ESSAY

Answer four questions selecting two questions only from each part.
Use the paper supplied for this purpose.
At the end of the time allotted for this paper, tie the three parts A, B, and C together so that part A is on top and hand them over to the supervisor.
You are permitted to remove only Parts B and C of the question paper from the Examination Hall.

Universal gas constant, R = 8.314 $JK^{-1}mol^{-1}$

PART A - STRUCTURED ESSAY

Answer all four questions. Each question carries 10 marks.

1. (a) Figure 1 shows the first five electronic energy levels of the H atom (n = 1,2,3,4,5)

Figure 2 shows six lines of the emission electronic spectrum of the H atom.

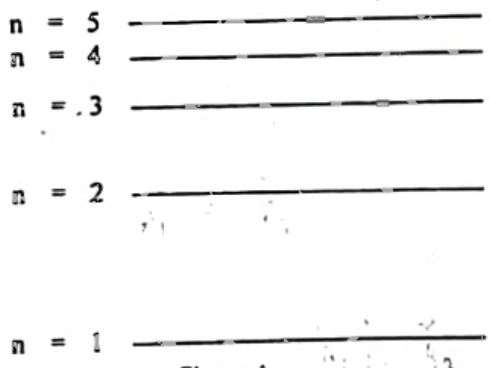


Figure 1

Figure 2

A_1, A_2 and A_3 are the first three lines belonging to the same series in this emission spectrum.
B_1, B_2 and B_3 are the first three lines of the subsequent series in the same emission spectrum.

(i) Draw six arrows between the energy levels in figure 1 to show the electronic transitions corresponding to the six spectral lines in figure 2.

(ii) Clearly label in figure 1 these arrows appropriately as A_1, A_2, A_3, B_1, B_2 and B_3.

(iii) Strike off the inappropriate word, within the bracket, in the following sentence.
The frequencies of the spectral lines {increase/ decrease} from A_1 to B_3.

(3.0 marks)

(b) (i) L and M are two p-block elements belonging to successive periods in the same group of the Periodic Table.

The highest chloride formed by L is LCl_3.

M forms MCl_3 and another chloride in a higher oxidation state.

Identify L and M below :

L is ..... M is .....

(ii) LCl_3 and MCl_3 are hydrolysed easily. On hydrolysis, LCl_3 gives a base and an acid while MCl_3 gives two acids.

Identify below the products of the hydrolysis by name :

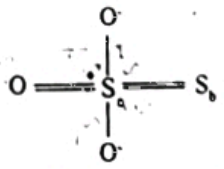
From LCl_3 hydrolysis .....and .....

From MCl_3 hydrolysis ..... and .....

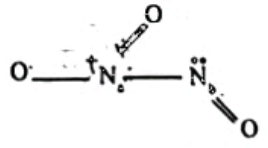
Using **chemical** symbols, write below separate **balanced** chemical equations for the hydrolysis of these two chlorides :

(3.8 marks)

(c) Write down separately in the relevant box below, the oxidation number and the valency of each of the two s atoms (labelled S_a and S_b) and the two N atoms (labelled N_a and N_b) in the structures indicated below :



atom	oxidation number	valency
S_a		
S_b		



atom	oxidation number	valency
N_a		
N_b		

(3.2 marks)

02. (a) When an Mn^{2+} salt is heated with PbO_2 in acid medium, a purple coloured solution is formed and PbO_2 is converted to Pb^{2+}

(i) Write down below the relevant balanced ionic half reactions :

.....

.....

(ii) Write down below the stoichiometry between Mn^{2+} and PbO_2 :

$Mn^{2+} : PbO_2$ = ... : .....

(2.5 marks)

(b) Calcium oxalate is converted to calcium carbonate, on heating, according to the equation

$$CaC_2O_4(s) \rightarrow CaCO_3(s) + CO(g)$$

Incomplete thermal decomposition of 2.00 g of pure $CaC_2O_4(s)$ yielded 1.78 g of the product. This product contained $CaCO_3$ and undecomposed CaC_2O_4. Calculate below the mass of undecomposed CaC_2O_4 remaining in the product.

(Relative atomic masses : Ca = 40 ; O = 16 ; C = 12)

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(2.5 marks)

(c) A and B are two fully miscible volatile liquids. On mixing, A and B form the ideal binary solution, AB, in which the mole fraction of A is x_A. The total vapour pressure of this solution is P_{AB} when the partial vapour pressures of A and B are P_A and P_B respectively.

R and S are also two fully miscible volatile liquids. On mixing, R and S form the binary solution, RS, in which the mole fraction of R is X_R. The forces of attraction between the molecules of R and S are slightly stronger than the forces of attraction between either R molecules or S molecules. The total vapour pressure of this solution is P_{RS} when the partial vapour pressures of R and S are P_R and P_S respectively.

At a given temperature T, the saturation vapour pressures of the pure liquids A, B, R and S are respectively P^o_A, P^o_B, P^o_R and P^o_S

At all temperatures, $P^o_A = P^o_R$; $P^o_B = P^o_S$; $P^o_A > P^o_B$

Using the above data, answer all the parts (i) - (iii)

(i) Prove below that at the temperature T,

$P^o_{AB} = P^o_B + x_A (P^o_A - P^o_B)$

.....

.....

.....

.....

State below the important assumption you made in proving the above equation.

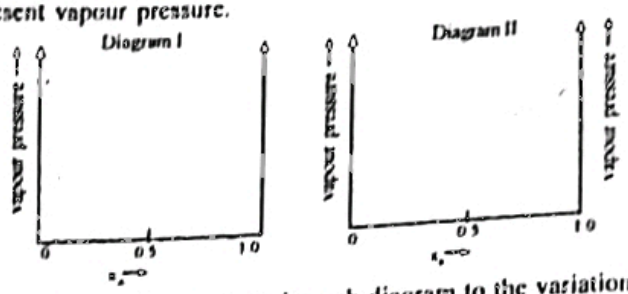
.....

(ii) In the diagrams given, sketch graphs to show clearly, the following variations

(I) the variation of each of the vapour pressures P_A, P_B and P_{AB} with x_A at the given temperature T on diagram I.

(II) the variation of each of the vapour pressures P_R, P_S and P_{RS} with x_R at the given temperature T on diagram II.

N.B : Use identical scales for the vertical axes in diagrams I and II to represent vapour pressure.



Label the graphs you drew in each diagram to the variations. Mark on the relevant axes, the points corresponding to P^o_A, P^o_B, P^o_R and P^o_S

(iii) Complete the passage given below by filling the blanks correctly with appropriate words / letters :

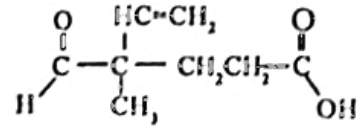
When the temperature of a solution is increased, there is a / an ..... in its vapour pressure. We say that the solution boils when its total vapour pressure is equal to the ..... pressure. At the normal boiling point, this pressure is equal to the ..... pressure.

The normal boiling point of pure liquid ..... is equal to the normal boiling point of pure liquid S. The normal boiling points of each of the pure liquids ..... and ..... are less than the normal boiling point of pure liquid B.

The solution RS shows a ..... deviation from ideal behaviour. The total vapour pressure of an equimolar solution of RS is ..... than the total vapour pressure of an equimolar solution of AB at any given temperature. The normal boiling point of an equimolar solution of RS will therefore take a ..... value than that of an equimolar solution of AB.

(5.0 marks)

(a) Write down the name of the compound with the following structure, in accordance with the IUPAC system of nomenclature.



.....

(1.5 marks)

(b) A compound Y has the molecular formula $C_3H_6O_3$. Calculate the percentages by mass of carbon, hydrogen and oxygen present in Y. (relative atomic masses : H = 1; C = 12 ; O = 16)

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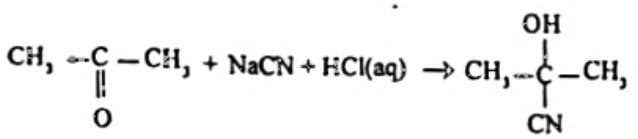
(1.5 marks)

(c) Consider the reaction of propanone with hydrogen cyanide :



Strike off the inappropriate words / symbols within each bracket in the statements (i), (ii), (iii) and (iv), given below :

In this reaction

(i) propanone undergoes an / a
{Electrophilic / Nucleophilic} {Addition / Substitution } reaction

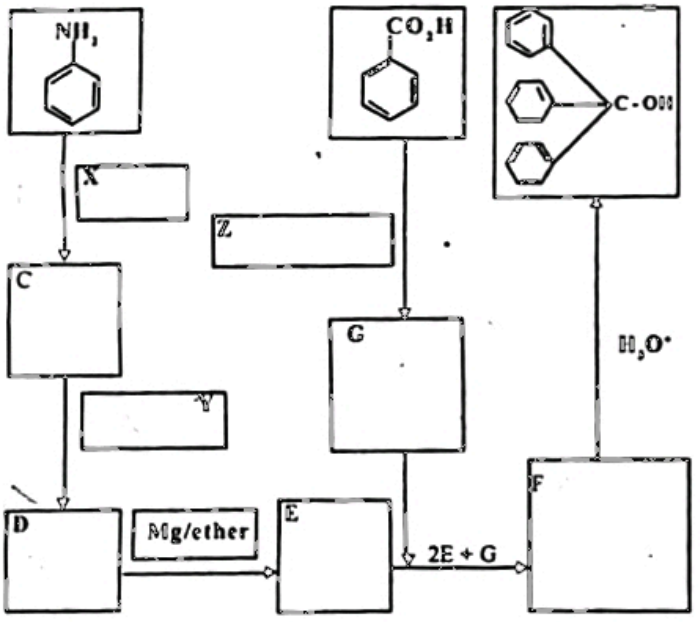
(ii) the OH group in the product arises from the reaction of
$>C=O$ with
{Cl^- followed by H_2O/ H_2O/ H^+}

(iii) the $>C=O$ carbon atom of propanone reacts as a / an
{Electrophile / Nucleophile / Free radical}

(iv) the hybridisation of the carbon atom of the carbonyl group of propanone changes from
{sp / sp^2 / sp^3} to {sp / sp^2 / sp^3}

(3.0 marks)

(d) Consider the reaction scheme represented through the boxes below for the synthesis of triphenyl methanol



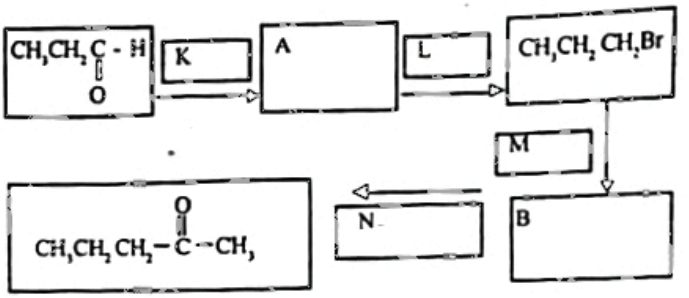
(i) Write the structural formulae of the compounds C,D,E,F and G in the relevant boxes.

(ii) Write the reagents and conditions corresponding to X in the relevant box.

(iii) Write the reagents corresponding to Y and Z in the relevant boxes.

(4.0 marks)

04. (a) Consider the reaction scheme represented through the boxes below for the synthesis of pentan - 2 - one.



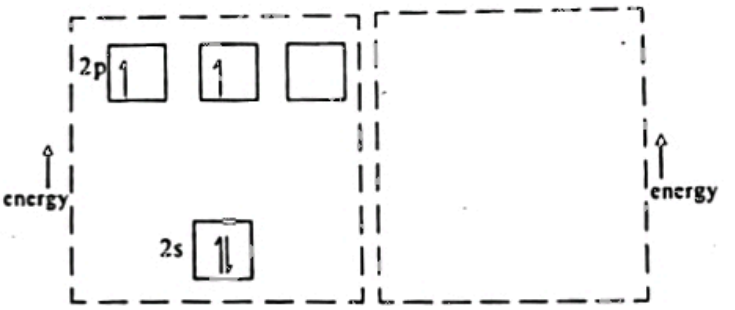
(i) Write the structural formulae of the compounds A and B in the relevant boxes.

(ii) Write the reagents corresponding to K, L, M and N in the relevant boxes.

(3.5 marks)

(b) Consider the state of hybridisation of the carbon atoms in the ethene molecule, C_2H_4.

Given below in Cage A is the schematic representation of the electron distribution in the outer shell of the ground state carbon atom, where each box represents an orbital.
N.B. The vertical position of the boxes represents the relative energy levels of the orbitals.



Cage A : Ground State of carbon atom.

Cage B : State of hybridisation of a carbon atom in C_2H_4

(i) Using boxes similar to those in Cage A, draw in Cage B, the outer orbitals of a hybridised carbon atom in ethene.
Label the boxes to indicate the types of orbitals repre sented by them.
Indicate, as in Cage A, the electron distribution in the boxes in Cage B.

N.B. In drawing these boxes in Cage B, pay attention to their vertical position with respect to the boxes in Cage A.

(ii) Complete the following sentences by filling in the blanks :-

(I) The electron in the ..... orbital of carbon is involved in the formation of the π bond in C_2H_4.

(II) The electrons in the ..... orbitals of carbon are involved in the formation of C-H bonds in C_2H_6.

(2.5 mrarks)

(c) Compounds P, Q and R all have the same molecular formula C_5H_{10}. All three compounds exhibit optical isomerism. However, none of them is a geometrical isomer or an optical isomer of any of the others.

The three compounds P, Q and R, undergo catalytic hydrogenation to yield the same compound S with molecular formula C_5H_{12}. S exhibits optical isomerism.

(i) Write in the relevant box below, the possible **structural formula** for each of the compounds P, Q, R and S.

Compound	Structural formula
P	
Q	
R	
S	

(ii) One out of the three compounds P, Q, R, exhibits geometrical isomerism.
Draw the structures of the two geometrical isomers of this compound in the cages below.

Geometrical Isomer I	Geometrical Isomer II

(4.0 marks)

PART B - ESSAY

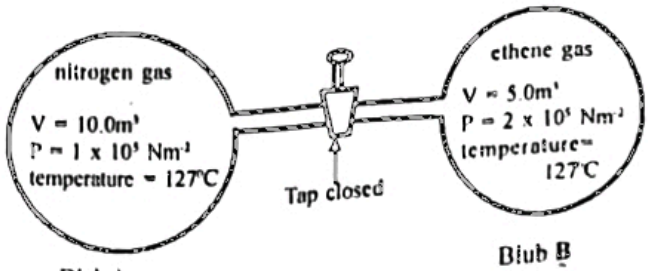
Answer two questions only. Each question carries 15 marks.

05. (a) (i) Write down Avogadro Law.
To what type of system would this law apply?

(ii) Starting from the equation $PV = \frac{1}{3}mNC^{\bar{2}}$, derive Avogadro Law.

(3.5 marks)

(b) Bulbs A and B are connected through a tap. The tap is initially closed. A contains only gaseous nitrogen and B contains only gaseous ethene. Each gas exists under the conditions indicated in the diagram given below.



Blub A Blub B

The tap is opened and the gases in the two blubs are allowed to mix freely and completely. However, the temperature of each bulb and its gaseous contents is kept unchanged at its initial value.

Assuming that gases nitrogen and ethene behave as ideal gases, and that the volume of the tap can be neglected, calculate the following in **SI units** :

(i) the number of moles of ethene gas initially present in bulb B

(ii) the number of moles of nitrogen gas initially present in bulb A

(iii) the total amount of gases present in the two bulbs.

(iv) the final pressure of the gaseous mixture in bulb B.

(v) the partial pressure of ethene gas in the final gaseous mixture in bulb A.

(6.0 marks)

(c) The weak acid HA dissolves in water. HA also dissolves in the organic liquid B but HA does not undergo either association or dissociation in this solution. B and water are completely immiscible with each other.

100.0 cm^3 of a 0.50 mol dm^{-3} aqueous solution of HA and 50.0 cm^3 of liquid B were placed in a separating funnel, shaken vigorously several times and the system was allowed to reach equilibrium at 27°C. The two liquids separated out into two immiscible layers and finally the pH of the aqueous layer was found to be 4.0.

The dissociation constant of HA at 27°C is 1.0×10^{-7} mol dm^{-3}.

Calculate the following :

(i) the concentration of hydrogen ions in the aqueous layer.

(ii) the concentration of undissociated HA in the aqueous layer.

(iii) the concentration of undissociated HA in the organic layer B.

(iv) the partition coefficient of HA between water and B, at 27°C.

(v) the degree of dissociation, α, of HA in the aqueous layer, at 27°C.

(5.5 marks)

6. (a) (i) Ag_2CrO_4 is an ionic compound sparingly soluble in water. Write down the **balanced** chemical equation for the equilibrium that exists between dissolved Ag_2CrO_4 and Ag_2CrO_4 (s) in a saturated aqueous solution of Ag_2CrO_4.

Using this equation, derive the expression for the solubility product, K_{sp}, of Ag_2CrO_4 (s).

(ii) K_{sp} of Ag_2CrO_4 (s) at 30°C is 4.0×10^{-12} mol^3 dm^{-9}. Calculate the solubility of Ag_2CrO_4 (s) in water at 30°C.

(iii) Calculate the maximum mass of Ag_2CrO_4 (s) that can be dissolved in 500.0 cm^3 of 0.20 mol dm^{-3} aqueous $AgNO_3$ solution at 30°C.

(Relative atomic masses : Ag = 108 ; Cr = 52; O = 16)

N.B. : The physical state corresponding to each chemical species appearing in your answers should be clearly indicated.

(5.5 marks)

(b) You are provided with the following data obtained at 25°C

$$E^\circ_{Mg^{2+}(aq)/\,Mg(s)} = -2.37V$$

$$E^\circ_{Pb^{2+}(aq)/\,Pb(s)} = -0.126\ V$$

(i) Calculate the electromotive force (e.m.f) at 25°C of an electro-chemical cell comprising a Pb^{2+} (aq) / Pb(s) electrode and a Mg^{2+}(aq) / Mg(s) electrode operating under standard conditions.

(ii) Using the conventional notation, write down the above mentioned electro-chemical cell.

(iii) Write down **balanced** chemical equations for the half-celll reactions that take place at the cathode and at the anode, when a current is drawn from the above mentioned electro-chemical ceil.

(3.5 marks)

(c) The following equilibrium exists in the gas phase above a temperature of 100°C.

$$A(g) + B(g) \rightleftharpoons P(g) + Q(g)$$

A glass bulb is filled with an equimolar mixture of gases A and B only. The bulb and its contents are heated to a temperature of 200°C (Experiment I). After equilibrium is reached, the mole fraction of P, x_p, in the bulb is found to be 0.2.

Thereafter, the temperature of the bulb and the contents is increased to 400°C and the system is allowed to reach equilibrium at this temperature. The mole fraction of A, x_A, in this equilibrium mixture is found to be 0.2.

(i) Calculate the equilibrium mole fractions of B, A and Q at 200°C.

(ii) Calculate K_p for the equilibrium at 200°C.

(iii) Calculate the equilibrium mole fractions of B, P and Q at 400°C.

(iv) Giving reasons, deduce from the above data and calculations, the sign of the enthalpy change of the forward reaction.

(v) Name the principle that can be used to predict the above equilibrium behaviour.

(vi) If experiment I at 200°C was repeated at the same temperature in a bulb whose volume is half that used earlier but using the same initial amounts of A and B as before, what would be the composition of the equilibrium mixture?

(6.0 marks)

7. (a) When 0.025 mol Na_2CO_3(s) was added to 25.0 cm^3 of 3.00 mol dm^{-3} HCl solution at room temperature, the temperature of the solution was observed to increase by 8.0°C. The specific thermal capacity of the resulting solution is 5000 Jkg^{-1}K^{-1} and its density is 1000 kg m^{-3}

(i) Calculate the heat liberated during the above mentioned reaction.

Assume that **all** the heat liberated by the reaction is used only to raise the temperature of the solution and that there is no loss of heat or change of volume in the solution whatsoever.

(ii) Calculate the enthalpy of neutralisation, **per mole of HCl reacted.**

State **any other** assumption you make in this calculation.

(iii) The enthalpy change, ΔH, for the reaction,

$$NaHCO_3(s) + HCl(aq) \rightarrow NaCl(aq) + CO_2(g) + H_2O\ (l)$$

Carried out under the same conditions as the above mentioned reaction, is -25.5 kJ mol^{-1}

Calculate the enthalpy change, ΔH for the reaction,

$$2\ NaHCO_3(s) \rightarrow Na_2CO_3(s) + H_2O\ (l) + CO_2(g)$$

carried out under the same conditions.

(5.5 marks)

(b) You are provided with the following thermo-chemical data :

Standard enthalpy of formation,
ΔH°_f, of KCl(s) = −437 kJ mol^{-1}

Standard enthalpy of sublimation,
ΔH°_s, of K(s) = +89 kJ mol^{-1}

Standard dissociation enthalpy,
ΔH°_D, of Cl_2(g) = +244 kJ mol^{-1}

Standard enthalpy of first ionisation,
ΔH°_1, of K(g) = +418 kJ mol^{-1}

Standard enthalpy of electron gain,
$\Delta H^\circ_{E.G.}$, of Cl(g) = −349 kJ mol^{-1}

Calculate the standard lattice enthalpy, ΔH°_L, of KCl (s)

(5.5 marks)

(c) (i) O_3(g) reacts with NO(g) producing NO_2(g) and O_2(g) in a single step reaction. State briefly, but as completely as possible, two essential requirements for a collision between an O_3(g) molecule and a NO(g) molecule in order that the above reaction may occur.

(ii) The decomposition of H_2O_2 in aqueous solution produces H_2O(l) and O_2(g).

The rate of decomposition is increased by the addition of OH^- ions to the solution.

Describe how you would experimentally establish that the role of OH^- ions in the above process is that of a catalyst.

(iii) The rate of reaction

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

can be expressed in the form,

$$\text{rate} \propto [Br^-(aq)]^x [BrO_3^-(aq)]^y [H^+(aq)]^z$$

where, $[Br^-(aq)]$ $[BrO_3^-(aq)]$ and $[H^+(aq)]$ are the concentrations of $Br^-(aq)$, $BrO_3^-(aq)$ and $H^+(aq)$ ions respectively in the reaction mixture at the time the rate of the reaction is measured.

Column 4 in the table below gives the amounts of $Br_2(aq)$ formed per unit volume of the reaction mixture per unit time (at a given temperature), when the concentrations of $Br^-(aq)$, $BrO_3^-(aq)$ and $H^+(aq)$ ions are as given in the columns 1,2 and 3, respectively.

1	2	3	4
$[Br^-(aq)]$/ mol dm^{-3}	$[BrO_3^-(aq)]$/ mol dm^{-3}	$[H^+(aq)]$ mol dm^{-3}	$Br_2(aq)$/formed. mol $dm^{-3}s^{-1}$
0.010	0.200	0.200	2.40×10^{-4}
0.040	0.200	0.200	9.60×10^{-4}
0.020	0.400	0.200	9.60×10^{-4}
0.020	0.400	0.100	2.40×10^{-4}

Calculate the values of x,y and z in the expression given above.

All necessary steps of the calculation must be given.

(5.5 marks)

PART C - ESSAY

Answer two questions only. Each question carries 15 marks.

08. (a) (i) Write the complete electronic configuration of the element 'X' having the atomic number 26.

(ii) Write doen two common stable oxidation states for 'X'

(iii) 'X' in one oxidation state is present in the aqueous solution A while 'X' is present in its other oxidation state in the aqueous solution B. Give one chemical test to distinguish between the two solutions A and B.

(3.0 marks)

(b) (i) Draw the "cross and dot" diagrams to show the arrangement of valence electrons in the outermost shell of each atom in each of the following molcules :

$POCl_3$

HNO_2

(ii) State the shape of each of the following species :

ClO_4^-

PH_3

(4.0 marks)

(c) (i) Write the chemical formula of pentaamminechlorocobalt (III) bromide.

(ii) Name the compound with the following formula in accordance with the IUPAC sistem of nomenclature :

$K_2Fe\ [Fe(CN)_6]$

(2.0 marks)

(d) The following observations were made with a soluble salt of a metal M :

(i) The salt when dissolved in water gave a blue solution

(ii) When excess ammonia was added to an aqueous solution of the salt, a deep blue solution was obtained

(iii) When the salt was dissolved in excess concentrated HCl, a yellow solution was obtained.

(iv) When the solution from (iii) above was diluted with water and reacted with H_2S, it gave a black precipitate.

Identify M.

Write down the chemical equations relevant to each of the above observations.

(3.0 marks)

(e) You are provided with several samples of a solution containing Cr^{3+}, Zn^{2+} and Ni^{2+} cations.

How would you experimentally confirm the presence of each of the cations in the solution?

(2.0 marks)

(f) Explain briefly why the boiling point of H_2O is higher than that of H_2S.

(1.0 marks)

09. (a) Give one balanced chemical equation in each case to show the

(i) reducing action of H_2S

(ii) oxidising action of H_2S

(iii) reducing action of NH_3

(iv) oxidising action of NH_3

(2.0 marks)

(b) (i) Draw the structure of the repeat unit for each of the forms, cis - polyisoprene and trans-polyisoprene.

(ii) Which one of these two forms of polyisoprene is present in the latex obtained form the rubber tree?

(iii) Giving reasons, indicate which of these two forms of polyisoprene is more elastic.

(iv) State two important physical properties that make vulcanised rubber more useful than natural rubber?

(v) State one important structural change that takes place when natural is vulcanised.

(4.0 marks)

(c) A student mixed 50.0 cm^3 of 0.2 mol dm^{-3} H_2SO_4 with 50.0 cm^3 of 0.8 mol dm^{-3} solution of CH_3COONa and observed that this solution possessed buffer properties.

With appropriate chemical equations and calculations, explain this observation.

(3.0 marks)

9. An iron nail with a rusty (corroded) surface, having a total mass of 0.30 g was dissolved completely in 50.0 cm^3 of 0.2 mol dm^{-3} H_2SO_4. The resultant solution required 25.00 cm^3 of 0.02 mol dm^{-3} $KMnO_4$ for complete reaction. The rust could be assumed to consist entirely of ferric oxide, Fe_2O_3.

(i) Write down the **balanced** chemical equations for the dissolution of the rusty nail in H_2SO_4.

(ii) Write down the **balanced** chemical equation for the reaction between Fe(II) and $KMnO_4$.

(iii) Calculate the mass of the iron nail before corrosion.
(Relative atomic masses : O = 16, Fe = 56)

(6.0 marks)

10. (a) State briefly **three** harmful effects on the environment caused by the use of agrochemicals including chemical fertilisers. Indicate clearly how each of the effects are brought about.

(3.0 marks)

(b) A sulphuric acid manufacturing factory is situated in an area rich in dolomite, $CaCO_3.MgCO_3$. Due to an error in the construction of the factory, SO_2 gas continuously leaks into the atmosphere when it is in operation. This SO_2 gas emitted into the atmosphere dissolves in rain water which falls on the soil rich in dolomite, the groundwater of the area becomes contaminated as a result.

(i) Using **balanced** chemical equations, indicate the essential steps involved in the manufacture of sulphuric acid. The necessary conditions involved, if any, should be clearly indicated.

(ii) With the help of **balanced** chemical equations, indicate what reactions could take place subsequent to SO_2 gas dissolving in the rain water.

(iii) With the help of **balanced** chemical equations, indicate what reactions could occur when the rain water contaminated as in (ii) above falls on dolomite deposits in the area.

(iv) Indicate briefly the changes that could take place in the groundwater due to the contamination referred to above.

(v) Indicate two problems that people could encounter in using the groundwater in the area.

(6.0 marks)

(c) A commercial liquid fertiliser is prepared by dissolving ammonium sulphate and urea in water. In a quality control experiment to determine the concentrations of urea and ammonium sulphate in a sample of this fertiliser, the following results were obtained.

(i) 100.0 cm^3 of the liquid fertiliser required 100.0 cm^3 of 0.08 mol dm^{-3} NaOH for complete reaction.

(ii) 100.0 cm^3 of the liquid fertiliser when reacted with dilute nitric acid and excess barium chloride gave 0.233 g of barium sulphate.

Write down **balanced** chemical equations for the reactions involved in (i) and (ii) above.

Calculate the concentration of urea and the concentration of ammonium sulphate in the liquid fertiliser.

(Relative atomic masses : Ba = 137; S = 32; O = 16)

(6.0 marks)