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PART A — STRUCTURED ESSAY

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

1. (*a*) (i) Write the complete electronic configuration of the element X with the atomic number 33.

.....

(ii) What are the most common oxidation states of the element X?

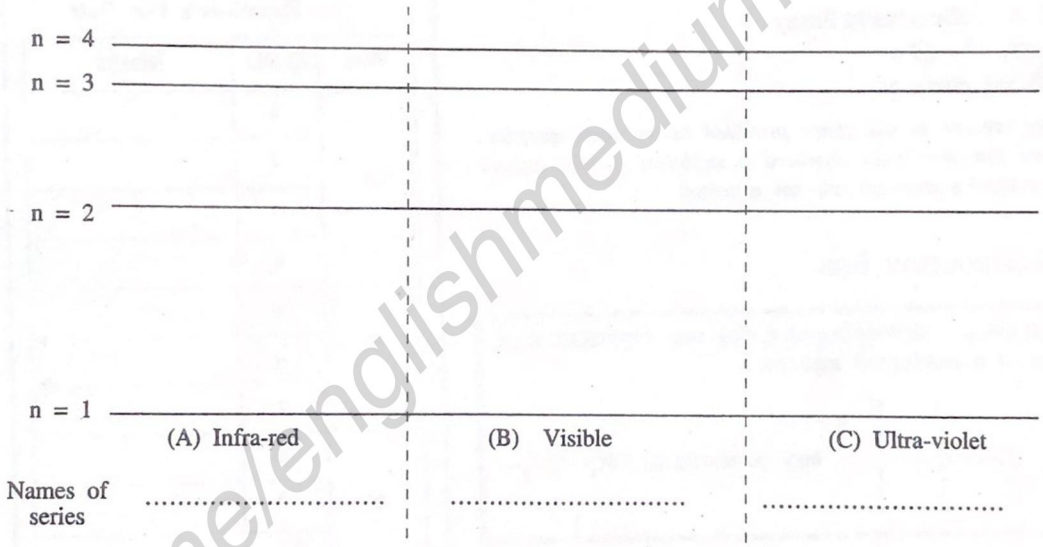
.....

(iii) Give the chemical formulae of the stable oxides of X.

.....

(2.5 marks)

(*b*) The first four electronic energy levels of the hydrogen atom are represented in the diagram given below.



Names of series ....

Indicate with **arrows** all electronic transitions that could occur between the above energy levels and which are responsible for emission lines in (A) the infra-red region (B) the visible region and (C) the ultra-violet region.

Write the **names of the series** to which each set of lines belongs, in the space provided in the diagram.

(2.7 marks)

(*c*) Y and Z are two non-transition elements belonging to the same group of the periodic table. They form the compounds YZ_2 and YZ_3.

(i) Identify the elements Y and Z.

Y = ... , Z = ...

(ii) Name the shapes of the molecules YZ_2 and YZ_3. (Diagrams are not acceptable.)

YZ_2 ....., YZ_3 .....

(3.0 marks)

(d) A, B, C and D are consecutive non-transition elements in the periodic table with atomic number increasing from A to D. Atomic number of D is less than 30.

The first ionization energies of these elements are in the order D << A < B < C.

Arrange these elements in the increasing order of electronegativity.

..... < ..... < ..... < .....

(1.8 marks)

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2. (a) (i) Magnetite, Fe_3O_4 is a mixed oxide of iron. Write the formulae of the constituent oxides of this mineral.

.....

(ii) A mixture contains Fe_2O_3 and Fe_3O_4. A 5.52 g sample of this mixture when dissolved in dil.H_2SO_4 required 20.0 cm^3 of 0.10 mol dm^{-3} $KMnO_4$ for complete reaction.

Calculate the molar ratio Fe_2O_3: Fe_3O_4 in the mixture. (Fe = 56.0 ; O = 16.0)

.....

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(iii) Calculate the maximum mass of iron that can be extracted from 1.0 kg of the mixture in (ii).

.....

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.....

.....

(5.0 *marks*)

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(b) (i) The pure liquids D, E and F form binary homogeneous solutions DE, EF and DF with each other at temperature T. The intermolecular forces between any two molecules of D, E and F are as indicated in the table below.

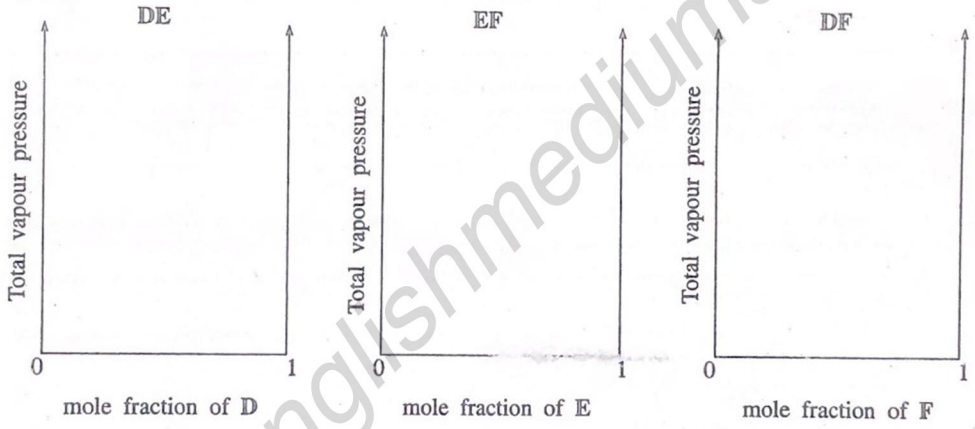
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Molecule	D	E	F
D	d	b	c
E	b	e	a
F	c	a	f

The following information is given :

- d = c = f.
- b is **slightly smaller** than d and e.
- a is **slightly greater** than e and f.
- The vapour pressures of the three liquids D, E and F are P_D, P_E and P_F respectively, at the given temperature with $P_D > P_E$ and $P_F > P_D$.

I. Mark P_D, P_E and P_F, as may be appropriate on each of the six vertical axes in the diagrams below.



II. Indicate in the relevant diagrams the likely variations of the total vapour pressure of each of the solutions **DE**, **EF** and **DF**.

(ii) α mol of D and γ mol of F are mixed to give a solution DF. The total equilibrium vapour pressure above DF at temperature T is P. Intermolecular forces in the vapour phase can be assumed to be absent.

Using the symbols given above in 2(*b*) (i) and (ii), **but no other**, write down mathematical expressions for the following :

I. The partial pressure of D in the vapour phase.

.....

II. The partial pressure of F in the vapour phase.

.....

III. The number of moles of D in the vapour phase.

.....

.....

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(5.0 marks)

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3. (*a*) The elements present in an organic compound A and their mass percentages are given below.

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organic

	C	H	N	Cl
mass%	55.6	6.2	10.8	27.4

(i) Deduce the empirical formula of A. (C = 12.0, H = 1.0, N = 14.0, Cl = 35.5)

.....

.....

.....

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.....

(ii) A is soluble in water and the solution is acidic. An aqueous solution containing 1.30 g A required 25.0 cm^3 of 0.40 mol dm^{-3} NaOH solution when titrated using phenolphthalein as the indicator.

Determine the relative molar mass of A. (1 mol of A reacts with 1 mol of NaOH)

.....

.....

.....

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.....

(iii) Write the molecular formula of A

.....

(iv) A undergoes the following reaction.

$$A \xrightarrow[0-5\,^{\circ}C]{\text{aq. } NaNO_2} B \xrightarrow[0-5\,^{\circ}C]{C_6H_5OH,\ \text{aq. NaOH}} C$$

Further, an aqueous solution of A gives a white precipitate with $AgNO_3$ solution.

Write the structures of A, B and C in the relevant cages.

A B C

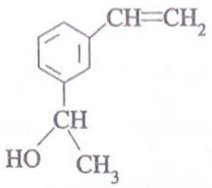
(5.1 marks)

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(*b*) Starting from benzene and selecting appropriate reagents and solvents only from those given below, show how you would synthesize the compound,

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Reagents and solvents :

$AlCl_3$, PCl_5, Br_2, I_2
$LiAlH_4$, Zn(Hg), Mg, Fe, $K_2Cr_2O_7$
CH_3COCH_3, CH_3COCl, CH_3CHO
dil.H_2SO_4, water, aq.NaOH
dry ether, ethanol,

- In the following scheme, each arrow indicates a single reaction.

However, consider

(A) Reaction with $LiAlH_4$ followed by hydrolysis

and (B) Reaction with RMgX followed by hydrolysis as a single reaction.

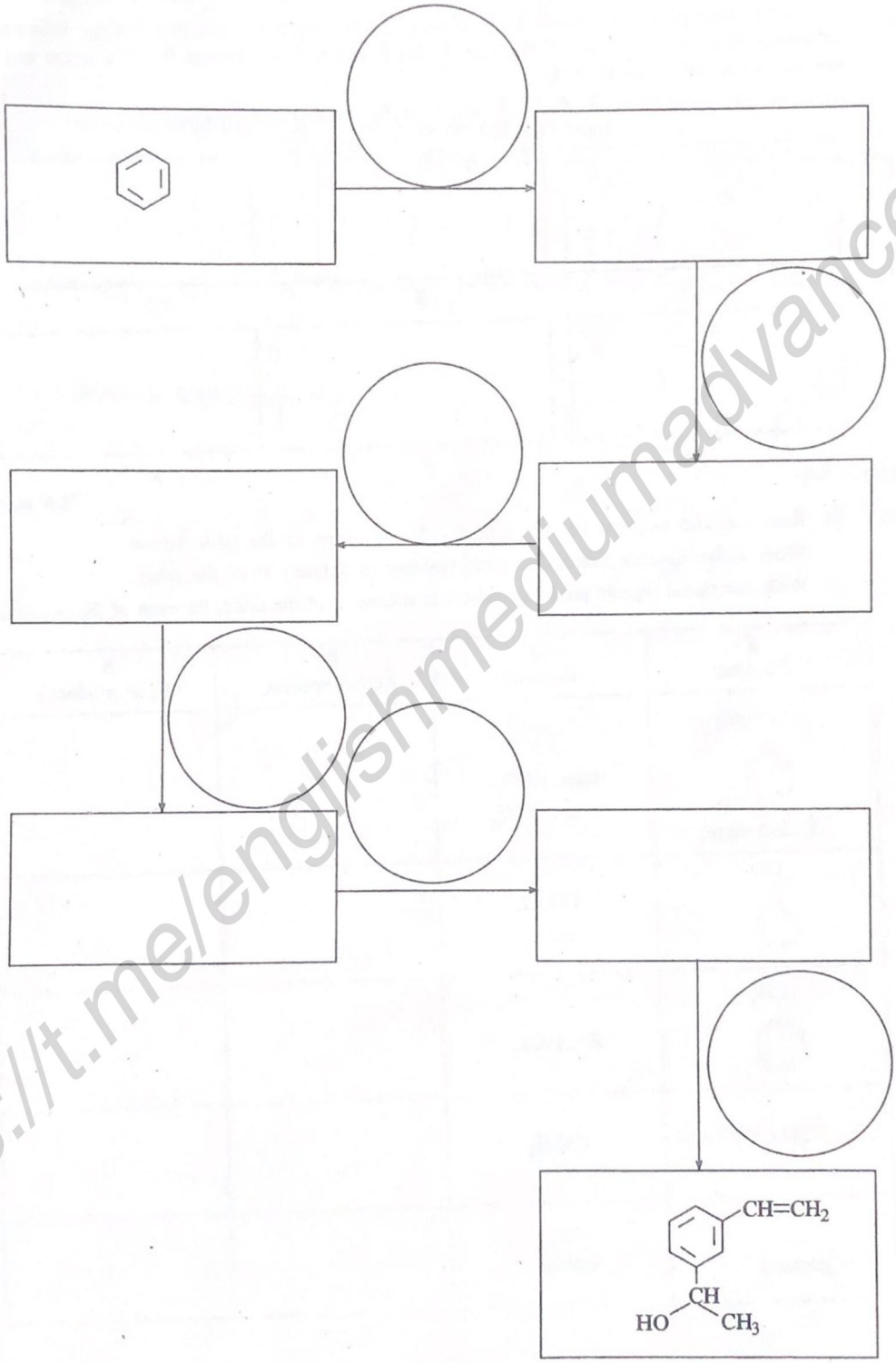
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- Write in the boxes the structures of the appropriate compounds and in the circles the reagents/ solvents required.

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(4.9 marks)

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Do not write in this column

4. (*a*) A, B and C are three isomeric hydrocarbons each having two sp^3 hybridized carbon atoms and two sp^2 hybridized carbon atoms only. A shows stereoisomerism. On bromination followed by dehydrobromination, A, B and C form D, E and F respectively. D and E are isomers but F is **not** an isomer of either D or E.

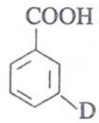
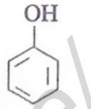
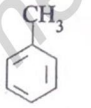
Give the structures of A, B, C, D, E and F in the appropriate cages.

A B C

D E F

(3.6 marks)

(*b*) (i) Reactants and reagents for reactions I – V are given in the table below.
Write active species relevant to each reaction in column R of the table.
Write the major organic product/products in column S of the table, for each of the reactions.

	P Reactant	Q Reagents	R Active species	S Major product/s
I.	 (D-deuterium)	conc. HNO_3, conc. H_2SO_4		
II.		CH_3Cl, $AlCl_3$		
III.		Br_2, $FeBr_3$		
IV.	$CH_3COCH_2CH_2COOH$	$NaBH_4$		
V.	CH_4 (excess)	Cl_2, sunlight		

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(ii) Consider the scheme of reactions given below.

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$$C_3H_4 \xrightarrow[HgSO_4]{dil.H_2SO_4} C_3H_6O \xrightarrow{aq.NaOH} C_6H_{12}O_2$$

X Y Z

Give the structures of X, Y and Z in the relevant boxes.

X	Y	Z

Write the IUPAC name of Z.

.....

(6.4 marks)

100

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02 E II

Department of Examinations, Sri Lanka

අධ්‍යයන පොදු සහතික පත්‍ර (උසස් පෙළ) විභාගය, 2007 අගෝස්තු
கல்விப் பொதுத் தராதரப் பத்திர (உயர் தர)ப் பரீட்சை, 2007 ஓகஸ்ற்
General Certificate of Education (Adv. Level) Examination, August 2007

රසායන විද්‍යාව II
இரசாயனவியல் II
Chemistry II

PART B — ESSAY

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

5. (*a*) (i) $NH_3(g)$ and $O_2(g)$ react with each other forming NO(g) and $H_2O(g)$. Write the balanced chemical equation for this reaction.

(ii) Calculate the standard enthalpy change, $\Delta H^{\ominus}$, for the reaction you wrote in (i) above using the following data :

Standard enthalpy of formation of $NH_3(g)$, $\Delta H_f^{\ominus}(NH_3, g) = -46 \text{ kJ mol}^{-1}$

Standard enthalpy of formation of NO(g), $\Delta H_f^{\ominus}(NO, g) = 90 \text{ kJ mol}^{-1}$

Standard enthalpy of formation of $H_2O(g)$, $\Delta H_f^{\ominus}(H_2O, g) = -242 \text{ kJ mol}^{-1}$

(iii) Using the data given and the value calculated, briefly explain which one of the two reactions I and II is likely to be more suitable to produce NO(g)

I. Reaction between $N_2(g)$ and $O_2(g)$.

II. Reaction between $NH_3(g)$ and $O_2(g)$. **(4.0 *marks*)**

(*b*) **A**(g) dissociates reversibly to form **B**(g) and **C**(g) at temperatures above 350 K.

An evacuated vessel of volume 4.157 dm^3 was filled with 2.0 mol of **A**(g), 1.0 mol of **B**(g) and 1.0 mol of **C**(g), and heated to 500 K. When the system attained equilibrium at this temperature, the vessel contained 1.6 mol of **A**(g), 1.2 mol of **B**(g) and 1.6 mol of **C**(g).

(i) Deduce the balanced chemical equation for the dissociation of **A**(g) forming **B**(g) and **C**(g).

(ii) Write an expression for the equilibrium constant, K_c, for the reaction in (i) above.

(iii) Calculate the value of K_p at 500 K.

(iv) If the numerical value of K_p of this reaction at 700 K in SI units is 5.1×10^{13}, deduce whether the dissociation of **A**(g) is exothermic. **(5.0 *marks*)**

(*c*) (i) The following chemical equilibrium exists among **X**(g), **Y**(g) and **Z**(g) at temperatures above 400 K.

$$\mathbf{X}(g) + \mathbf{Y}(g) \rightleftharpoons 2\,\mathbf{Z}(g)$$

An evacuated vessel of volume 16.628 dm^3 contains 2 mol of **X**(g) and 2 mol of **Y**(g). This vessel is heated to 500 K to reach the above equilibrium. The equilibrium constant, $K_p = 4$ at this temperature.

I. Calculate the number of moles of **X**(g), **Y**(g) and **Z**(g) inside the vessel.

II. Calculate the total pressure inside the vessel.

(ii) After equilibrium is reached in (i) above, 1 mol of **Z**(g) is added to the vessel maintaining the temperature at 500 K. Calculate the number of moles of **X**, **Y** and **Z** inside the vessel, when the new equilibrium is reached.

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(iii) After equilibrium is reached in (i) above, suppose, 1 mol of **Y**(g) and 1 mol of **Z**(g) are added to the vessel maintaining the temperature at 500 K. Deduce logically, without calculations, to which direction the equilibrium of the system shifts. **(6.0 *marks*)**

6. (*a*) (i) The following procedure was used by a student to determine the solubility product of $Ca(OH)_2$ at room temperature.

Procedure :

2.50 g of pure $Ca(OH)_2$ was added to 250.0 cm^3 of distilled water and shaken well. There after, half of the solution was filtered. Three 25.00 cm^3 portions of the filtrate were transferred to three titration flasks and titrated with a 0.050 mol dm^{-3} HCl solution using phenolphthalein as the indicator.

The following readings were then obtained.

12.50 cm^3, 12.05 cm^3, 11.95 cm^3

I. Calculate the solubility product of $Ca(OH)_2$ at room temperature using the above data.

II. Indicate the colour change at the end point of this titration.

III. Name another indicator which can be used for this titration.

IV. What is the importance of taking three measurements in the above titration?

V. Briefly explain how you assure that the solution used in this experiment was saturated with $Ca(OH)_2$.

VI. Is it possible to determine the solubility product of $CaCO_3$ using the above method? Explain your answer in brief. **(5.0 *marks*)**

(ii) A 2.50 g sample of $Mg(OH)_2$ containing 10% (w/w) NaOH was titrated using the procedure given in (*a*) (i) above. Calculate

I. the concentration of Mg^{2+} ions in the filtrate.

II. the expected end point.

State the assumptions you used in the calculations I and II above. Justify your assumptions using suitable calculations.

K_{sp} of $Mg(OH)_2$ at room temperature = 1.2×10^{-11} mol^3 dm^{-9} (H = 1, O = 16, Na = 23) **(4.0 *marks*)**

(*b*) 50.00 cm^3 of 0.10 mol dm^{-3} NaOH solution was mixed with 25.00 cm^3 of a monobasic weak acid solution. The pH of the mixture was found to be 11.0. Calculate the concentration of the weak acid solution. When 20.00 cm^3 of 0.10 mol dm^{-3} NaOH solution was mixed with 25.00 cm^3 of the above weak acid solution, the pH of the mixture was 4.0. Calculate the dissociation constant of the weak acid. State assumptions, if any, you used in the above calculations. **(6.0 *marks*)**

7. (*a*) In an experiment to ditermine the kinetic parameters of the reaction between acidified $KMnO_4$ and oxalic acid, $(H_2C_2O_4)$ the reagents were mixed in closed containers as shown in the table below. The experiment was carried out at 50 °C and the volume of CO_2 evolved during the first 2 minutes after mixing the reagents was measured at 25 °C and a pressure of 1 atm. Note that the reactions in containers 1 - 3 were conducted at the same pH value (1.0) and the reaction in container 4 was conducted at a different pH value (1.3). The measurements obtained are given in the table below.

Container No.	Solution mixed		pH	Volume of CO_2/cm^3
	$KMnO_4$	$H_2C_2O_4$		
1.	0.01 mol dm^{-3} ; 50.0 cm^3	0.01 mol dm^{-3} ; 50.0 cm^3	1.0	9.5
2.	0.02 mol dm^{-3} ; 75.0 cm^3	0.02 mol dm^{-3} ; 25.0 cm^3	1.0	29.0
3.	0.01 mol dm^{-3} ; 50.0 cm^3	0.02 mol dm^{-3} ; 50.0 cm^3	1.0	19.5
4.	0.01 mol dm^{-3} ; 50.0 cm^3	0.01 mol dm^{-3} ; 50.0 cm^3	1.3	10.0

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(i) Write the balanced ionic equation for this reaction between $KMnO_4$ and $H_2C_2O_4$.

(ii) Using the data given in the above table, derive an expression for the rate of the reaction you wrote in (i) in terms of the concentrations of MnO_4^-, $C_2O_4^{2-}$ and H^+ ions.

(iii) Deduce by what factor the reaction rate would be increased if 50.0 cm^3 of 0.02 mol dm^{-3} $KMnO_4$ were used in container 4.

(iv) Is it possible to use your expression in (ii) above to predict the changes in reaction rate when the reactions are carried out at (I) pH = 2.0 and (II) pH = 10.0? Give reasons for your answers.

(9.0 *marks*)

(*b*) (i) Details of two electrochemical cells **A** and **B** constructed using three standard electrodes are given below. **P** and **Q** are metals. (e.m.f. = electromotive force)

	Electrode 1 (Positive)	Electrode 2	e.m.f./V
A	$H^+(aq)/H_2(g)$	$P^{2+}(aq)/P(s)$	1.25
B	$P^{2+}(aq)/P(s)$	$Q^{2+}(aq)/Q(s)$	0.95

I. Calculate the standard electrode potential, $E^{\ominus}$ of metal **Q**.

II. Write the cell reaction of the electrochemical cell **B**.

III. Predict qualitatively the expected change in cell e.m.f. if the $P^{2+}(aq)$ concentration in cell **B** is increased to 2.0 mol dm^{-3}.

(ii) Using your knowledge of the electrolysis of salts, outline an electrochemical method to obtain a pure sample of $Mg(OH)_2$ starting with an aqueous solution of $MgCl_2$.

Write the electrode reaction involved in the method you have outlined.

(6.0 *marks*)

PART C - ESSAY

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

8. (*a*) (i) How would you identify the aqueous solutions in each of the following groups, by using **only** the method/materials given against each group.

Group	Method/Materials
I. $Na_2S_2O_3$ solution, dil.H_2SO_4 solution, Na_2CO_3 solution	By mixing solutions pairwise
II. $NaNO_3$ solution, NH_4NO_3 solution, NH_4Cl solution	By heating with NaOH and/or Al powder

(ii) A mixture **X** contains salts of two metallic elements **only**. Tests performed with this mixture and the observations made are given below.

Test	Observations
I. Dissolved the mixture in distilled water	A coloured solution was obtained.
II. Added dil. HCl to an aqueous solution of the mixture.	No precipitate
III. Passed H_2S through solution from II and filtered.	A black precipitate was obtained.
IV. The precipitate from III was treated with dil.HNO_3	The precipitate dissolved forming a turbid light-blue solution.
V. NH_4OH was added dropwise to filtrate from III.	A white precipitate was formed.

State the inferences that you can make from each of the tests I – V.

Identify the cations in **X**.

Give **one** test to confirm the identity of the cation revealed in test V.

(8.0 *marks*)

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(*b*) An aqueous solution of an inorganic covalent compound **Y** (relative molar mass < 40) undergoes the following reactions.

(A) It decolorizes an acidified $KMnO_4$ solution with the evolution of O_2 gas.

(B) It gives a brown precipitate with alkaline $KMnO_4$ with evolution of O_2 gas.

(C) It turns a colourless acidic solution of NaBr, yellow.

(D) It slowly decomposes at room temperature but the decomposition can be accelerated by exposing it to sunlight.

(E) When oil paintings are exposed to polluted air containing H_2S, white $PbCO_3$ pigments become black due to formation of PbS. **Y**, can be used to restore the original white colour.

(i) Identify **Y**.

(ii) Give the Lewis (dot and cross) structure of **Y**.

(iii) Draw the shape of **Y**.

(iv) Give balanced chemical equations for the reactions of **Y** in (A) to (E) above.

(v) Name the type of reaction in (D).

(vi) Give **one** common use of a dilute aqueous solution of **Y**.

(vii) Pure **Y** is a syrupy liquid with the boiling point around 150 °C. Give a reason for this high boiling point.

(7.0 *marks*)

9. (*a*) (i) Write balanced chemical equations for reactions of aqueous NaOH with (I) urea and (II) ammonium sulphate.

(ii) A fertilizer solution contains urea and ammonium sulphate and the following procedure was used to determine their concentrations.

Two, 50.0 cm^3 portions of the fertilizer solution were boiled separately with 35.0 cm^3 of 2.0 mol dm^{-3} NaOH solution (excess) until the evolution of NH_3 ceased. One portion of the solution required 30.0 cm^3 of 1.0 mol dm^{-3} HCl when titrated using phenolphthalein as the indicator. The other portion required 50.0 cm^3 of 1.0 mol dm^{-3} HCl when titrated using methyl orange as the indicator.

Calculate the concentrations of urea and ammonium sulphate in the fertilizer solution.

(9.0 *marks*)

(*b*) (i) A green salt dissolves in water and the solution turns purple with time. When dil. HCl is added, this solution turns green forming a unipositive complex ion. Identify the complex ions responsible for (I) the purple colour and (II) the green colour in **solution**.

(ii) Consider the 'hydroxides', XOH of the elements **X** = Na, K, Cl and Br. Explain the variation of acidic / basic character of these compounds on the basis of electronegativity.

Element	:	H	O	Na	K	Cl	Br
Electronegativity	:	2.1	3.5	0.9	0.8	3.0	2.8

(6.0 *marks*)

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10. (*a*) N_2 is reduced to NH_3 in the Haber process. This is carried out at a temperature of about 550 °C and under a pressure of 250 atm.

(i) Give **one** reason as to why the reduction of $N_2(g)$ is difficult.

(ii) For the reaction,

$$3H_2\ (g) + N_2\ (g) \rightleftharpoons 2NH_3(g) \quad \Delta H^{\ominus} = -\ 92.0\ kJ$$

the yield of NH_3 at various temperatures is given below.

Temperature/°C	Yield of NH_3 at 250 atm
200	88%
550	15%
1000	negligible

Briefly explain why a temperature of 550 °C is chosen when the yield is only 15%.

(iii) Name the catalyst used in Haber process.

(iv) Why the catalyst is used in a finely divided state? Explain your answer.

(v) Give a balanced chemical reaction (along with conditions) to convert $NH_3(g)$ to $N_2(g)$.

(vi) Give **two** industrial uses of NH_3. **(7.5 *marks*)**

(*b*) (i) Selecting compounds **only** from those given below, write one chemical equation in each case to illustrate the formation of a thermoplastic polymer by (I) Addition polymerization (II) condensation polymerization (type of polymerization must be stated clearly with each reaction).

Indicate the repeat units clearly.

$$ClCO(CH_2)_4COCl,\quad C_6H_5OH,\quad NH_2(CH_2)_6NH_2,$$
$$HCHO,\quad CH_2{=}CH{-}Cl,\quad CH_2{=}CH{-}CH_3$$

(ii) Using your knowledge on the structure of natural rubber, draw the structure of the more elastic polymer formed by the polymerization of butadiene,

$$CH_2{=}CH{-}CH{=}CH_2$$

Indicate the repeat unit clearly.

(iii) State **one** common problem associated with using powdered (I) dolomite and (II) apatite, in their natural form as fertilizers.

Outline **two** methods by which apatite can be converted to a useful fertilizer. **(7.5 *marks*)**

* * *

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