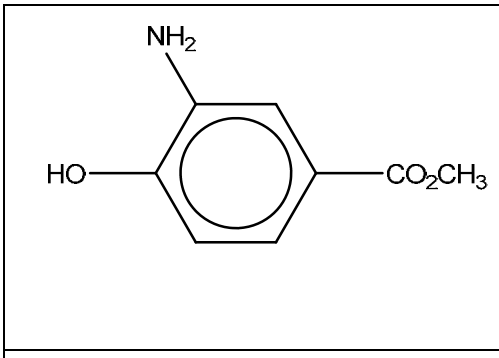
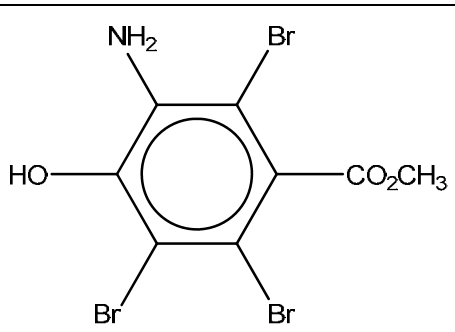
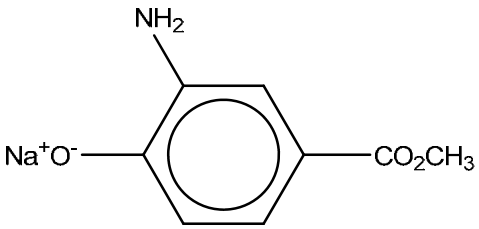
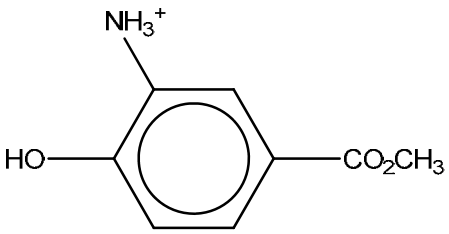
H2 Chemistry (9647) Prelims 2013 Paper 3

1 (a)

	
Orthocaine	A
	
B	C

[9]

1 mark for each correct structure.

C:H ratio in orthocaine ≈ 1:1⇒ Presence of **benzene ring.**

Orthocaine gives violet complex with neutral FeCl_3 (aq) ⇒ Presence of **phenol.**

Orthocaine undergoes **electrophilic substitution** with aq Br_2. ⇒ Presence of **phenylamine/ phenol.**

Orthocaine undergoes **acid – base rxn** with NaOH(aq). ⇒ Presence of **phenol/ carboxylic acid.**

Orthocaine undergoes **acid – base rxn** with HCl(aq). ⇒ Presence of **amine.**

Orthocaine undergoes **acid hydrolysis** in hot acid to give **CH_3OH.**

CH_3OH is **oxidized** by hot acidified $KMnO_4$ to give **CO_2** , colourless gas.

Allow alternative answers

(b) (i) Using Expt 2 & 3, [NO] x 1.5 times while keeping $[O_2]$ constant, rate x 2.25 times (i.e. $(1.5)^2$ times). Therefore second order with respect to NO.

Using Expt 1 & 2, let rate = $k[NO]^2[O_2]^n$

$$\frac{\text{rate(1)}}{\text{rate(2)}} = \frac{1.4\times10^{-5}}{8.4\times10^{-5}} = \frac{k[0.001]^2[0.002]^n}{k[0.002]^2[0.003]^n}$$

$\left(\frac{2}{3}\right)^n = \frac{2}{3}$ so n = 1

First order with respect to O_2.

Using Expt 1, rate = $k[NO]^2[O_2]$

$1.40 \times 10^{-5} = k(0.001)^2(0.002)$

$k = 7000\ mol^{-2}dm^6s^{-1}$

(ii) rate of formation of NO_2

$= k[NO]^2[O_2] = 7000(0.002)^2(0.002)$

$= 5.60 \times 10^{-5}\ moldm^{-3}s^{-1}$

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$

rate of depletion of O_2

= ½ x rate of formation of NO_2

= ½ x $5.60 \times 10^{-5} = 2.80 \times 10^{-5}\ moldm^{-3}s^{-1}$ **[5]**

(c) (1): $CH_3COOAg\ (s) + aq \rightleftharpoons CH_3COO^- + Ag^+$

(2): $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

CH_3COO^- is a **strong conjugate base of a weak acid**.

C*l*$^-$ and Br^- are **weak conjugate bases of strong acids.**

When nitric acid is added, **position of eqm (POE) in (2) shifts to the left** , concentration of CH_3COO^- decreases.

As a result, **POE in (1) shifts right** to counter the decrease in concentration of CH_3COO^-. This continues until all of CH_3COOAg dissolves.

[3]

(d) $K_{sp} = (1.30 \times 10^{-5})^2 = 1.69 \times 10^{-10}\ mol\ dm^{-3}$

$[Ag^+] = (0.025/ 170) \div 2 = 7.353 \times 10^{-5}\ mol\ dm^{-3}$

$(7.353 \times 10^{-5} + s)(s) = 1.69 \times 10^{-10}$

Since K_{sp} is small, assume s is small, $7.353 \times 10^{-5} + s \approx 7.353 \times 10^{-5}$

Solving, $s = 2.298 \times 10^{-6}\ mol\ dm^{-3}$

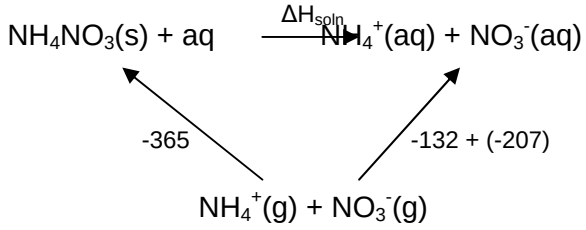
Mass of AgC*l* ppt **[3]**

$= (1.30 \times 10^{-5} - 2.298 \times 10^{-6})\ (2)\ (108 + 35.5)$

$= 3.07 \times 10^{-3}$ g

2 **(a)** **(i)** The enthalpy change of solution of a substance is the enthalpy change when **one mole of the substance is completely dissolved in enough (or excess) solvent (or water)** so that **no further enthalpy change takes place on adding more solvent**.

(ii)



Using Hess' Law,

$\Delta H_{soln} = -\Delta H(\text{LE}) + \Sigma\, \Delta H_{hyd} = 365 + (-132-207) = +26.0$ kJmol^{-1}

(iii) Ammonium nitrate is a **giant ionic lattice structure** and water molecules are **simple covalent molecules**. When ammonium nitrate dissolves in water, **the energy released in the formation of ion-dipole interactions** between the ions and water molecules is **less that the energy absorbed in breaking up the ionic bonds between ammonium and nitrate ions and hydrogen bonds between water molecules**.

(iv) $\Delta S = 186 + 256 - 151 = +291$ Jmol^{-1}K^{-1}

$\Delta G = \Delta H - T\Delta S$

For the instant cold pack to work,

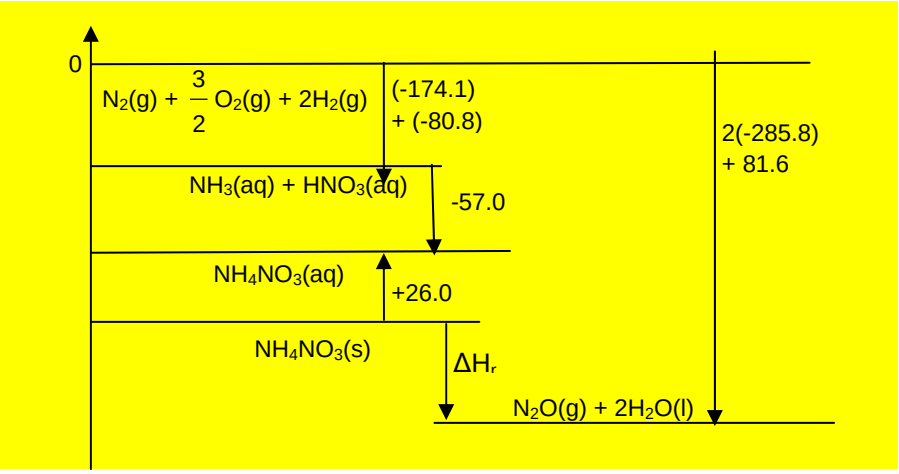
$\Delta G < 0$ i.e. $\Delta H - T\Delta S < 0$

$$T > \frac{\Delta H}{\Delta S}$$

$$T > \frac{+(26.0 \times 10^3)}{+291}$$ i.e. T > 89.3 K

[7]

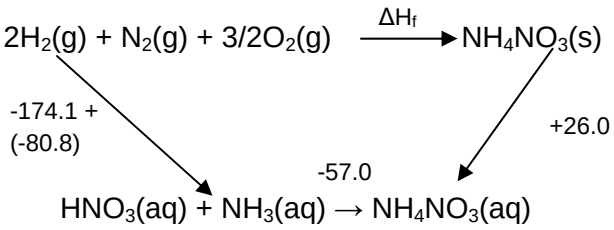
(b) **(i)** **Method 1:**



ΔH_r = [2(-285.8) + 81.6] – [-174.1 - 80.8 - 57.0 - 26.0]

= -152.1 kJmol^{-1}

Method 2:

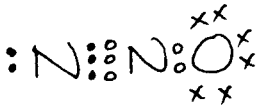


$\Delta H_f(NH_4NO_3(s))$ = -174.1 – 80.8 – 57.0 - 26.0 = -337.9

$\Delta H_r = 2\Delta H_f(H_2O(l)) + \Delta H_f(N_2O(g)) – \Delta H_f(NH_4NO_3(s))$

= -152.1 kJmol^{-1}

(ii)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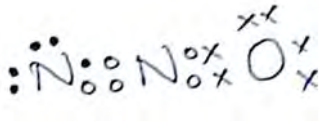


[4]

(c) (i) Denaturation is the process by which a protein **loses its tertiary or secondary / quarternary structure** by application of external stress and **loses its function**

(ii) **pH changes:**

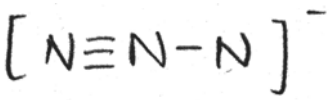
-Disrupts hydrogen bonds in the tertiary structure. At low pH, –NH_2 becomes –NH_3^+.At high pH, phenol becomes phenoxide ion.

Or

- Disrupts ionic interactions in the tertiary structure. At low pH,

phenoxide becomes phenol while at high pH, $-NH_3^+$ becomes $-NH_2$.

(iii) 7 **[4]**

(d) **(i)** 

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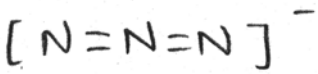


Linear **[2]**

(i) Volume of gas = 3.0 x 24.0 = 72.0 dm^3

(ii) $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$ i.e. $\frac{(1)(72.0)}{273+25} = \frac{(0.8)(V_2)}{(273-10)}$

Therefore, V_2 = 79.4 dm^3

It is assumed that N_2 was behaving as an ideal gas. **[3]**

3 **(a)** **(i)** $n_{NaOH} = n_{HCl}$ in 5.00 cm^3 sample

At equilibrium, V_{NaOH} = 30.00 cm^3

$n_{NaOH} = n_{HCl} = 0.0300 \times 0.100 = 0.00300$ mol

$[HCl] = 0.00300 \div 0.005 = 0.600$ mol dm^{-3}

$C_2F_4 \equiv 2HCl$

$[C_2F_4] = ½ [HCl] = 0.300$ mol dm^{-3}

$CHCl F_2 \equiv HCl$

$[CHCl F_2] = 1.00 - [CHCl F_2]_{reacted}$

$= 1.00 - 0.600 = 0.400$ mol dm^{-3}

(ii) $K_c = \frac{[C_2F_4][HCl]^2}{[CHClF_2]^2}$

$K_c = \frac{[0.300][0.600]^2}{[0.400]^2} = 0.675$ mol dm^{-3}

(iii) Comparing Experiment 1 and 2, when the temperature is increased, the equilibrium [HCl] increased/ the volume of NaOH required to neutralise the HCl increases. The equilibrium position shifted to the right to absorb energy. Therefore, forward reaction is endothermic. **[6]**

OR

ΔH = 2BE(C-H) + 2BE(C-C*l*) + 4BE(C-F)

– BE(C=C) – 4BE(C-F) – 2BE (H-C*l*)

= +28.0 kJ mol^{-1}

Since ΔH is positive, the forward reaction is endothermic.

(b) **(i)** At the start of reaction, there is only forward reaction since there is no product for backward reaction to take place.

Therefore, to find the rate of forward reaction, draw a **tangent to the graph at t = 0 min**. The **gradient of the tangent is the initial rate** of forward reaction.

(ii) From the respective tangent of the graphs for experiment 2 and 3,

Expt2 : Expt3

$\frac{35}{30} : \frac{9}{30}$

4 : 1

When [CHC*l*F$_2$] is halved, the rate of forward reaction decreased by ¼ . Therefore, the reaction is second order with respect to CHC*l*F$_2$(g).

(iii) If conclude first order in (b)(ii):

CHC*l*F$_2$ = CF_2 + HC*l* (slow)

2 CF_2 → C_2F_4

OR

CHC*l*F$_2$ = CF_2 + HC*l* (slow)

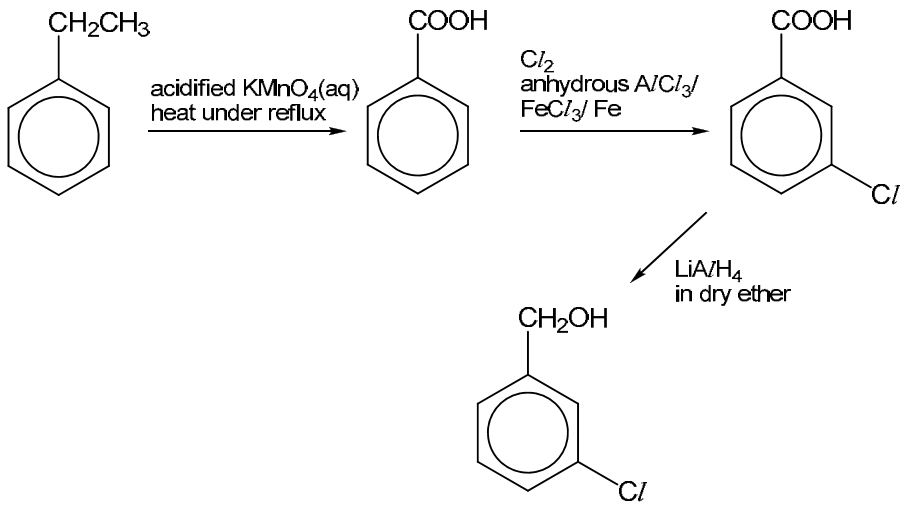
CF_2 + CHC*l*F$_2$ → C_2F_4 + HC*l*

If conclude 2nd order in (b)(ii):

2nd step is the slow step

[6]

(c) **(i)**



(ii) Electrophilic Substitution

Step 1: Generation of Cl^+ electrophile.

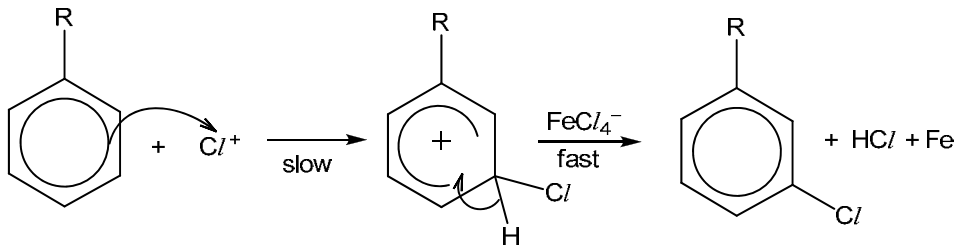
If $FeCl_3$ is used, $FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

If Fe is used, $Fe + {}^3/_2 Cl_2 \rightarrow FeCl_3$

$FeCl_3 + Cl_2 \rightarrow FeCl_4^- + Cl^+$

If $AlCl_3$ is used, $AlCl_3 + Cl_2 \rightarrow AlCl_4^- + Cl^+$

Step 2: Electrophilic attack of benzene by Cl^+.



[8]

4 **(a)** **(i)** $Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$ **[1]**

(ii) $Ni(s) + Fe^{2+}(aq) \rightarrow Ni^{2+}(aq) + Fe(s)$

$E^{\ominus} = -0.44 - (-0.25)$

$= -0.19V, < 0V$

Since $E^{\ominus}$ is less than 0V, the reaction is not spontaneous and will not be feasible. **[2]**

(iii) When excess $NH_3(aq)$ is added:

Oxidation: $[Ni(NH_3)_6]^{2+}(aq) + 2e^- \rightarrow Ni(s) + 6NH_3(aq)$ $-0.51V$

Reduction: $Fe^{2+}(aq) + 2e^- \rightarrow Fe(s)$ $-0.44V$

Overall: $Ni(s) + 6NH_3(aq) + Fe^{2+}(aq) \rightarrow Fe(s) + [Ni(NH_3)_6]^{2+}(aq)$

Overall $E^{\ominus} = -0.44 - (-0.51)$

$= +0.07$ V

Hence, since $E^{\ominus} > 0V$, the reaction can take place.

$$Fe(OH)_2(s) \rightleftharpoons Fe^{2+}(aq) + 2OH^-(aq)$$

Fe^{2+} is consumed/ $[Fe^{2+}]$ drops. (By le chatelier's principle) more $Fe(OH)_2(s)$ is able to dissolved/ The equilibrium position shift right to replenish the loss of Fe^{2+} and removing $Fe(OH)_2(s)$. **[3]**

(iv) Grey ppt: Iron/ Fe(s)

Pale blue solution: $[Ni(NH_3)_6]^{2+}$ OR $[Ni(NH_3)_6]Cl_2$ **[2]**

(b) **(i)** $\Delta S^{\ominus} > 0$ as there is an increase in disorder due to the increase of number of moles of aqueous/liquid produts from 4 to 7.

This increase in disorder will result in ΔG value to be more likely negagtive, and hence the reaction is expected to be favourable.

[2]

(ii)

$Fe(OH)_2(s)$	$\rightleftharpoons$	$Fe^{2+}(aq)$	+	$2OH^-(aq)$
		0		0
		a		2a

$a(2a)^2 = 1.8 \times 10^{-15}$

$a = 7.66 \times 10^{-6}$ mol dm^{-3} **[2]**

(iii) $$K_s = \frac{[Fe(en)_3^{2+}]}{[Fe(H_2O)_6^{2+}][en]^3}$$ **[2]**

$$5.00 \times 10^{9} = \frac{0.117}{x(0.149)^3}$$

$$x = 7.07 \times 10^{-9}\ mol dm^{-3}$$

Total $n_{Fe(OH)_2} = (0.117 + 7.07 \times 10^{-9})$ mol

$$m_{Fe(OH)_2} = (0.117 + 7.07 \times 10^{-9}) \times (55.8 + 2 \times 16.0 + 2 \times 1.0)$$

$$m_{Fe(OH)_2} = 10.5g$$

(iv) When dissolved and after equilibrium is established, [Fe^{2+}] in the solution **A** is 7.07 × 10^{-7} mol dm^{-3} which is less than 7.66 X 10^{-6} mol dm^{-3}. Hence, IP < K_{sp} and all of the y grams of $Fe(OH)_2$(s) is able to dissolve.

[1]

(c) **(i)** (I) Heat (under reflux) with H2SO4(aq).

(II) Carefully neutralise, and add $FeCl_3$(aq)

P: Purple coloration observed

Q: No purple coloration observed.

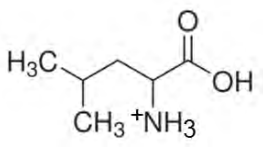
[2]

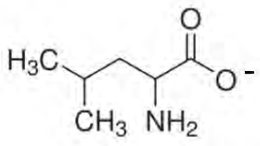
(ii) Heat both compounds with $KMnO_4$ in H_2SO_4(aq)

R: Purple solution turned colourless.

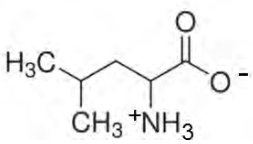
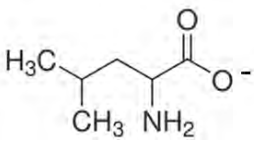
S: Purple solution remains. **[2]**

5 **(a)** **(i)**

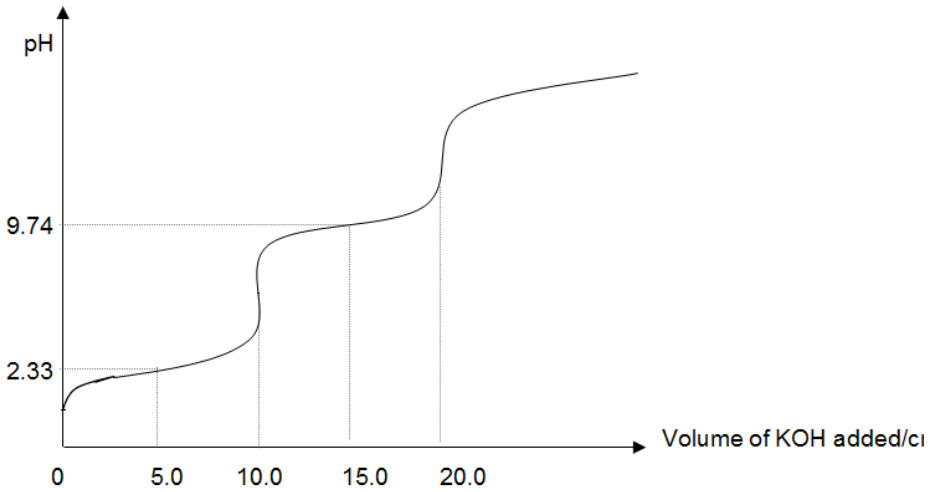
pH 2: 

pH 10: 

[2]

(ii)  + OH^- →  + H_2O **[1]**

(iii)



[3]

(iv) Amount of leucine = 10.0/1000 x 0.150 = 0.00150 mol

At pH 2.33, [HA] = [A^-]

Amount of HA = Amount of A^- = 0.00150/2 = 0.000750 mol

Amount of H^+ added from HC*l* = 5.00/1000 x 0.0300 = 0.000150 mol

$A^- + H^+ \rightarrow HA$

Amount of remaining HA = 0.000750 + 0.000150 = 0.000900 mol

Amount of remaining A^- = 0.000750 – 0.000150 = 0.000600 mol

$pH = pK_a + \lg([A^-]/[HA])$

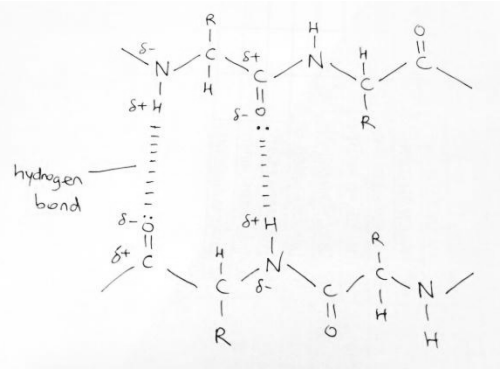
$= 2.33 + \lg((0.000600 \div V)/(0.000900 \div V))$

$= 2.15$

Change in pH = 2.15 – 2.33 = –0.18 **[3]**

(b) **(i)** The secondary structure of a protein is the regular coils and folds in localised segments of the polypeptide chain, as stabilised by hydrogen bonding between the *backbone* C=O and N–H groups of the polypeptide chain. **[1]**

(ii)



[3]

(c) **(i)** Barium sulfate / $BaSO_4$ **[1]**

(ii) $4Br_2(aq) + S_2O_3^{2-}(aq) + 5H_2O(l) \rightarrow 8Br^-(aq) + 2SO_4^{2-}(aq) + 10H^+(aq)$

[1]

(iii) $I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$

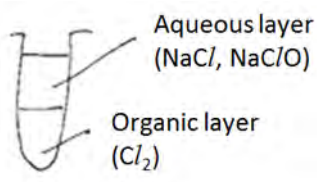
[1]

(iv) $Br_2 + e^- \rightleftharpoons 2Br^-$ $E^\ominus = +1.07$ V

$I_2 + e^- \rightleftharpoons 2I^-$ $E^\ominus = +0.54$ V

As observed from $E^\ominus$ values, Br_2 is a stronger oxidising agent than I_2. Hence, Br_2 can oxidise $S_2O_3^{2-}$ to SO_4^{2-} (oxidation state of sulfur increases from +2 to +6). Iodine can only oxidise $S_2O_3^{2-}$ to $S_4O_6^{2-}$ (oxidation state of sulfur increases from +2 to +2.5). **[2]**

(v)



[2]