

5.2.4 Metal redox evidence, complete tests and complex preparation

Name: _____ Class: _____ Date: _____

Total: 36 marks

KEY WORDS evidence • conditions

Objective

Metal redox evidence, complete tests and complex preparation. All questions and marking guidance are original.

1 Key knowledge and worked examples

A coloured ion can change by redox, proton transfer or ligand exchange. Check oxidation numbers and conditions before choosing an equation. Zinc reduces acidic vanadium species through V(V), V(IV), V(III), V(II). Hydrogen peroxide oxidises chromium(III) to chromate in alkaline conditions; acid then gives dichromate.

■ Worked method

If $\text{VO}^{2+}/\text{V}^{3+}$ has reduction potential +0.34 V and Zn^{2+}/Zn -0.76 V, zinc reduction of V(IV) to V(III) gives $E^\circ_{\text{cell}} = 0.34 - (-0.76) = +1.10$ V. The vanadium half-equation is $\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$. It is a one-electron reduction even though oxygen and hydrogen also need balancing.

2 Practice

2.1 Complete the observations for initial hydroxide precipitates of Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} , using fresh room-temperature samples. [8]

2.2 Write precipitation equations with OH^- for Mn^{2+} and Ni^{2+} , and a net equation with NH_3 for Fe^{3+} . [3]

2.3 Write the equation for $\text{Cr}(\text{OH})_3$ dissolving in OH^- to $[\text{Cr}(\text{OH})_6]^{3-}$. Explain what amphoteric means. [2]

3 Exam-style questions

3.1 Given $\text{VO}^{2+}/\text{V}^{3+} \text{ E}^\circ = +0.34 \text{ V}$ and $\text{Zn}^{2+}/\text{Zn} \text{ E}^\circ = -0.76 \text{ V}$, write the full zinc/vanadium reaction in acid and calculate its standard voltage. [4]

3.2 Chromium(III) hydroxide is oxidised by H_2O_2 in alkaline solution. Balance $2\text{Cr}(\text{OH})_3 + 3\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + \text{H}_2\text{O}$. State what acidifying the chromate then changes. Explain two stages of catalytic-converter action. [5]

3.3 A complex synthesis has limiting metal amount 0.0100 mol , product ratio 1:1 and product $M = 250 \text{ g mol}^{-1}$. Dry crystals weigh 1.75 g . Find percentage yield. Explain one low-yield cause and one cause of misleadingly high mass. [4]

3.4 A supplied reduction potential for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is -0.41 V ; Zn^{2+}/Zn is -0.76 V . Test zinc reduction of Cr^{3+} and give the overall equation. State the expected Cr^{2+} colour and a reason to exclude air. [4]

3.5 Write the excess-ammonia dissolution equations for $\text{Ni}(\text{OH})_2$ to $[\text{Ni}(\text{NH}_3)_6]^{2+}$ and $\text{Zn}(\text{OH})_2$ to $[\text{Zn}(\text{NH}_3)_4]^{2+}$. Explain why their different ligand counts must be retained. [3]

3.6 Supplied reduction potentials at the same specified alkaline conditions are $\text{H}_2\text{O}_2/2\text{OH}^- = +0.88\text{ V}$ and $\text{CrO}_4^{2-}/\text{Cr}(\text{OH})_3 = -0.13\text{ V}$. Predict whether peroxide oxidation of $\text{Cr}(\text{III})$ to $\text{Cr}(\text{VI})$ is thermodynamically favoured. Explain which half-reaction reverses and one limitation of the prediction. [3]

Solutions

Original marking guidance: M1 method, A1 accuracy, B1 explanation.

2.1 Cr^{3+} green/grey-green; Mn^{2+} off-white/very pale precipitate, darkens in air; Fe^{2+} green; Fe^{3+} red-brown; Co^{2+} blue initially; Ni^{2+} green; Cu^{2+} pale blue; Zn^{2+} white. Observations on standing can differ because of oxidation/slow changes.

2.2 $\text{Mn}^{2+} + 2\text{OH}^- \rightarrow \text{Mn}(\text{OH})_2(\text{s})$; $\text{Ni}^{2+} + 2\text{OH}^- \rightarrow \text{Ni}(\text{OH})_2(\text{s})$; $\text{Fe}^{3+} + 3\text{NH}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3(\text{s}) + 3\text{NH}_4^+$. Hydrated-complex equivalents accepted.

2.3 $\text{Cr}(\text{OH})_3(\text{s}) + 3\text{OH}^- \rightarrow [\text{Cr}(\text{OH})_6]^{3-}$. The hydroxide reacts with both acids and bases.

3.1 $\text{VO}^{2+} + 2\text{H}^+ + \text{e}^- \rightarrow \text{V}^{3+} + \text{H}_2\text{O}$. Double it and combine $\text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^-$ to give $2\text{VO}^{2+} + 4\text{H}^+ + \text{Zn} \rightarrow 2\text{V}^{3+} + 2\text{H}_2\text{O} + \text{Zn}^{2+}$. $E^\circ = +1.10 \text{ V}$.

3.2 $2\text{Cr}(\text{OH})_3 + 3\text{H}_2\text{O}_2 + 4\text{OH}^- \rightarrow 2\text{CrO}_4^{2-} + 8\text{H}_2\text{O}$. Acidification favours dichromate without changing Cr(VI) oxidation state. CO/NO adsorb and react on the surface through weakened bonds/lower barrier; CO_2/N_2 desorb.

3.3 Theoretical mass = $0.0100 \times 250 = 2.50 \text{ g}$; yield = $1.75/2.50 \times 100 = 70.0\%$. Solubility/transfer loss or incomplete reaction lowers recovery; retained solvent/water or impurity raises apparent mass.

3.4 $E^\circ = -0.41 - (-0.76) = +0.35 \text{ V}$. $\text{Zn} + 2\text{Cr}^{3+} \rightarrow \text{Zn}^{2+} + 2\text{Cr}^{2+}$. Cr^{2+} is blue; oxygen readily oxidises it back to Cr^{3+} , so air changes the observed product.

3.5 $\text{Ni}(\text{OH})_2 + 6\text{NH}_3 \rightleftharpoons [\text{Ni}(\text{NH}_3)_6]^{2+} + 2\text{OH}^-$. $\text{Zn}(\text{OH})_2 + 4\text{NH}_3 \rightleftharpoons [\text{Zn}(\text{NH}_3)_4]^{2+} + 2\text{OH}^-$. Coordination counts differ, so changing both to the same ligand coefficient changes the specified complex and fails species/atom balance.

3.6 Peroxide is reduced while the chromium reduction half-reaction reverses to oxidation. $E_{\text{cell}} = 0.88 - (-0.13) = +1.01 \text{ V}$, so that direction is favoured under the stated conditions. Actual rate may be slow, or changing conditions changes the potentials.