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PART A — STRUCTURED ESSAY

*Answer **all four** questions. Each question carries **10** marks.*

1. (*a*) Complete each of the statements given below by filling the blanks with a compound from the following list.

BCl_3, PCl_5, Cl_2O_7, N_2O_5, SiO_2, HF, HI, HCl, H_2S, H_2O

(i) The most acidic oxide is ..... .

(ii) The hydrogen halide showing the highest acidity in aqueous solution is ..... .

(iii) The compound with the highest melting point is ..... .

(iv) The compound forming the strongest hydrogen bonds is ..... .

(v) The compound most likely to act as a Lewis acid is ..... .

(vi) The element with the numerically highest oxidation number is found in the compound ..... .

(3·6 marks)

(*b*) **X** is a non-transition element which does not react with deuterium oxide (D_2O) at room temperature. The hydroxide of **X** is not amphoteric but shows basic properties. The sulphate of **X** is very soluble in water.

(i) Identify **X**.

.....

(ii) Give balanced chemical equations for the reactions that occur when **X** is burnt in air.

.....

.....

.....

(3·4 marks)

(*c*) **A**, **B**, **C** and **D** are four non-transition elements whose atomic numbers are Z, Z + 1, Z + 2 and Z + 3 respectively. Of these elements, **C** has the highest first ionization energy. Identify the group in the periodic table to which **C** belongs, if

(i) the atomic radius of **D** is smaller than that of **C**.

.....

(ii) the atomic radius of **D** is larger than that of **C**.

.....

(3·0 marks)

100

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2. (*a*) **Y** is a hydrated salt containing Na, S, H and O **only**. It contains 18·5% of Na, 25·8% of S and 4·0% of H, by mass. In this compound H is present as H_2O **only**.
(Na = 23·0, S = 32·0, H = 1·0, O = 16·0)

(i) Determine the empirical formula of **Y**.

.....

.....

.....

.....

.....

(2·5 marks)

(ii) If the relative molecular mass of **Y** is 248, deduce its molecular formula.

.....

.....

.....

.....

(0·6 marks)

(iii) Draw the structure of the anion of salt **Y**.

.....

.....

.....

.....

(1·0 marks)

(iv) Give a commonly used name for **Y**.

.....

(0·3 marks)

(v) Give two uses of **Y**.

.....

.....

.....

(0·6 marks)

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(b) The reversible reaction $2A(g) \rightleftharpoons B(g)$ reaches equilibrium at temperatures above 100 °C. Figure I, shows the activation energy curve for the above reaction. Figure II, shows the Maxwell-Boltzmann distributions of speeds for the molecules **A** and **B** at temperatures T_1 and T_2 where $T_2 > T_1 > 100$ °C.

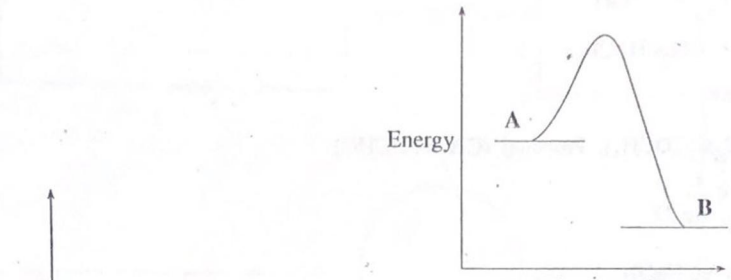


Figure I

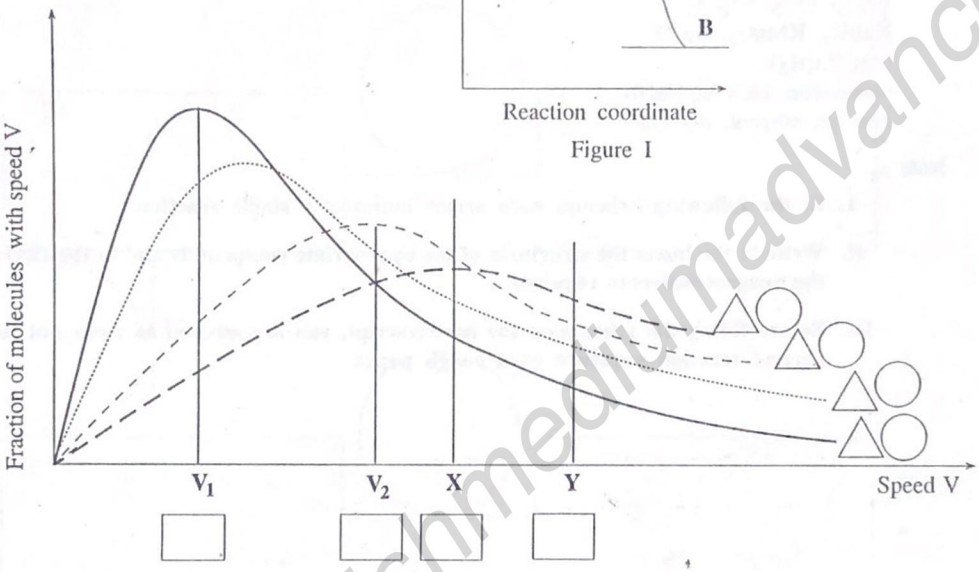


Figure II

(i) In figure I, draw vertical arrows to show the activation energy of the forward reaction, **F**, and the activation energy of the reverse reaction, **R**. Label them **F** and **R**.

(ii) Delete the **inappropriate** words in the following statement:

'The forward reaction is **endothermic/exothermic** and its enthalpy change is **negative/positive**.'

(iii) In figure II, **X** and **Y** are the speeds of molecules with energy equal to each activation energy. Identify the activation energies corresponding to **X** and **Y**, by writing **F** and **R** in the appropriate cages placed below **X** and **Y** in the figure.

(iv) In figure II, V_1 and V_2 refer to the mean speeds of the two types of molecules at the same temperature. The mean molecular speed is inversely proportional to molecular mass. Identify as to which type of molecules the mean speeds V_1 and V_2 refer to by writing **A** and **B** in the appropriate cages placed below V_1 and V_2 in the figure.

(v) Hence identify the different distributions in figure II, by writing **A** and **B** in the appropriate triangles and T_1 and T_2 in the appropriate adjacent circles, which are placed at the ends of the curves.

(vi) Delete the **inappropriate** words in the following statements:

'The equilibrium concentration of **A** at T_1 is **greater/smaller**, than its value at T_2.'

'The equilibrium concentration of **B** at T_1 is **greater/smaller**, than its value at T_2.'

'When the temperature is increased from T_1 to T_2, the rate of the forward reaction **increases/decreases** and the rate of the reverse reaction **increases/decreases**.'

(5·0 marks)

100

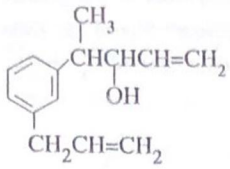
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(Organic)

3. Selecting appropriate reagents and solvents **only** from the list below, show how you would synthesize the following compound:



List of reagents and solvents:

acetophenone ($C_6H_5COCH_3$), Propenal (CH_2=CHCHO)
$AlCl_3$, PCl_5, Cl_2, I_2
$NaBH_4$, $KMnO_4$, Ag_2O
Mg, Zn(Hg)
water, conc.HCl, aq.NaOH
acetone, ethanol, dry ether

Note :

I. In the following Schemes each arrow indicates a single reaction.

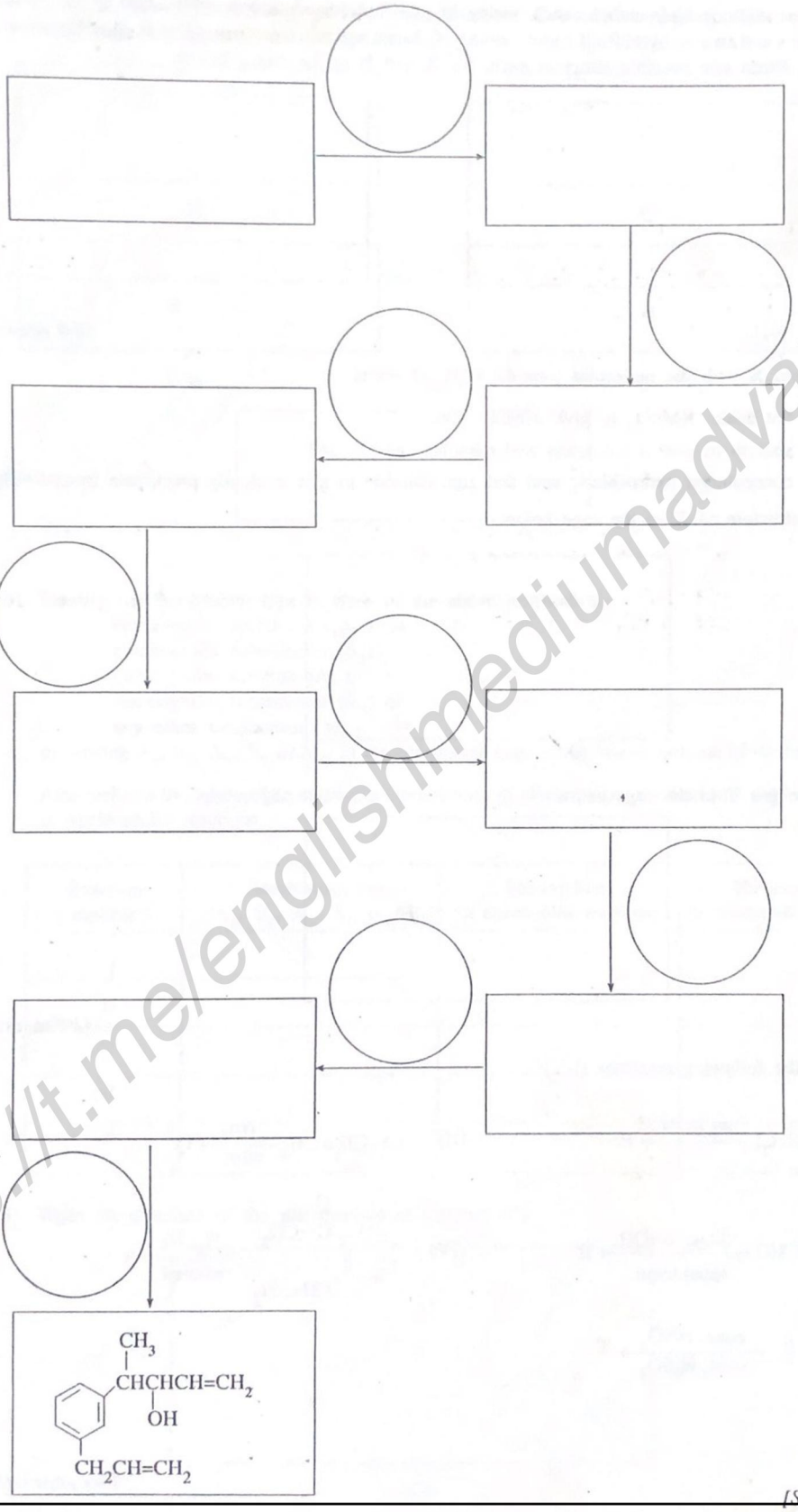
II. Write in the boxes the structures of the appropriate compounds and in the circles the reagents/solvents required.

III. Before filling the scheme on the answerscript, you are advised to work out the correct reaction sequence on a rough paper.

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(10·0 marks)

100

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4. (*a*) **A** and **B** are isomeric hydrocarbons each having **two** sp^3-hybridized carbon atoms, **two** sp^2-hybridized carbon atoms and **two** sp-hybridized carbon atoms. **A** shows optical isomerism while **B** shows geometric isomerism. Write **one** possible structure each, for **A** and **B** in the cages below.

A **B**

(2·0 marks)

(*b*) A compound **X** with the molecular formula, $C_9H_{12}O$ reacts

(i) with hot acidic $KMnO_4$ to give benzoic acid,

(ii) with sodium to give a colourless and odourless gas **Y**, and

(iii) with concentrated hydrochloric acid and zinc chloride to give a cloudy precipitate immediately.

Write the structure of **X** in the cage below.

X

Identify the gas **Y** in the cage below.

Y

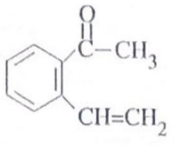
(2·0 marks)

(*c*) Consider the following reactions (I-V):

(I) $CH_3CH_2I \xrightarrow{\text{aq. KCN}} \mathbf{P}$

(II) $CH_3CH=CH_2 \xrightarrow[\text{ether}]{\text{HBr}} \mathbf{Q}$

(III) $CH_3CHO \xrightarrow[\text{room temp.}]{\text{dil.aq. NaOH}} \mathbf{R}$

(IV)  $\xrightarrow[\text{ethanol}]{H_2, Ni} \mathbf{S}$

(V)  $\xrightarrow[\text{conc. } H_2SO_4]{\text{conc. } HNO_3} \mathbf{T}$

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(i) **P**, **Q**, **R**, **S** and **T** are the respective major products of the above reactions, (I) - (V). Write their structures in the appropriate cages.

P

Q

R

S

T

(ii) Identify the mechanism type of each of the above reactions as,
electrophilic addition (A_E),
electrophilic substitution (S_E),
nucleophilic addition (A_N),
nucleophilic substitution (S_N) or
any other mechanism (M_O)
by writing A_E, S_E, A_N, S_N or M_O in the appropriate cage in the second column of the table below.

Also write in the appropriate cages the electrophiles in electrophilic reactions and the nucleophiles in nucleophilic reactions.

Reaction number	Mechanism-type (A_E, S_E, A_N, S_N or M_O)	Electrophile (in electrophilic reactions)	Nucleophile (in nucleophilic reactions)
I			
II			
III			
IV			
V			

(iii) Write the structure of the intermediate in reaction (V).

100

(6·0 marks)

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இலங்கைப் பரீட்சைத் திணைக்களம்
Department of Examinations, Sri Lanka

02 E II

අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2005 අප්‍රේල්
கல்விப் பொதுத் தராதரப் பத்திர(உயர் தர)ப் பரீட்சை, 2005 ஏப்பிரல்
General Certificate of Education (Adv. Level) Examination, April 2005

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

PART B — ESSAY

* *Answer two questions only. (Each question carries 15 marks.)*

5. Answer part (*a*) and ***either*** part (*b*) ***or*** (*c*) **only.**

(*a*) At temperatures above 400 K, A(g) dissociates to give B(g) and D(g) resulting in the equilibrium,

$$aA(g) \rightleftharpoons B(g) + D(g)$$

(i) The equilibrium constants K_c and K_p for the above equilibrium have the same numerical value. Starting with the definitions of K_c and K_p for the above reaction, deduce that the balancing coefficient, '*a*', in the above equation is equal to 2.

(ii) In a certain equilibrium mixture of the gases **A**, **B** and **D**, at 500 K, the respective partial pressures of the gases are as follows;

$$p_A = 2 \times 10^5 \text{ Pa}, \quad p_B = 8 \times 10^5 \text{ Pa} \quad \text{and} \quad p_D = 2 \times 10^5 \text{ Pa}.$$

Calculate K_p for the above equilibrium at 500 K.

(iii) A rigid vessel of volume 4·157 m^3 is filled with only A(g) at 27° C and the pressure of the gas under these conditions is X. When the vessel and its contents are heated to 500 K, and the system allowed to reach equilibrium at this temperature, it is found that, the total pressure in the vessel is Y and the partial pressure of **B** in the vessel is Z. Assuming that the volume of the vessel is unchanged on heating, show that,

$$Y = \frac{5}{2}Z \quad \text{and} \quad \frac{Y}{X} = \frac{5}{3}$$

State any assumption/s you have used.

If Y is 8×10^5 Pa, calculate the values of X and Z.

(iv) To the equilibrium mixture in (iii) above where $Y = 8 \times 10^5$ Pa, n moles of **A** are added. When the system reaches equilibrium again at 500 K, the total pressure in the vessel is found to be $2{\cdot}5 \times 10^6$ Pa. Calculate the value of n and the partial pressures of A(g), B(g) and D(g) under the new equilibrium conditions.

(8·0 *marks*)

(*b*) Write down balanced chemical equations for the processes appropriate to each of the following statements from (i) to (vii).

(i) The standard electron gain enthalpy, $\Delta H^{\ominus}_{EA}$, of bromine is −328·0 kJ mol^{-1}.

(ii) The standard enthalpy of formation, $\Delta H^{\ominus}_{f}$, of $MgCl_2(s)$, is −641·0 kJ mol^{-1}.

(iii) The standard enthalpy of combustion, $\Delta H^{\ominus}_{C}$, of stearic acid, $C_{17}H_{35}COOH$, is −11 380·0 kJ mol^{-1}.

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(iv) The standard enthalpy of first ionisation, $\Delta H_{I_1}^{\ominus}$ and the standard enthalpy of second ionisation, $\Delta H_{I_2}^{\ominus}$ of Mg are respectively, 737·0 kJ mol^{-1} and 1451·0 kJ mol^{-1}.

(v) The standard enthalpy of atomisation, $\Delta H_{A}^{\ominus}$, of Mg is 148·0 kJ mol^{-1}.

(vi) The standard lattice enthalpy, $\Delta H_{L}^{\ominus}$, of $MgBr_2(s)$, is −2440·0 kJ mol^{-1}.

(vii) The standard bond dissociation enthalpy, $\Delta H_{D}^{\ominus}$, of Br_2 is 193·0 kJ mol^{-1}.

Given that the standard state for bromine is $Br_2(l)$ and that its standard enthalpy of vaporisation $\Delta H_{vap}^{\ominus}$, is 15·0 kJ mol^{-1}, calculate the standard enthalpy changes of the following reactions (viii) and (ix).

(viii) $Mg(s) + Br_2(l) \longrightarrow MgBr_2(s)$

(ix) $Cl_2(g) + MgBr_2(s) \longrightarrow MgCl_2(s) + Br_2(l)$

(7·0 marks)

(c) A closed vessel contains a solution of three volatile liquids **A**, **B** and **C**, in equilibrium with a vapour phase containing **A**, **B** and **C** molecules only, at a temperature Q. The total vapour pressure is H. There are no interactions between the molecules in the vapour phase, while there is complete uniformity of forces amongst the molecules in the liquid phase. Some selected properties of the above system and its pure components are given in the table below.

compound	Pure liquid		liquid phase		vapour phase	
	vapour pressure	relative molecular mass	number of molecules	number of moles	number of molecules	number of moles
A	H/2	L	a	b	a/3	b
B		M	2a			
C		N		3b		

Using **only** the symbols given in this question and **no other**, write down expressions for the following and simplify them as far as possible.

(i) Avogadro Constant N_A.

(ii) q, the number of moles of **B**, in the liquid phase.

(iii) c, the number of molecules of **C** in the liquid phase.

(iv) the mole fractions of **A**, **B** and **C**, in the liquid phase.

(v) the partial pressure of **B**, in the vapour phase.

(vi) the total number of moles T, in the vapour phase.

(vii) the mole fractions of **A**, **B** and **C** in the vapour phase.

(viii) the partial pressure of **A** and **C** in the vapour phase.

(ix) the volume G, of the vapour phase, if the gas constant is R.

(x) the mean square speed of **A** molecules, $\overline{C_A^2}$, in the vapour phase.

(N.B. Answers with symbols other than those given in the question will not be given marks.)

(7·0 marks)

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6. Answer **all** parts.

(*a*) A procedure used in a student project to investigate the pollution of ground water in a village by an agrochemical **X** of relative molecular mass 125, is given below.

(I) 500·0 cm^3 of an aqueous solution containing 90·0 ppm of **X**, was shaken well with 100·0 cm^3 of ether and the two layers allowed to reach equilibrium at 25 °C. The ether layer was then separated and evaporated to dryness. A residue containing 40·0 mg of **X** was obtained.

(II) Experiment (I) was repeated using 1000·0 cm^3 of water from a well, in place of the 500·0 cm^3 of the aqueous solution of **X**. The residue obtained contained 43·2 mg of **X**.

(III) 2000·0 cm^3 of the above well water was shaken with 100·0 g of ground redbrick powder for 30 minutes. The water was then filtered to remove brick particles. Experiment (I) was repeated, this time using 1000·0 cm^3 of the above filtrate in place of the 500·0 cm^3 of the aqueous solution of **X**. The residue obtained contained 6·0 mg of **X**.

(i) Calculate the content of **X** in the water obtained directly from the well and in the well water after treatment with brick powder, in ppm and in mol dm^{-3}, in each case.
(1 ppm = 1 mg dm^{-3})

(ii) Giving reasons for your answer, explain the observations in (III) above.

(iii) What additional measurements are needed to make the results more reliable and generally applicable to the ground water quality of the village?

(iv) The World Health Organisation (WHO) recommendation for the maximum content of **X** in drinking water is 9·0 ppm. Suggest a method based on the above procedure, to bring the well water to the above WHO standard.

(8.0 *marks*)

(*b*) A student prepared 100·0 g each of three mixtures **P**, **Q** and **R** by mixing the finely ground metals Al, Zn and Mg. The masses of the metals used for each mixture are given in the table below.

Mixture	Mass of metal / g			Total mass/g
	Al	Zn	Mg	
P	21.6	13.0	65.4	100.0
Q	27.0	52.0	21.0	100.0
R	32.4	65.0	2.6	100.0

(Al = 27.0, Zn = 65.0, Mg = 24.0)

The student however, failed to label the mixtures and they cannot be identified visually. You are provided with 1.0 g samples of each of the three mixtures. Show, with necessary calculations, how you would identify the three mixtures using only the following:

0·2 mol dm^{-3} HCl solution
Three identical empty bottles
Three identical balloons, the open ends of which fit tightly over the mouths of the bottles.

Write balanced chemical equations for any reactions you may use.

(7.0 *marks*)

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7. Answer **all** parts.

(*a*) **A** is a saturated aqueous solution of AgCl and **B** is a 0·1 mol dm^{-3} aqueous solution of NaCl, saturated with AgCl.

At 25 °C, the solubility product of AgCl = 1×10^{-10} mol^2 dm^{-6}

(Ag = 107·0, Cl = 35·5)

(i) Calculate the concentration of $Ag^+(aq)$ and the solubility of AgCl in mg dm^{-3}, in each of the solutions **A** and **B** at 25 °C.

(ii) Draw a labelled sketch of an experimental arrangement for electroplating a small copper ring with silver, using one of the solutions **A** and **B**. Indicate the polarity (+ve or –ve) of the electrodes and clearly label the anode and cathode. Name the metals used for the anode and cathode.

(iii) It is known that the lower the rate of electroplating, the finer and shinier the metal coating obtained. Using your knowledge of chemical kinetics, deduce giving reasons as to which of the solutions **A** and **B** is more suitable for the above experiment (ii).

(iv) The following equilibrium occurs when a silver salt is dissolved in an aqueous solution of KCN:

$$[Ag(CN)_2]^-(aq) \rightleftharpoons Ag^+(aq) + 2CN^-(aq)$$

Explain why a solution of a silver salt in aqueous KCN is more suitable than an aqueous solution of the silver salt of the same concentration for the commercial electroplating with Ag.

Comment on the magnitude of the equilibrium constant of the above equilibrium.

(v) Explain why an ammoniacal solution of $AgNO_3$ and not an aqueous solution of $AgNO_3$, is used as the oxidising agent, in the Tollen's silver mirror test for organic reducing agents.

(vi) The copper ring was silver plated at a constant current of 0·15 A for 40 minutes. Calculate the increase in mass of the copper ring.

(Faraday Constant, F = 96 540 C mol^{-1})

(vii) The electrode potential of a $Ag|Ag^+$ electrode becomes more positive as the concentration of $Ag^+(aq)$ in the electrolyte increases. Sketch an electrochemical cell which can be made using the solutions **A** and **B**, two silver rods and a salt bridge as the only components. Label the sketch to show clearly the anode and cathode and identify the anode and cathode solutions as **A** or **B**.

(10.0 *marks*)

(*b*) Deduce by means of suitable calculations, what you would expect to observe when 100·0 cm^3 of a 1×10^{-5} mol dm^{-3} aqueous solution of barium hydroxide is mixed with 100·0 cm^3 of a $2{\cdot}5 \times 10^{-5}$ mol dm^{-3} aqueous solution of cadmium sulphate at 25 °C.

At 25 °C

solubility product of barium sulphate = 1×10^{-10} mol^2 dm^{-6}

solubility product of cadmium hydroxide = $1{\cdot}2 \times 10^{-14}$ mol^3 dm^{-9}

(5.0 *marks*)

PART C - ESSAY

* *Answer **two** questions only. (Each question carries **15** marks.)*

---

8. Answer **all** parts.

(*a*) (i) **M** is a 3d-transition element. **M** forms a stable dioxide MO_2, which is white in colour.

(A) Identify **M**.

(B) Write the complete electronic configuration of **M**.

(C) Give **one** industrial application in each case for **M** and MO_2.

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(ii) The tests performed on a solution prepared by dissolving two 3d-transition metal chlorides in water (solution S) and the relevant observations are given below.

Test	Observation
(A) Aqueous NaOH was added to solution S.	A blue-green precipitate was obtained.
(B) Solution S was warmed with aqueous NaOH and H_2O_2 and filtered.	A precipitate and a yellow filtrate were obtained.
(C) Conc. HCl was added to the precipitate obtained in (B).	A yellow solution was obtained.
(D) Diluted the yellow solution obtained in (C) and passed H_2S.	A black precipitate was obtained.

Identify the cations present in S.

Identify the respective ions responsible for the yellow colour of the filtrate from test (B) and the yellow colour of the solution obtained in test (C). Write balanced chemical equations for the formation of these two ions in the above reactions.

What do you expect to observe when the filtrate from (B) is acidified? Give the relevant balanced chemical equation.

(8.0 *marks*)

(*b*) Ammonia is produced industrially using N_2 and H_2. The following questions refer to the 'Haber' process for the manufacture of NH_3.

(i) What are the sources of N_2 and H_2 used for this process?

(ii) What are the specific reaction conditions (temperature, pressure and catalyst) used?

(iii) How does the catalyst affect the rate of the forward reaction, the rate of the reverse reaction and the equilibrium constant?

(iv) Name **one** industry in which NH_3 is oxidized. What are the reaction conditions employed in this oxidation?

(v) Give **one** household use of ammonia.

(vi) Write balanced chemical equations and the necessary reaction conditions for the reactions of ammonia with each of the following :

CuO, I_2 and Na

(vii) Give, in each case, **one** ammonium compound that is used in
(A) the fertilizer industry.
(B) the rubber industry.
What is the role of each of the above compounds in the relevant industry?

(7.0 *marks*)

9. Answer **all** parts.

(*a*) (i) NH_3 is one of the starting materials used for the production of Na_2CO_3 by the 'Solvay' process. What are the other starting materials used for this process? How are these other materials obtained?

(ii) Give **two** by-products of this process.

(iii) Give balanced chemical equations for the reactions taking place during this process of production and during the recycling of by-products.

(iv) Give **two** reasons as to why a low temperature (<15 °C) is used in this process.

(v) Give **three** important factors that need to be considered in choosing a site for this industry.

(vi) Give **one** industrial use in each case for Na_2CO_3 and $NaHCO_3$.

(7.5 *marks*)

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(*b*) A test kit for determining the chloride ion concentration of domestic water supplies contains a $AgNO_3$ solution and a K_2CrO_4 solution. $AgNO_3$ solution is added dropwise to a 24·0 cm^3 sample of the water to be tested, to which K_2CrO_4 indicator has been added. When sufficient $AgNO_3$ has been added to convert all Cl^- ions to AgCl, the end point is indicated by the formation of orange coloured Ag_2CrO_4. The concentration of $AgNO_3$ is such that each drop of $AgNO_3$ solution consumed corresponds to 12·5 mg of Cl^- ions in 1·0 dm^3 of water tested, when the sample size of water tested is 24·0 cm^3.

(i) What mass of Cl^- (in mg) is contained in a cubic decimetre of water sample which requires 12 drops of $AgNO_3$ solution to reach the end point indicated by the orange colour change?

(ii) What is the molar concentration of Cl^- ions in the water sample tested in (i)?

(iii) If experiment (i) is repeated using 6·0 cm^3 only of the same sample of water used in (i) above, how many drops of $AgNO_3$ will be required to reach the end point? Under these conditions, what Cl^- ion content in mg dm^{-3} of the water sample corresponds to one drop of $AgNO_3$ solution used?

(iv) What is the molar concentration of the $AgNO_3$ solution? (Volume of 20 drops = 1.0 cm^3)
(Cl = 35·5, Ag = 107·0, N = 14·0, O = 16·0)

(4.0 *marks*)

(*c*) Consider the polymers poly(styrene), poly(vinyl chloride) and natural rubber.

For each of these polymers,

(i) Write the structure of the repeat unit.

(ii) Write the structure of the monomer which polymerizes to form the above polymer.

Give **one** simple test that can be carried out at your home to distinguish between PVC and bakelite (phenol-formaldehyde).

(3.5 *marks*)

10. Answer **all** parts.

(*a*) You are provided with unlabelled samples of $(NH_4)_2CO_3$, $ZnCO_3$, $MgCO_3$ and $BaCO_3$, a furnace that can be heated to high temperatures, distilled water, dilute HCl, test tubes and crucibles. Show how you would identify these carbonates, using only the materials mentioned above.

Write balanced chemical equations for the reactions you use.

(5.0 *marks*)

(*b*) Give **one** sulphur containing and **one** chlorine containing compound, each of which acts as a bleaching agent. Explain the bleaching action of each compound. Give **one** method in each case for the industrial production of the bleaching agents you mentioned above.

(4.0 *marks*)

(*c*) Antacid tablets are used to control excessive acid (HCl) in the gastric solution present in the stomach. One make of antacid tablets contains 0·520 g of $Mg_2Si_3O_8$ and 0·087 g of $Mg(OH)_2$ per tablet, both of which react with HCl.

The stomach of a patient contains 0·365 g of HCl per 100·0 cm^3 of gastric solution. The total volume of the gastric solution is 500·0 cm^3.

Calculate,

(i) the pH of the gastric solution of the patient.

(ii) the pH of the gastric solution after the patient has taken two of these antacid tablets. Assume that the tablets have reacted completely with the gastric solution and that no further acid has been secreted during this period.

$Mg_2Si_3O_8$ reacts with HCl as follows:

$$Mg_2Si_3O_8 + 4HCl \longrightarrow 2MgCl_2 + 3SiO_2 + 2H_2O$$

(Mg = 24·0, Si = 28·0, O = 16·0, H = 1·0, Cl = 35·5)

(6.0 *marks*)

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