## PART A — STRUCTURED ESSAY

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

**1.** (*a*) The 3d transition element **M** shows the highest oxidation state of +7.

(i) Identify **M** .....

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

.....

(iii) Give the chemical formula and the colour of the most stable oxide of **M**.

.....

**(2.2 marks)**

(*b*) Fill in the blanks in the following table selecting the most appropriate words/phrases from **only** those given below the table under categories **A**, **B**, **C** and **D** for the respective columns.

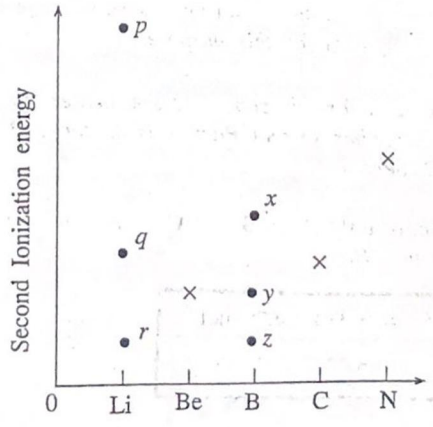
| Material | A<br>Type of material | B<br>Particles occupying lattice positions | C<br>Interactions between particles | D<br>Electrical properties |
|---|---|---|---|---|
| Diamond | | | | |
| KF(s) | | | | |
| Ice | | | | |
| Li(s) | | | | |

**A** : Ionic lattice, giant covalent lattice, metallic lattice, molecular lattice, amorphous material
**B** : Atoms, positive ions, negative ions, positive ions and negative ions, molecules, electrons
**C** : Covalent bonds, van der Waals interactions, hydrogen bonds, metallic bonds, electrostatic interactions
**D** : Conductor, nonconductor, electrolyte **(4.8 marks)**

(*c*) The points corresponding to the **second** ionization energy of Be, C and N are shown by × in the figure given below.

(i) Select the most appropriate point corresponding to the second ionization energy of Li out of the points *p*, *q* and *r*, and mark it with a circle (⊙).

(ii) Select the most appropriate point corresponding to the second ionization energy of B out of the points *x*, *y* and *z*, and mark it with a square (⊡).




**(3.0 marks)**

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2. (*a*) A sample of $Na_2SO_4$ is contaminated with some NaCl. The following procedure was used to determine the percentage of NaCl in the sample.

(Basic)

1.000 g of the sample was dissolved in water in a 250 $cm^3$ volumetric flask and diluted upto the mark to form the solution **A**.

The following solutions (1) - (5) were prepared by diluting a $4.0 \times 10^{-4}$ mol $dm^{-3}$ $Cl^-$ ion solution.

| | (1) | (2) | (3) | (4) | (5) |
|---|---|---|---|---|---|
| $4.0 \times 10^{-4}$ mol $dm^{-3}$ $Cl^-$ ion solution/$cm^3$ | 1.00 | 2.00 | 3.00 | 4.00 | 5.00 |
| Distilled water/$cm^3$ | 9.00 | 8.00 | 7.00 | 6.00 | 5.00 |

Into each of the solutions (1)-(5), 1.00 $cm^3$ of dil. $HNO_3$ and 1.00 $cm^3$ of $AgNO_3$ were added. Similarly into 10.00 $cm^3$ of solution **A**, 1.00 $cm^3$ dil. $HNO_3$ and 1.00 $cm^3$ $AgNO_3$ were added. It was observed that the turbidity produced by solution **A** was equal to that of solution (3).

Calculate the mass percentage of NaCl in the sample of $Na_2SO_4$.
(Na = 23.0, Cl = 35.5) **(5.0 marks)**

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(b) **A** and **B** are pure liquids miscible in all proportions forming ideal solutions at temperature T. The boiling point of **A** is higher than that of **B**. Mark/draw the following in Figure 1.

(i) $p_A^0$ and $p_B^0$ : Relative points representing vapour pressures of pure **A** and pure **B** respectively.

(ii) $p_A$ : Line/curve showing the variation of the vapour pressure of **A** with composition.

(iii) $p_B$ : Line/curve showing the variation of the vapour pressure of **B** with composition.

(iv) $p_T$ : Line/curve showing the variation of the total vapour pressure with composition.

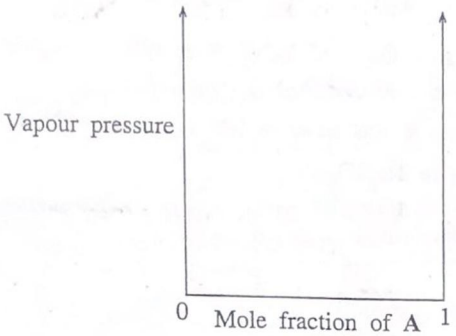



Figure 1

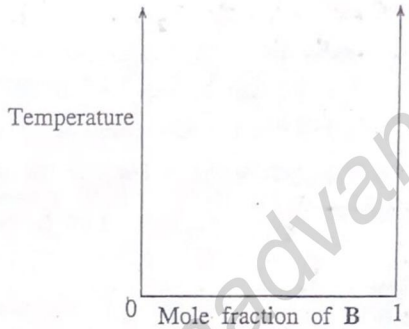



Figure 2

(v) Show that for an equimolar solution of **A** and **B** in equilibrium with its vapour, the mole fraction of **A** in the vapour phase is,

$$\frac{p_A^0}{p_A^0 + p_B^0}$$

.....

.....

.....

.....

(vi) Draw the temperature-composition phase diagram for the solutions of **A** and **B** in Figure 2. Mark in your diagram,

I. the boiling point, $T_A^0$, of pure **A**.

II. the boiling point, $T_B^0$, of pure **B** and

III. the regions where the following phases exist.
liquid, vapour and liquid + vapour together

**(5.0 marks)**

100

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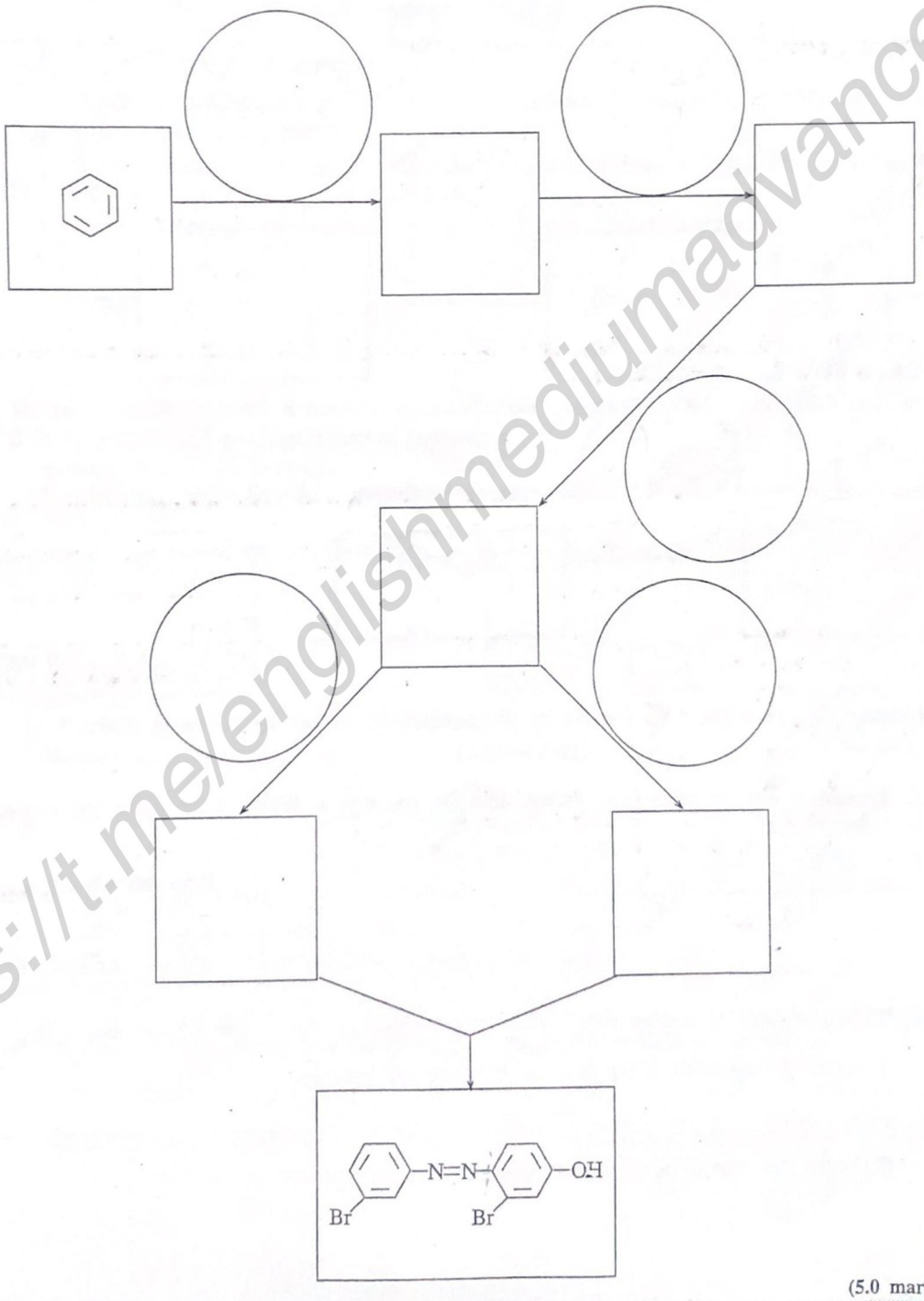
3. Complete the following synthesis, schemes **A** and **B** selecting reagents and solvents only from those given with each scheme.

   * Write the structures of appropriate compounds in the boxes and the reagents/solvents in the circles.
   * Indicate temperature where important.

(i) **Scheme A:**

Reagents and solvents :

dil. HCl, Conc. HCl, Conc. $H_2SO_4$, Conc. $HNO_3$, aq. NaOH, $NaNO_2$, CuBr, $Br_2$, $FeBr_3$, Fe, $PBr_3$, $LiAlH_4$, Sn




**(5.0 marks)**

*[see page six*

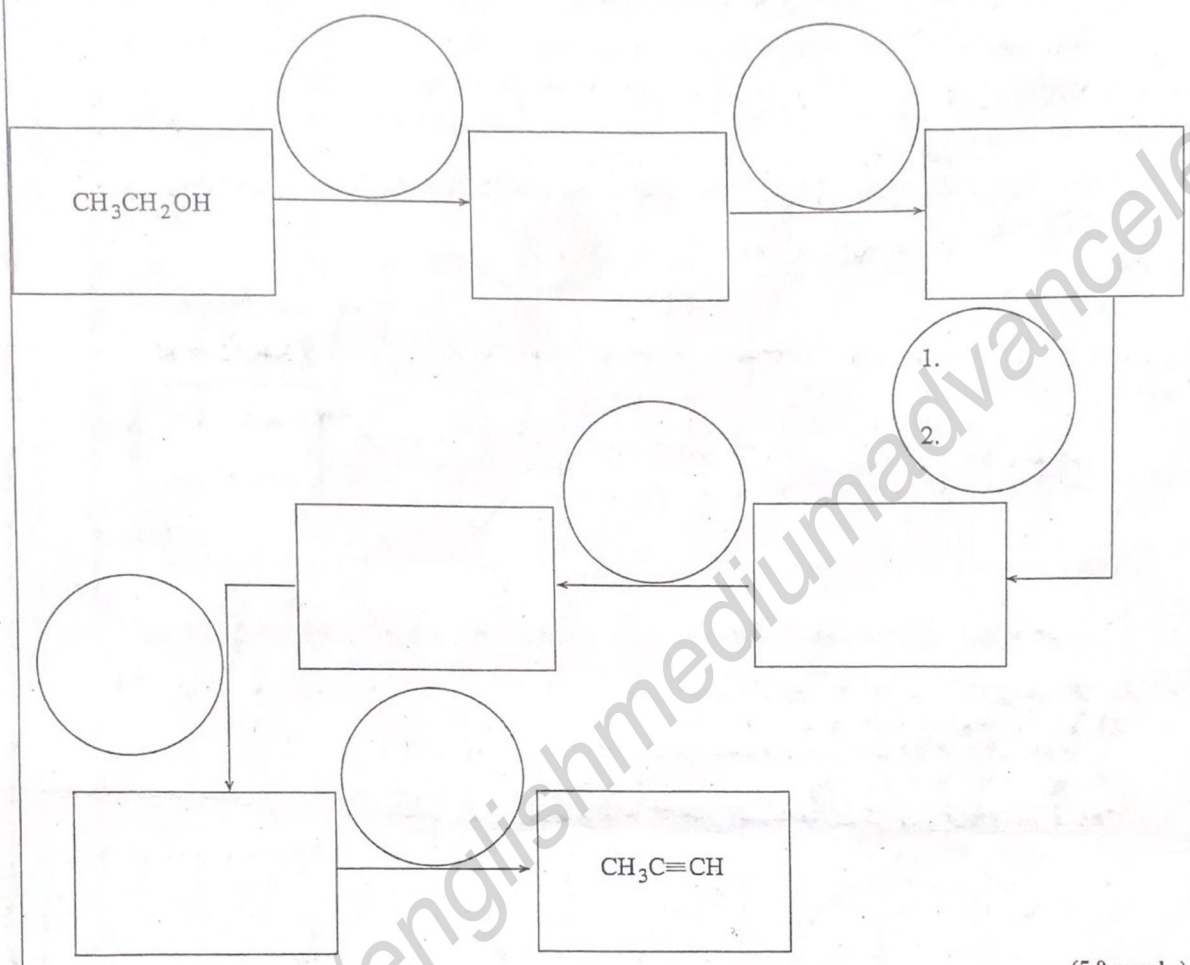
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(ii) Scheme B:

Reagents and solvents :

Conc. $H_2SO_4$, $Br_2$, $FeBr_3$, $PBr_3$, HCHO, alcoholic KOH, $CH_3CHO$, Mg, Fe, dry ether, $H_2O$




(5.0 marks)

100

4. (*a*) Cinnamaldehyde is the main constituent of cinnamon oil. It has the following structure.

$$C_6H_5-CH=CH-CHO$$

(i) Suggest a test, to show that cinnamaldehyde contains a double bond. Give the expected observation/s.

| Test | Observation/s |
|---|---|
| ..... | ..... |
| ..... | ..... |

(ii) Cinnamaldehyde is reacted with $LiAlH_4$ and reaction mixture is treated with dil. acid.

I. Draw the structure of the final organic product obtained.

.....

II. Name the type of reaction occurring between cinnamaldehyde and $LiAlH_4$.

.....

(see page seven)

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(iii) Cinnamaldehyde reacts with isopropyl magnesium bromide, $(CH_3)_2CHMgBr$

I. Give the name of a solvent used in this reaction.

.....

II. Why is it important to keep the solvent dry?

.....

III. Write the structural formula of the product obtained when cinnamaldehyde is reacted with $(CH_3)_2CHMgBr$ and the intermediate hydrolysed.

.....

IV. Recall the condensation reaction that occurs between two molecules of $CH_3CHO$ in the presence of aqueous NaOH.

Write the structures of the two molecules that would undergo a similar reaction under the same conditions forming cinnamaldehyde.

(5.0 marks)

(*b*) The two compounds **A** and **B** have the same molecular formula $C_3H_6O$. Both **A** and **B** react with Brady's reagent giving orange coloured precipitates.

**A** reacts with HCN forming a single product **C**.

**B** reacts with HCN forming a mixture of two stereo-isomers **D** and **E**.

(i) Write the structures of **A**, **B**, **C**, **D** and **E** in the appropriate cages.

**A** **B**

**C** **D** **E**

(ii) State the specific type of isomerism shown by **D** and **E**.

.....

(iii) State a physical property that can be used to distinguish between **D** and **E**?

.....

(iv) What difference is shown by **D** and **E** in respect of the physical property given by you in (iii) above?

.....

.....

(5.0 marks)

100

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இலங்கைப் பரீட்சைத் திணைக்களம்
Department of Examinations, Sri Lanka

02 E II

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கல்விப் பொதுத் தராதரப் பத்திர(உயர் தர)ப் பரீட்சை, 2008 ஓகஸ்ற்
General Certificate of Education (Adv. Level) Examination, August 2008

රසායන විද්‍යාව II
இரசாயனவியல் II
**Chemistry II**

PART B — ESSAY

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

$R = 8{\cdot}314 \text{ J K}^{-1} \text{ mol}^{-1}$
$N_A = 6{\cdot}022 \times 10^{23} \text{ mol}^{-1}$

**5.** (*a*) $NH_4SH$ undergoes decomposition at 27° C as follows :

(Chemical equilibrium)

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

The equilibrium constant, $K_c$, for this reaction at 27 °C is $1.44 \times 10^2 \text{ mol}^2 \text{ m}^{-6}$

(i) Calculate the equilibrium constant, $K_p$, for the above reaction at 27 °C.

**Note :** • Derivation of the relevant equations is not necessary.
• Assume that $NH_3(g)$ and $H_2S(g)$ behave ideally.
• At 27 °C, $RT$ = 2.5 kJ mol$^{-1}$

(ii) Calculate the minimum mass of $NH_4SH$ that must be placed in an evacuated vessel of volume $1.0 \times 10^{-2} \text{ m}^3$ to attain the state of equilibrium at 27° C.

(The relative molecular mass of $NH_4SH$ = 51) **(7.5 marks)**

(*b*) Using the descriptions provided for solutions **A** to **G**, answer the questions (i) - (vi).

(Ionic equilibrium)

| Solution | Description |
|---|---|
| **A** | Freshly distilled water in a stoppered bottle |
| **B** | An aqueous solution of 0.20 mol dm$^{-3}$ HCl |
| **C** | An aqueous solution of 0.10 mol dm$^{-3}$ $CH_3COOH$ |
| **D** | An aqueous solution of 0.01 mol dm$^{-3}$ $CH_3COOH$ |
| **E** | An aqueous solution which is 0.10 mol dm$^{-3}$ in $CH_3COOH$ and 0.10 mol dm$^{-3}$ in $CH_3COONa$ |
| **F** | An aqueous solution which is 0.10 mol dm$^{-3}$ in $CH_3COOH$ and 0.05 mol dm$^{-3}$ in $CH_3COONa$ |
| **G** | An aqueous solution which is $C_1$ mol dm$^{-3}$ in $CH_3COOH$ (dissociation constant $K_1$) and $C_2$ mol dm$^{-3}$ in HCOOH (dissociation constant $K_2$) |

(i) Arrange solutions **A** to **E** in the order of **increasing** their pH. **No** explanation is necessary.

(ii) Solution **E** was diluted 10 times. Would the pH change? Explain your answer in brief.

(iii) Which of the solutions **E** or **F** would resist more to a change in pH upon addition of a small quantity of an HCl acid solution? Explain your answer in brief.

(iv) Solution **I** was prepared by mixing 50.0 cm$^3$ of **B** and 50.0 cm$^3$ of **C**. What is the pH of **I**? State assumptions, if any, you used in this estimation.

(v) What change in pH would you expect when **A** is exposed to air? Explain your answer in brief.

(vi) Derive an expression for the total $H^+$ ion concentration of solution **G** in terms of the initial concentrations ($C_1$, $C_2$) and the acid dissociation constants ($K_1$, $K_2$) of acetic acid and formic acid respectively.

**(7.5 marks)**

*[see page ten*

6. (*a*) Calculate the lattice energy of $CaBr_2(s)$ by constructing an appropriate enthalpy level diagram. Necessary thermochemical data are given below. (Physical states of all chemical species must be given for full marks.)

| | |
|---|---|
| Enthalpy of evaporation of $Br_2(l)$ | $= 31$ kJ mol$^{-1}$ |
| Bond dissociation enthalpy of $Br_2(g)$ | $= 193$ kJ mol$^{-1}$ |
| Electron affinity of Br(g) | $= -331$ kJ mol$^{-1}$ |
| Enthalpy of atomization of Ca(s) | $= 177$ kJ mol$^{-1}$ |
| Sum of first and second ionization energies of Ca(g) | $= 1740$ kJ mol$^{-1}$ |
| Enthalpy of formation of $CaBr_2(s)$ | $= -683$ kJ mol$^{-1}$ |

**(6.0 marks)**

(*b*) A 20.0 g sample of dry clay was thoroughly stirred with 100.0 cm$^3$ of 0.100 mol dm$^{-3}$ $KNO_3$ solution, and the resulting clay suspension was allowed to settle. The supernatant solution was then separated, and to 50.0 cm$^3$ of this solution, 100.0 cm$^3$ of 0.0500 mol dm$^{-3}$ ammonium oxalate solution was added. The resulting solution was filtered, and the precipitate was dried and weighed. The mass of the dry precipitate was 256 mg.

(i) Calculate the concentration of $Ca^{2+}$ in this filtrate.

(ii) Calculate the quantity of Ca in the clay sample in mg/kg.

State assumptions, if any, you used in these calculations.

(C = 12.0, O = 16.0, Ca = 40.0)

Solubility product of calcium oxalate $\left(CaC_2O_4\right)$ at the relevant temperature = $2.30 \times 10^{-9}$ mol$^2$ dm$^{-6}$.

**(9.0 marks)**

7. (*a*) Few drops of phenolphthalein were added to a freshly prepared aqueous solution of 0.10 mol dm$^{-3}$ KI. This solution was well stirred, and thereafter, it was electrolysed using carbon electrodes for a specific period of time. The current passed through the solution was kept constant.

(i) What was the colour of the solution before electrolysis?

(ii) Write the balanced chemical equations for

I. the anode reaction

II. the cathode reaction, and

III. the cell reaction.

(iii) Indicate the colour changes that would occur around the electrodes with the start of electrolysis.

(iv) Propose a method to determine the fraction of $I^-$ ions left at the end of electrolysis. (No experimental details necessary.)

(v) Would the fraction of remaining $I^-$ be different from the value in (iv) if 0.50 mol dm$^{-3}$ KI was used instead of 0.10 mol dm$^{-3}$ KI? Briefly explain your answer.

(vi) In a separate experiment, a solution of $CuSO_4$ was electrolysed using carbon electrodes. What changes would you observe,

I. on the electrodes

II. in solution?

Write down the relevant electrode reactions. **(9.0 marks)**

(*b*) (i) "The order of a particular reactant appearing in the rate expression of a given chemical reaction may **not** necessarily be the same as the stoichiometric coefficient of that reactant in the balanced chemical equation." Clarify this statement in brief.

(ii) $FeCl_3$ is reduced by $SnCl_2$ according to the following reaction.

$$2\ FeCl_3(aq) + SnCl_2(aq) \longrightarrow 2\ FeCl_2(aq) + SnCl_4(aq)$$

A 50.0 cm$^3$ sample of 0.0360 mol dm$^{-3}$ $FeCl_3$ solution was mixed with a $SnCl_2$ solution of the same concentration and of the same volume. It was found that, after 4.00 minutes, 24% of the initial quantity of Fe(III) had been converted to Fe(II). Calculate

I. the rate of reduction of Fe(III).

II. the rate of oxidation of Sn(II). **(6.0 marks)**

*[see page eleven*

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## PART C - ESSAY

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

8. (*a*) $X_2Y$ and $YZ_2$ are two gases formed by the element Y. Y is a solid at room temperature whereas $X_2$ and $Z_2$ are gases.

(A) $X_2Y$ and $YZ_2$ dissolve in water giving acidic solutions.

(B) The oxidation state of Y in $X_2Y$ is –2 and in $YZ_2$ it is +4.

(C) $X_2Y$ and $YZ_2$ (moist) react together forming Y and $H_2O$.

(D) When $X_2Y$ is passed into an acidified $CuSO_4$ solution, a black precipitate is formed.

(E) When $YZ_2$ is passed into an acidified $CuSO_4$ solution, the solution turns colourless.

(i) Identify the gases $X_2Y$ and $YZ_2$.

(ii) Write balanced chemical equations for reactions occurring in (C), (D) and (E).

(iii) Give **two** industrial uses of the gas $YZ_2$.

(iv) Describe briefly a chemical method to identify each of these gases when present as a mixture. Give the relevant balanced chemical equations. **(9.0 marks)**

(*b*) A solution **B** contains $C_2O_4^{2-}$ and $CO_3^{2-}$ ions. A 25.00 $cm^3$ portion of this solution was treated with excess $Ca(NO_3)_2$ solution to completely precipitate $C_2O_4^{2-}$ and $CO_3^{2-}$ ions. The precipitate so obtained after drying had a mass of 0.820 g. This precipitate was then dissolved in dil. $H_2SO_4$ and titrated with 0.05 mol $dm^{-3}$ $KMnO_4$ solution. The titration required 20.00 $cm^3$ of the $KMnO_4$ solution.

Calculate the concentrations of $C_2O_4^{2-}$ and $CO_3^{2-}$ ions in the solution **B**.
(Ca = 40.0, C = 12.0, O = 16.0) **(6.0 marks)**

9. (*a*) (i) The density of an aqueous solution prepared using pure $Na_2CO_3$ was found to be 1.0212 g $cm^{-3}$. Calculate the concentration of this solution. Assume that the density of water at the very same temperature is 1.000 g $cm^{-3}$ and that there is no change in volume during the dissolution of $Na_2CO_3$.

(ii) With the solution in (i) above (in the burette) 25.00 $cm^3$ aliquots of a $H_2SO_4$ solution were titrated using phenophthalein as the indicator. The average of three appropriate end points obtained was 12.50 $cm^3$. Calculate the concentration of the $H_2SO_4$ solution.

(iii) Would it be possible to carry out the above titration in the same way using methyl orange as the indicator? If yes, what is the end-point you expect? If no, give reasons.
(Na = 23.0, C = 12.0, O = 16.0) **(6.0 marks)**

(*b*) The 3d transition element **M** reacts with dil. $H_2SO_4$ forming a pale green solution. On addition of $NH_4OH$ this solution gives a light green precipitate. This precipitate turns yellow-brown with time when kept exposed to air.

(i) Identify **M**.

(ii) What are the most common (positive) oxidation states of **M**?

(iii) Give **one** test to distinguish between the oxidation states given in (ii).

(iv) Outline a method to determine quantitatively the concentrations of **M** in each of the oxidation states given in (ii) when present together in a sample.

(v) Identify the species responsible for the light green and the yellow-brown precipitates mentioned above.

(vi) Give **one** instance where **M** is used as a catalyst in chemical industry.

(vii) Give the chemical formulae and the names of **two** ores used for the extraction of **M**.
**(9.0 marks)**

*[see page twelve*

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10. (a) (i) I. What is meant by the temporary hardness of water?

II. What chemical species are responsible for the temporary hardness?

III. Give **two** domestic problems caused by the temporary hardness.

IV. Give **two** methods by which temporary hardness can be removed. Write chemical equations where appropriate.

(ii) Briefly explain the variation of the acids strength of the following.

$HClO$, $HClO_2$, $HClO_3$, $HClO_4$ **(7.0 marks)**

(b) Ostwald process is used for the manufacture of $HNO_3$ acid.

(i) What are the starting materials used in this process?

(ii) State the sources/methods of obtaining these starting materials.

(iii) Give the chemical steps involved in the Ostwald process together with balanced chemical equations and the necessary conditions (temperature, pressure, catalyst).

(iv) In the manufacture of $HNO_3$, rather than oxidizing $N_2(g)$ directly to $NO(g)$, it is first reduced and the product obtained then oxidized.

Explain the reason for this briefly using the thermochemical data given below.

Values of standard enthalpy of formation, $\left(\Delta H_f^{\ominus}\right)$, of $NO(g)$, $NH_3(g)$ and $H_2O(g)$ are respectively $+90$ kJ mol$^{-1}$, $-46$ kJ mol$^{-1}$ and $-242$ kJ mol$^{-1}$.

**(8.0 marks)**

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