



STARTER FOR 10...

13.6. Redox chemistry of transition metals

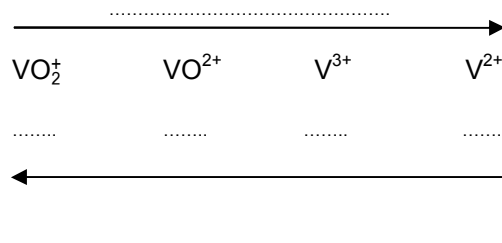
One of the important properties of transition metals is that they can exist in a range of oxidation states in their compounds. The different oxidation states can be readily inter-converted.

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.

Oxidⁿ state



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

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

Reduction half equation	E° / V
$\text{Zn}^{2+}(\text{aq}) + 2 \text{e}^{-} \rightleftharpoons \text{Zn}(\text{s})$	-0.76
$\text{V}^{3+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{V}^{2+}(\text{aq})$	-0.26
$\text{VO}^{2+}(\text{aq}) + 2 \text{H}^{+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{V}^{3+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+0.34
$\text{NO}_3^{-}(\text{aq}) + 4 \text{H}^{+}(\text{aq}) + 3 \text{e}^{-} \rightleftharpoons \text{NO}(\text{g}) + 2 \text{H}_2\text{O}(\text{l})$	+0.96
$\text{VO}_2^{+}(\text{aq}) + 2 \text{H}^{+}(\text{aq}) + 1 \text{e}^{-} \rightleftharpoons \text{VO}^{2+}(\text{aq}) + \text{H}_2\text{O}(\text{l})$	+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 $[\text{Cr}(\text{OH})_6]^{3-}$ to CrO_4^{2-} using hydrogen peroxide under alkaline conditions.

.....
 (2 marks)

- (b) The oxidation of $[\text{Co}(\text{NH}_3)_6]^{2+}$ to $[\text{Co}(\text{NH}_3)_6]^{3+}$ by oxygen in the air under alkaline conditions.
 (HINT: O_2 is reduced to OH^{-} ions under these conditions)

.....
 (2 marks)



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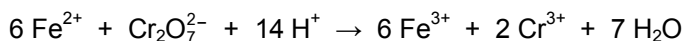
13. Transition metal chemistry answers

Therefore the % by mass of iron in Tablet B = $(1.085 \text{ g} / 2.10 \text{ g}) \times 100\% = 51.6 \%$

Therefore Tablet B comes from the **FeRICH** tablets.

(1 mark)

Tablet C



No. of moles in 10.5 cm^3 of $0.0022 \text{ mol dm}^{-3} \text{K}_2\text{Cr}_2\text{O}_7 = 2.31 \times 10^{-5} \text{ mol}$

Therefore, no. of moles of Fe^{2+} in 20.00 cm^3 aliquot = $(2.31 \times 10^{-5} \text{ mol}) \times 6 = 1.386 \times 10^{-4} \text{ mol}$

Therefore, no. of moles of Fe^{2+} in 500 cm^3 and hence in one of Tablet C = $(1.386 \times 10^{-4} \text{ mol} / 20) \times 500$

$$= 3.465 \times 10^{-3} \text{ mol} \quad (1 \text{ mark})$$

Molar mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} = 151.9 + (7 \times 18.0) = 277.9 \text{ g mol}^{-1}$

Therefore mass of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ per tablet = $3.465 \times 10^{-3} \text{ mol} \times 277.9 \text{ g mol}^{-1} = 0.96 \text{ g}$

(1 mark)

Therefore Tablet C comes from the **Fe4U** tablets.

(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.

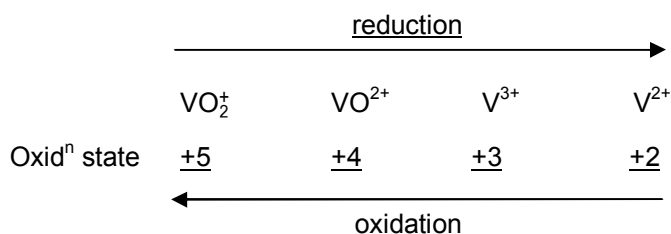
or

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

(1 mark for either method)

13.6. Redox chemistry of transition metals

1. (a)



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

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



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13. Transition metal chemistry answers

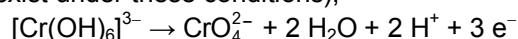
which will then be oxidised further to VO^{2+} . Since the electrode potential for the $\text{VO}_2^+/\text{VO}^{2+}$ electrode is more negative than that of the NO_3^-/NO electrode no further oxidation is possible.

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

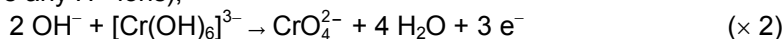
- (ii) The electrode potential of the Zn^{2+}/Zn electrode is more negative than each of the $\text{VO}_2^+/\text{VO}^{2+}$, $\text{VO}^{2+}/\text{V}^{3+}$ and the $\text{V}^{3+}/\text{V}^{2+}$ electrodes. Therefore it will reduce each of the vanadium species in turn i.e. VO_2^+ will be reduced to VO^{2+} 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 $[\text{Cr}(\text{OH})_6]^{3-}$ would not exist under these conditions);



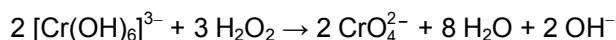
But the oxidation is in alkali conditions so it becomes (just add enough OH^- equally to both sides of the equation to remove any H^+ ions);



The hydrogen peroxide half equation is;

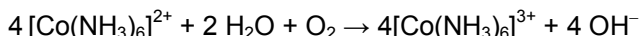
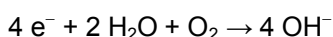


Combining to give the full redox equation;



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

- (b) $[\text{Co}(\text{NH}_3)_6]^{2+} \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 1 \text{e}^- \quad (\times 4)$



(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)