STARTER FOR 10...

13.6. Redox chemistry of transition metals

One of the important properties of transition metals is that they can exist in a range of oxidation states in their compounds. The different oxidation states can be readily inter-converted.

1. Vanadium has an extensive redox chemistry.

(a) Complete the diagram by;

(i) Identifying the oxidation state of vanadium in each of the vanadium containing species.

(ii) Adding labels to indicate if the change shown by the arrows is oxidation or reduction. (2 marks)

....

$\longrightarrow$

	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Oxid^n state	....	....	....	....

$\longleftarrow$

....

(b) Use the electrode potentials in the table to explain the following;

Reduction half equation	**E$^\ominus$ / V**
$Zn^{2+}(aq) + 2\,e^- \rightleftharpoons Zn(s)$	–0.76
$V^{3+}(aq) + 1\,e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$VO^{2+}(aq) + 2\,H^+(aq) + 1\,e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$NO_3^-(aq) + 4\,H^+(aq) + 3\,e^- \rightleftharpoons NO(g) + 2\,H_2O(l)$	+0.96
$VO_2^+(aq) + 2\,H^+(aq) + 1\,e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00

(i) Nitric acid will oxidise V^{2+} to VO^{2+} but no further.

....

....(2 marks)

(ii) Zinc will reduce VO_2^+ to V^{2+}.

....

....(2 marks)

2. Write two half equations and combine to give a full redox equation for the following oxidations;

(a) The oxidation of $[Cr(OH)_6]^{3-}$ to CrO_4^{2-} using hydrogen peroxide under alkaline conditions.

....

....(2 marks)

(b) The oxidation of $[Co(NH_3)_6]^{2+}$ to $[Co(NH_3)_6]^{3+}$ by oxygen in the air under alkaline conditions.
(HINT: O_2 is reduced to OH^- ions under these conditions)

....

....(2 marks)

13. Transition metal chemistry answers

Therefore the % by mass of iron in Tablet B = (1.085 g / 2.10 g) × 100% = 51.6 %
Therefore <u>Tablet B comes from the ***FeRICH*** tablets.</u> *(1 mark)*

Tablet C

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

No. of moles in 10.5 cm^3 of 0.0022 mol dm^{-3} $K_2Cr_2O_7$ = 2.31×10^{-5} mol
Therefore, no. of moles of Fe^{2+} in 20.00 cm^3 aliquot = (2.31×10^{-5} mol) × 6 = 1.386×10^{-4} mol
Therefore, no. of moles of Fe^{2+} in 500 cm^3 and hence in one of Tablet C = (1.386×10^{-4} mol / 20) × 500
= 3.465×10^{-3} mol *(1 mark)*

Molar mass of $FeSO_4.7H_2O$ = 151.9 + (7 × 18.0) = 277.9 g mol^{-1}
Therefore mass of $FeSO_4.7H_2O$ per tablet = 3.465×10^{-3} mol × 277.9 g mol^{-1} = 0.96 g *(1 mark)*
Therefore <u>Tablet C comes from the ***Fe4U*** tablets.</u> *(1 mark)*

BONUS MARK

Either

Add an excess of zinc to a 25.0 cm^3 aliquot of the original solution. This will reduce any Fe^{3+} ions to Fe^{2+} ions. Filter off the unreacted zinc and titrate the mixture against $KMnO_4$. If the titre is the same (i.e. the amount of $KMnO_4$ needed for complete oxidation has not changed) then only Fe^{2+} ions were present in the original solution. If the titre has increased (i.e. more $KMnO_4$ is needed for complete oxidation) then the original sample must have contained some Fe^{3+} ions.

or

Dissolve the tablet in water and add sodium hydroxide solution until present in excess. If Fe^{2+} is present a green precipitate of $[Fe(H_2O)_4(OH)_2]$ would form. Any Fe^{3+} present would form an orange/brown precipitate of $[Fe(H_2O)_3(OH)_3]$.

(1 mark for either method)

13.6. Redox chemistry of transition metals

1. (a)

<u>reduction</u> $\longrightarrow$

	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
Oxid^n state	<u>+5</u>	<u>+4</u>	<u>+3</u>	<u>+2</u>

$\longleftarrow$ <u>oxidation</u>

(1 mark for correct oxidation states, 1 mark for correct identification of oxidation and reduction)

(b) (i) The electrode potentials for the V^{3+}/V^{2+} electrode and the VO^{2+}/V^{3+} electrode are each more negative that the NO_3^-/NO electrode potential. Therefore, NO_3^- will initially oxidise V^{2+} to V^{3+}

which will then be oxidised further to VO^{2+}. Since the electrode potential for the VO_2^+/VO^{2+} electrode is more negative than that of the NO_3^- / NO electrode no further oxidation is possible.

(2 marks; 1 mark for comment on electrode potentials and 1 mark for explaining comment)

(ii) The electrode potential of the Zn^{2+}/Zn electrode is more negative than each of the VO_2^+/VO^{2+}, VO^{2+}/V^{3+} and the V^{3+}/V^{2+} electrodes. Therefore it will reduce each of the vanadium species in turn i.e. VO_2^+ will be reduced to VO^{2+} which in turn will be reduced to V^{3+} which in turn will be reduced to V^{2+}.

(2 marks; 1 mark for comment on electrode potentials and 1 mark for explaining comment)

2. (a) In acid conditions the first half equation would be (this is purely a theoretical simplification, as $[Cr(OH)_6]^{3-}$ would not exist under these conditions);

$$[Cr(OH)_6]^{3-} \rightarrow CrO_4^{2-} + 2\,H_2O + 2\,H^+ + 3\,e^-$$

But the oxidation is in alkali conditions so it becomes (just add enough OH^- equally to both sides of the equation to remove any H+ ions);

$$2\,OH^- + [Cr(OH)_6]^{3-} \rightarrow CrO_4^{2-} + 4\,H_2O + 3\,e^- \qquad (\times 2)$$

The hydrogen peroxide half equation is;

$$2\,e^- + H_2O_2 \rightarrow 2\,OH^- \qquad (\times 3)$$

Combining to give the full redox equation;

$$2\,[Cr(OH)_6]^{3-} + 3\,H_2O_2 \rightarrow 2\,CrO_4^{2-} + 8\,H_2O + 2\,OH^-$$

(2 marks; 1 for correct half equations, 1 for correct full redox equation)

(b) $[Co(NH_3)_6]^{2+} \rightarrow [Co(NH_3)_6]^{3+} + 1\,e^-$ $\qquad (\times 4)$

$4\,e^- + 2\,H_2O + O_2 \rightarrow 4\,OH^-$

$4\,[Co(NH_3)_6]^{2+} + 2\,H_2O + O_2 \rightarrow 4[Co(NH_3)_6]^{3+} + 4\,OH^-$

(2 marks; 1 for correct half equations, 1 for correct full redox equation)

13.7. Transition metals as catalysts

1. (a) Nickel, heterogeneous

(b) Iron, heterogeneous

(c) Vanadium pentoxide (V_2O_5), heterogeneous

(d) Platinum, palladium or rhodium, heterogeneous

(e) Fe^{2+} ions, homogeneous

(f) Manganese dioxide, MnO_2, heterogeneous

(g) Mn^{2+} ions, homogeneous *(7 marks)*

2. (a) Autocatalysis is when one of the products of the reaction acts as a catalyst for the reaction.

(1 mark)