

Answer **all** questions in the spaces provided.

1 (a)

Repulsion between two negatively charged ions causes the activation energy to be high.

[1]

(b)

Preparation of reaction mixture

1. Using a 50.0 cm³ measuring cylinder, add 25.0 cm³ of peroxodisulfate ions into a 250 cm³ conical flask.
2. Using a 10.0 cm³ measuring cylinder, add 2.0 cm³ of aqueous copper (II) ions into the same conical flask.
3. Using a 50.0 cm³ measuring cylinder, add 45.5 cm³ of deionised water into the conical flask.
4. Using a 10.0 cm³ measuring cylinder, measure out 2.5 cm³ of ethanedioate ions.
5. Transfer the ethanedioate ions into the conical flask and insert a rubber bung into the conical flask. The rubber bung has a delivery tube connected to rubber tubing with the other end of the tubing inserted into an inverted burette filled with water.
6. Start the stopwatch immediately and gently swirl the conical flask continuously.
7. Monitor the water level in the burette and stop the stopwatch when 40.00 cm³ of CO₂ is produced. Record the time taken.
8. Repeat step 1 to 7 using the following volumes of reactants, copper (II) ions and deionised water shown in experiment 2 to 4, at the same temperature.

| Experiment | Volume of S ₂ O ₈ ²⁻ / cm ³ | Volume of C ₂ O ₄ ²⁻ / cm ³ | Volume of Cu ²⁺ / cm ³ | Volume of water / cm ³ |
|------------|---|---|--|-----------------------------------|
| 1 | 25.0 | 2.5 | 2.0 | 45.5 |
| 2 | 25.0 | 5.0 | 2.0 | 43.0 |
| 3 | 2.5 | 25.0 | 2.0 | 45.5 |
| 4 | 5.0 | 25.0 | 2.0 | 43.0 |

Treatment of results

1. Relative rates (= 1/t) of expt 1 to 4 are calculated. Since total volume of mixture is constant in expt 1 to 4, concentration of reactant is proportional to its volume used.
2. Compare the relative rates of expt 1 to 2 and 3 to 4, to find the order of reaction with respect to (w.r.t) C₂O₄²⁻ and S₂O₈²⁻ respectively. If volume of C₂O₄²⁻ doubles and rate remains the same, it is zero order w.r.t C₂O₄²⁻. If volume of C₂O₄²⁻ doubles, and rate remains doubles, it is first order w.r.t C₂O₄²⁻. If volume of C₂O₄²⁻ doubles and rate quadruples, it is second order w.r.t C₂O₄²⁻. The same applies for S₂O₈²⁻.
3. The rate law of reaction can then be found, rate = k[S₂O₈²⁻]ⁿ[C₂O₄²⁻]^m, where n and m are the orders of reaction w.r.t to S₂O₈²⁻ and C₂O₄²⁻ respectively.

[8]

(c)

1. Repeat one of the experiments (e.g. expt 2) at two (at least) different temperatures, other than that for experiment 1 to 4 above. This can be done by immersing conical flasks in water bath maintained at different constant temperatures e.g. 40 °C and 60 °C.
2. Using the results in experiment 2 and that of the two further experiments, relative rate, followed by \ln (relative rate) for each expt is calculated.
3. A graph of \ln (relative rate) against $\frac{1}{T}$ is plotted. The gradient of the best fit line is then determined, where gradient = $-\frac{E_a}{R}$. E_a is given by | gradient x R |.

[3]

[Total: 12]

2 (a) (i)

| | Half-equations | Polarity |
|---------|--|----------|
| Anode | $\text{Pb(s)} + \text{SO}_4^{2-}(\text{aq}) \rightarrow \text{PbSO}_4(\text{s}) + 2\text{e}^-$ | – |
| Cathode | $\text{PbO}_2(\text{s}) + 4\text{H}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + 2\text{e}^- \rightarrow \text{PbSO}_4(\text{s}) + 2\text{H}_2\text{O(l)}$ | + |

[3]

(ii)

The relative density of the sulfuric acid will decrease.

During discharging, as sulfuric acid is used up to produce PbSO_4 , the concentration of sulfuric acid will decrease, resulting in a decrease in density.

[2]

(iii)

Overcharging will result in electrolysis of water.
Identity of other gas: Oxygen

[2]

(iv)

$$E^\ominus = 1.47 - (-0.13) = +1.60 \text{ V}$$

[2]

(v)

Lead-acid battery has a higher voltage as PbSO_4 formed is insoluble, which resulted in a lower concentration of Pb^{2+} in the electrolyte, thus driving the forward reaction.

[2]

(b) (i)

To 1 cm³ of halide ions, add AgNO₃(aq) dropwise. Then add aqueous NH₃ in excess.

Cl⁻ ions form white ppt with AgNO₃ which is soluble in excess NH₃(aq).

Br⁻ ions form cream ppt with AgNO₃ which is insoluble in excess NH₃(aq) [2]

(ii)

$\text{Ag}^+(\text{aq}) + \text{X}^-(\text{aq}) \rightleftharpoons \text{AgX}(\text{s})$, where X⁻ is Cl⁻ and Br⁻

Both halide ions form insoluble ppt with Ag⁺.

$\text{Ag}^+(\text{aq}) + 2\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Ag}(\text{NH}_3)_2]^+(\text{aq})$

Ag⁺ ions form soluble diammine complex which decreases the [Ag⁺], resulting in a corresponding decrease in ionic product (i.e. I.P = [Ag⁺][X⁻]) for both halide ions.

As K_{sp} value of AgCl is much larger than that of AgBr, the ionic product of AgCl will fall below its K_{sp} but not for AgBr.

[2]

[Total: 15]

3 (a) (i)

Co³⁺: 1s²2s²2p⁶3s²3p⁶3d⁶

[1]

(ii) Suggest the identities of X and Y.

X: Co(OH)₃

Y: [Co(NH₃)₆]³⁺

[2]

(iii)

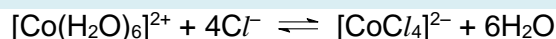
$[\text{Co}(\text{H}_2\text{O})_6]^{3+} + 3\text{OH}^- \rightleftharpoons \text{Co}(\text{OH})_3 + 6\text{H}_2\text{O} \text{ ———(1)}$

When aqueous ammonia is added in excess, a ligand exchange reaction occurs. The stronger NH₃ ligands replace weaker H₂O ligands in the [Co(H₂O)₆]³⁺ ions to form [Co(NH₃)₆]³⁺ complex.

$[\text{Co}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons [\text{Co}(\text{NH}_3)_6]^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l}) \text{ ———(2)}$

This decreases the concentration of [Co(H₂O)₆]³⁺ in solution. By Le Chatelier's Principle, equilibrium (1) shifts left to increase the concentration of [Co(H₂O)₆]³⁺(aq). Hence the brown precipitate of Co(OH)₃ dissolves [1].

[3]

(b)

There is a change of co-ordination number from 6 to 4.

[2]

(c) (i)

The partially-filled d orbitals of V^{2+} are split into two groups of different energy levels by H_2O ligands. When white light shines on the complex, a d electron undergoes d-d transition and is promoted to a higher energy d orbital. During the transition, the d electron absorbs light from the yellow region of the visible spectrum. The colour observed is the colour of transmitted light, which is a mixture of remaining wavelengths that have not been absorbed.

[2]

(ii)

The reactant molecules are physically adsorbed onto the catalyst surface. This allows for formation of weak bonds between reactants and the surface catalyst, thus weakening the intramolecular bonds in the reactants and helps to catalyse the reaction. After reaction, the reactant molecules desorb from the catalyst surface.

[2]

(iii)

| | $2\text{SO}_2(\text{g})$ | + | $\text{O}_2(\text{g}) \rightleftharpoons$ | $2\text{SO}_3(\text{g})$ |
|---------------------------|--------------------------|---|---|--------------------------|
| Initial pressure /atm | 0.6667x | | 0.3333x | 0 |
| Change in pressure /atm | -0.6333x | | -0.3167x | +0.6333x |
| Equilibrium pressure /atm | 0.0334x | | 0.0166x | 0.6333x |

Let the initial total pressure be x atm.

$$K_p = (0.6333x)^2 / (0.0166x)(0.0334x)^2 = 7200$$

$$\therefore x = (0.6333)^2 / 7200(0.0166)(0.0334)^2$$

$$= 3.01 \text{ atm}$$

[2]

(iv)

Rate of conversion will slow down/decrease due to poisoning of the catalyst.

[1]

[Total: 15]

4 (a) (i)

$$\text{No. of moles of } \text{HY}^{3-} \text{ required} = 0.0149 \times \frac{25.55}{1000}$$

$$= 0.00038070 \text{ mol}$$

No. of moles of Ca^{2+} present = 0.00038070 mol

No. of moles of CaCO_3 = 0.00038070 mol

Mass of CaCO_3 = 0.00038070 x [40.1 + 12 + 3(16)]
= 0.0381g (3 sf)

[1]

(ii)

$\text{ppm CaCO}_3 = \frac{0.038107}{50} \times 10^6 = 762$ (3 sf)
The water is very hard.

[2]

(b)

Ca^{2+} can be removed by heating the water sample.

By Le Chatelier's Principle, the position of equilibrium will shift right to remove the heat supplied causing a decrease in the concentration of Ca^{2+} ions.

OR

Ca^{2+} can be removed by heating the water sample.

Heating the water sample removes CO_2 (g) hence decreasing the concentration of CO_2 (aq).

By Le Chatelier's Principle, the position of equilibrium will shift right to increase the concentration of CO_2 (aq) causing a decrease in the concentration of Ca^{2+} ions.

[2]

(c) (i)

$[\text{C}_{18}\text{H}_{29}\text{SO}_3^-] = \sqrt{(1.2 \times 10^{-17} / 2.5 \times 10^{-4})}$
= $2.1908 \times 10^{-7} \text{ mol dm}^{-3}$
= $2.19 \times 10^{-7} \text{ mol dm}^{-3}$

[1]

(ii)

Mass of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ added to 1.0 dm^3 = 0.174 g

No of moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3\text{Na}$ added to $1.0 \text{ dm}^3 = \frac{0.174}{348} = 5.00 \times 10^{-4} \text{ mol}$

[1]

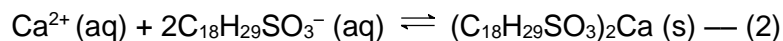
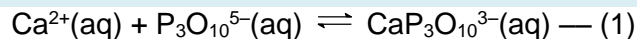
(iii)

Maximum moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3^-$ dissolved in $1.0 \text{ dm}^3 = 2.1908 \times 10^{-7} \text{ mol}$

No of moles of $\text{C}_{18}\text{H}_{29}\text{SO}_3^-$ precipitated out = $5.00 \times 10^{-4} - 2.1908 \times 10^{-7}$
= $4.9978 \times 10^{-4} \text{ mol}$

$$\begin{aligned}\text{Percentage of } \text{C}_{18}\text{H}_{29}\text{SO}_3^- \text{ precipitated} &= \frac{4.9978 \times 10^{-4}}{5.00 \times 10^{-4}} \times 100\% \\ &= 99\% \text{ (shown)}\end{aligned}$$

[2]

(d) (i)

$\text{P}_3\text{O}_{10}^{5-}$ form complexes with Ca^{2+} causing a decrease in the concentration of Ca^{2+} .

By Le Chatelier's Principle, the equilibrium position of (2) shifts left to increase the concentration of Ca^{2+} . Hence reducing the amount of $(\text{C}_{18}\text{H}_{29}\text{SO}_3)_2\text{Ca}$ formed.

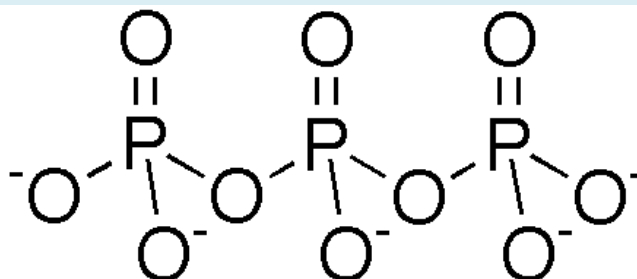
Hence, preventing the formation of precipitate when detergent is added into hard water.

[2]

(ii)

+5

[1]

(iii)

[1]

(iv)

Concentration of $\text{P}_3\text{O}_{10}^{5-}$ decreases as it complexes with the added Mg^{2+} to form $\text{MgP}_3\text{O}_{10}^{3-}$.

By Le Chatelier's Principle, the equilibrium position of (1) will shift left to increase the concentration of $\text{P}_3\text{O}_{10}^{5-}$.

There is no change to the value of K_c as temperature is kept constant.

[2]

[Total: 15]

5 (a)

CH_3OH and $\text{CH}_3\text{CH}_2\text{OH}$.

[1]

(b)

Two epoxide rings.

Two alcoholic groups are produced for every epoxide ring that will be hydrolysed. Since there are four alcoholic groups formed after 'juvenile hormone' undergoes hydrolysis, this implies that there are two epoxide rings in 'juvenile hormone'.

[2]

(c) State the type of reaction that T has undergone and the functional group that it contains other than the four alcoholic groups.

T undergoes basic hydrolysis to give methanol and U. T is likely to contain an ester.

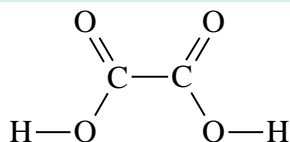
[1]

(d)

Two tertiary alcohol groups.

T has four alcohol groups which were retained in U even after basic hydrolysis. Since V has only two alcohol groups left after mild oxidation, this implies that the two alcohol groups must be tertiary in order to resist oxidation.

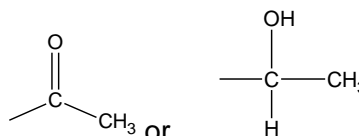
[2]

(e)

[1]

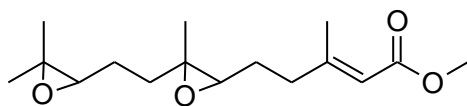
(f)

Condensation. W contains either

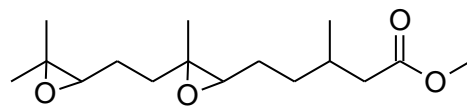
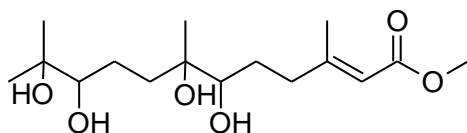
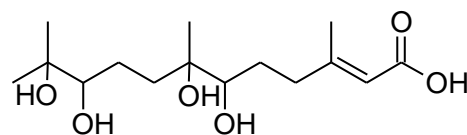
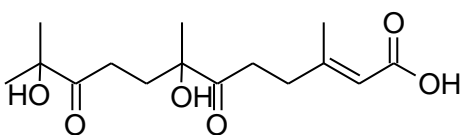
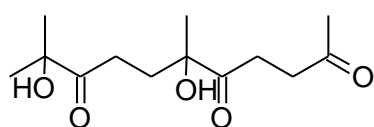


[2]

(g)



Juvenile hormone

**S****T****U****V****W**

[6]

[Total: 15]