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General Certificate Of Education (Adv. Level) Examination, August 2023

රසායන විද්‍යාව I
Chemistry I

02 | S/E | I

Universal gas constant $R = 8.314\ J\ K^{-1}\ mol^{-1}$ Plank's constant $h = 6.626 \times 10^{-34}\ J\ s$

Avogadro constant $N_A = 6.022 \times 10^{23}\ mol^{-1}$ Velocity of light $c = 3 \times 10^{8}\ m\ s^{-1}$

Introduction to paper Class- 07 -2023 A/L

❖ **Answer all the Questions.**

1. (*b*) The water sample **Y** contains the anions SO_3^{2-}, SO_4^{2-} and NO_3^-. The following procedures were carried out for the quantitative analysis of the anions present in the water sample.

Procedure 1

To 25.00 cm^3 of sample **Y**, an excess of a dilute solution of $BaCl_2$ was added with stirring. Thereafter, excess dilute HCl was added with stirring to the precipitate formed until there was no further evolution of a gas with pungent odour. The solution was allowed to stand for 10 minutes and filtered. The precipitate was washed with distilled water and dried in an oven at 105 °C until a constant mass was obtained. The mass of the precipitate was 0.174 g. The filtrate obtained was kept for further analysis (**see procedure 3**).

Procedure 2

To 25.00 cm^3 of sample **Y**, an excess of dilute H_2SO_4 and acidified 5% KIO_3 solutions were added. The liberated I_2 was immediately titrated with 0.020 mol dm^{-3} $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ used was 20.00 cm^3. (Assume that in this procedure, SO_3^{2-} ions are oxidized to sulphate ions $\left(SO_4^{2-}\right)$ without any loss to the atmosphere.)

Procedure 3

The filtrate from **procedure 1** was neutralized with dilute NaOH and to it excess Al powder and dilute NaOH were added. The solution was heated and the gas evolved was transferred quantitatively to react with a 20.00 cm^3 volume of 0.11 mol dm^{-3} HCl solution. Completion of the reaction was tested with litmus. The HCl remaining after reacting with the gas evolved was titrated with 0.10 mol dm^{-3} NaOH solution using methyl orange as the indicator. The volume of NaOH required was 10.00 cm^3.

(i) Write balanced ionic/non-ionic equations for the reactions taking place in **procedures 1, 2 and 3**.

(ii) Determine the concentrations (mol dm^{-3}) of SO_3^{2-}, SO_4^{2-} and NO_3^- in water sample **Y**. (Ba = 137; S = 32; O = 16)

<u>Procedure I</u>

SO_3^{2-} + $BaCl_2$ → $BaSO_3$↓ + $2Cl^-$ **OR** Ba^{2+} + SO_3^{2-} → $BaSO_3$↓ **(02)**

SO_4^{2-} + $BaCl_2$ → $BaSO_4$↓ + $2Cl^-$ **OR** Ba^{2+} + SO_4^{2-} → $BaSO_4$↓ **(02)**

$BaSO_3$↓ + $2HCl$ → $BaCl_2$ + $SO_2 + H_2O$ **(03)**

$BaSO_4$ will remain insoluble

<u>Procedure 2</u>

$2IO_3^-$ + $12H^+$ + 10e → I_2 + $6H_2O$ **(02)**

5(SO_3^{2-} + H_2O → SO_4^{2-} + $2H^+$ + 2e) **(02)**

$2IO_3^-$ + $5SO_3^{2-}$ + $2H^+$ → I_2 + $5SO_4^{2-}$ + H_2O **(03)**

OR

$2IO_3^-$ + $12H^+$ + 10e → I_2 + $6H_2O$ **(02)**

5(SO_2 + $2H_2O$ → SO_4^{2-} + $4H^+$ + 2e) **(02)**

$2IO_3^-$ + $5SO_2$ + $4H_2O$ → I_2 + $5SO_4^{2-}$ + $8H^+$ **(03)**

I_2 + 2e → $2I^-$ **(02)**

$2S_2O_3^{2-}$ → $S_4O_6^{2-}$ + 2e **(02)**

I_2 + $2S_2O_3^{2-}$ → $S_4O_6^{2-}$ + $2I^-$ **(03)**

Therefore, $5SO_3^{2-} \equiv 2S_2O_3^{2-}$ **OR** $5SO_2 \equiv 2S_2O_3^{2-}$ & $SO_2 \equiv SO_3^{2-}$ **(02)**

<u>Procedure 3</u>

$3NO_3^-$ + 8Al + $5OH^-$ + $2H_2O$ → $8AlO_2^-$ + $3NH_3$ **(02)**

NH_3 + HCl → NH_4Cl **(02)**

HCl + NaOH → NaCl + H_2O **(02)**

Procedure 2 – Determination of SO_3^{2-}

Moles of $S_2O_3^{2-}$ $= \frac{0.02}{1000} \times 20$ **(02)**

Therefore, moles of SO_3^{2-} $= \frac{0.02}{1000} \times 20 \times \frac{5}{2}$ **(02)**

Concentration of SO_3^{2-} $= \frac{0.02}{1000} \times 20 \times \frac{5}{2} \times \frac{1000}{25}$ **(02)**

= **0.04 mol dm^{-3}** **(03 + 01)**

Procedure 3 – Determination of NO_3^-

Moles of HCl $= \frac{0.11}{1000} \times 20$ **(02)**

Moles of NaOH $= \frac{0.10}{1000} \times 10$ **(02)**

Since NaOH and HCl react in the ratio of 1:1

Moles of HCl reacted with NH_3 $= \frac{0.11}{1000} \times 20 - \frac{0.10}{1000} \times 10$ **(02)**

$= \frac{1}{1000}(2.2 - 1) = \frac{1.2}{1000}$ **(02)**

Therefore, moles of NH_3 $= \frac{1.2}{1000}$ **(02)**

Therefore, moles of NO_3^- $= \frac{1.2}{1000}$ **(02)**

Concentration of NO_3^- $= \frac{1.2}{1000} \times \frac{1000}{25}$ **(02)**

= **0.048 mol dm^{-3}** **(03 + 01)**

Procedure I – Determination of SO_4^{2-}

Molar mass of $BaSO_4$ = 137 + 32 + 64 = 233 **(02)**

Mass of $BaSO_4$ precipitate = 0.174 g

Therefore, moles of $BaSO_4$ $= \frac{0.174}{233}$ **(02)**

Therefore, moles of SO_4^{2-} $= \frac{0.174}{233} = 7.47 \times 10^{-4}$ **(02)**

Concentration of SO_4^{2-} $= \frac{7.47 \times 10^{-4}}{25} \times 1000$ **(02)**

= **0.029 (0.03) mol dm^{-3}** **(03 + 01)**

2.

2011 AL

(*b*) Solution **P** contains SO_4^{2-}, Cu^{2+} and H^+. The following procedures (1-3) were used to determine their concentrations.
Procedure:

(1) Excess $BaCl_2$ solution was added to 25.00 cm^3 of the solution **P**, to precipitate SO_4^{2-} as $BaSO_4$ The precipitate was filtered, washed and dried till a constant mass was observed. The mass of the precipitate was 2.335 g. Determine the concentration of SO_4^{2-} in solution **P** in mol dm^{-3}. (O = 16, S = 32, Ba = 137)

(2) H_2S was bubbled through 25.00 cm^3 of solution **P** to precipitate Cu^{2+} as CuS. The precipitate was filtered, washed with water, and the filtrate was kept to be used in procedure (3). The precipitate was transferred into a titration flask containing 30.00 cm^3 of 0.28 mol dm^{-3} acidic $KMnO_4$ to produce Cu^{2+} Mn^{2+} and SO_2. The solution was boiled to remove SO_2, and the excess $KMnO_4$ was titrated with 0.10 mol dm^{-3} Fe^{2+} solution. The burette reading at the end point was 10.50 cm^3. Determine the concentration of Cu^{2+} in solution P in mol dm^{-3}.

(3) The filtrate from procedure (2) above was placed in a titration flask, boiled to remove H_2S and cooled to room temperature. To this, both 5% KIO_3 and 5% KI were added in excess. The volume of 0.40 mol dm^{-3} $Na_2S_2O_3$ solution required to titrate the liberated iodine was 25.00 cm^3. Determine the concentration of H^+ in solution **P** in mol dm^{-3}. **(7.5 *marks*)**

8. (b) 1.

Weight of $BaSO_4$	= 2.335 g	
Molar mass of $BaSO_4$	= 233 g mol^{-1}	**(02)**
Moles of $BaSO_4$	= 2.335/233 = 0.010	 **(03)**
Therefore, moles of SO_4^{2-}	= 0.010	**(02)**
$[SO_4^{2-}]$	= 0.010 x 1000/25 mol dm^{-3} = 0.40 mol dm^{-3}	**(03)** **(03 + 02)**

(15 marks)

2. $5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$ ---------(1) **(05)**

$5CuS + 6MnO_4^- + 28H^+ \rightarrow 6Mn^{2+} + 5Cu^{2+} + 5SO_2 + 14H_2O$ ---(2) **(05)**

or

$5S^{2-} + 6MnO_4^- + 28H^+ \rightarrow 6Mn^{2+} + 5SO_2 + 14H_2O$ **(03)**

Moles of MnO_4^- reacted with CuS $= (8.4 \times 10^{-3}) - (2.1 \times 10^{-4})$
$= 8.2 \times 10^{-3}$ **(02)**

$5SO_2 + 2H_2O + 2MnO_4^- \rightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$ ----------(3) **(05)**

Combining eqs. (2) & (3), $5CuS \equiv 8MnO_4^-$ ----------(4) **(03)**

From relationship (4), moles of CuS $= 5/8 \times 8.2 \times 10^{-3}$ **(03)**
$= 5.1 \times 10^{-3}$ **(01)**

Therefore, moles of Cu^{2+} in 25.00 cm^3 $= 5.1 \times 10^{-3}$ **(01)**

$[Cu^{2+}] = 5.1 \times 10^{-3}/25 \times 1000 \text{ mol dm}^{-3}$ **(01)**

$[Cu^{2+}] = 0.20 \text{ mol dm}^{-3}$ **(03 + 02)**

(40 marks)

3. $IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$
$\underline{3(I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-)}$
$IO_3^- + 6S_2O_3^{2-} + 6H^+ \rightarrow I^- + 3S_4O_6^{2-} + 3H_2O$ -----------(5) **(06)**
For first two reactions only, award (02) + (02) marks

Moles of $S_2O_3^{2-} = 0.4/1000 \times 25$ **(03)**
From eq.(5), moles of H^+ in 25.00 $cm^3 = 0.4/1000 \times 25$ **(03)**

$[H^+] = 0.4/1000 \times 25 \times 1000/25 \text{ mol dm}^{-3}$ **(03)**

$[H^+] = 0.4 \text{ mol dm}^{-3}$ **(03 + 02)**

(20 marks)

Total 8(b) = 75 marks

3. **2012 AL**

(*b*) (i) A 3*d* block element **M** forms an ion $\mathbf{M}^{n+}$. This ion can be oxidized by MnO_4^- in a dil. H_2SO_4 medium to give the MO_2^+ ion. In an experiment, 30.0 cm^3 of 0.100 mol dm^{-3} $KMnO_4$ was required to oxidize 5.00×10^{-3} mol of $\mathbf{M}^{n+}$ to MO_2^+. Use this data to calculate the value of *n*.

(ii) The following procedures I and II were used to determine the percentage of Cu in the Cu-containing alloy **Z**.
Procedures:

I. A sample of 2.80 g of the alloy Z was dissolved in 500.0 cm^3 of dil. H_2SO_4. Addition of excess KI to 25.0 cm^3 of this solution produced the white precipitate CuI, and I_2 as the only products. The liberated I_2 was titrated with $Na_2S_2O_3$ solution using starch as the indicator. The volume of $Na_2S_2O_3$ solution required was 30.0 cm^3.

II. To 25.0 cm^3 of $K_2Cr_2O_7$ solution, prepared by dissolving 1.18 g in 500.0 cm^3 of distilled water, 20 cm^3 of dil. H_2SO_4 and excess KI were added. The liberated I_2 was titrated with the $Na_2S_2O_3$ solution used in procedure I with starch as the indicator. The volume of $Na_2S_2O_3$ required was 24.0 cm^3.

1. Give balanced chemical equations for the reactions taking place in procedures I and II.
2. Determine the percentage of Cu in alloy **Z**.
3. Indicate the colour changes you would observe at the end points of the titrations in procedures I and II.

(O = 16, K = 39, Cr = 52, Cu = 63.5) **(8.0 *marks*)**

(ii) 1. Procedure I

$2Cu^{2+} + 4I^- \rightarrow 2CuI + I_2$ .... (eq. 1) (03)

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ .... (eq. 2) (03)

Procedure II

$Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$

$3(2I^- \rightarrow I_2 + 2e)$

$Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 3I_2 + 2Cr^{3+} + 7H_2O$ ....(eq. 3) (06) ~~(03)~~

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$ ....(eq. 4) ~~(03)~~

2. **METHOD 1**

Considering Procedure II

Combining (eq. 3) + (3 x eq. 4)

$Cr_2O_7^{2-} \equiv 6S_2O_3^{2-}$ (03)

Molar mass of $K_2Cr_2O_7 = 294\ g\ mol^{-1}$ (02)

Concentration of $K_2Cr_2O_7$ solution $= \dfrac{1.18}{294} \times \dfrac{1000}{500}$

$= 0.008\ mol\ dm^{-3}$ (03)

Moles of $K_2Cr_2O_7$ in $25.0\ cm^3 = \dfrac{0.008}{1000} \times 25$ (03)

Therefore, Moles of $S_2O_3^{2-} = \dfrac{0.008}{1000} \times 25 \times 6$ (03)

$[S_2O_3^{2-}] = \dfrac{0.008}{1000} \times 25 \times 6 \times \dfrac{1000}{24}$

Concentration of $Na_2S_2O_3$ solution = $0.05\ mol\ dm^{-3}$ (03)

<u>Considering Procedure I</u>

No. of moles of $S_2O_3^{2-}$ = $\frac{0.05}{1000} \times 30$ (03)

Combining (eq. 1) + (eq. 2)

$2Cu^{2+} \equiv 2S_2O_3^{2-}$

Hence, $Cu^{2+} \equiv S_2O_3^{2-}$ (03)

Therefore, Moles of Cu^{2+} present in 25.0 cm^3 = $\frac{0.05}{1000} \times 30$ (03)

Moles of Cu^{2+} in 500.0 cm^3 = $\frac{0.05}{1000} \times 30 \times \frac{500}{25}$ (03)

Therefore, weight of Cu^{2+} $= \frac{0.05}{1000} \times 30 \times \frac{500}{25} \times 63.5$

$= 1.9$ g (03)

% Cu in alloy Z $= \frac{1.9}{2.80} \times 100$

= **68%** (05)