

5.4 ANSWERS TO EXERCISES

5.4 Exercise 1

1.

a) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$
c) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^7$	d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$
d) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$	
2.

a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$	b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$
c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2$	d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$
d) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$	
3.
 - a) They do not form any stable ions with partially filled d-orbitals
 - b) They have empty d-orbitals of low energy which can accept electron pairs
 - c) The presence of ligands causes the d-orbitals to split. In the presence of visible light, electrons are excited from low energy d-orbitals to high energy d-orbitals, absorbing the light in the process. The resultant light is coloured.
 - d) Cu^+ has a full 3d sublevel, so there are no available d-orbitals into which electrons can be excited.
4. Prepare samples of the transition metal ion over a range of known concentrations. Add a small quantity of a suitable ligand to each in order to identify the colour. Choose the filter which gives the largest absorbance, and measure the absorbance of each sample using this filter.
Plot a graph of absorbance against concentration.
Take the sample of unknown concentration, add the ligand to intensify the colour, and measure its absorbance using the same filter.
Use the graph to deduce the concentration of the solution.

5.4 Exercise 2

1.
 - a) ion containing a central metal ion attached to one or more ligands by means of co-ordinate bonds
 - b) species containing a lone pair of electrons which can form a co-ordinate bond with a metal ion
 - c) the total number of co-ordinate bonds formed between the metal ion and the ligands

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| 2. | a) | $\text{Fe}^{2+} + 6\text{H}_2\text{O} \rightarrow \text{Fe}(\text{H}_2\text{O})_6^{2+}$ | unidentate |
| | b) | $\text{Fe}^{2+} + 6\text{CN}^- \rightarrow \text{Fe}(\text{CN})_6^{4-}$ | unidentate |
| | c) | $\text{Fe}^{3+} + 6\text{CN}^- \rightarrow \text{Fe}(\text{CN})_6^{3-}$ | unidentate |
| | d) | $\text{Cr}^{3+} + 6\text{NH}_3 \rightarrow \text{Cr}(\text{NH}_3)_6^{3+}$ | unidentate |
| | e) | $\text{Ag}^+ + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}$ | unidentate |
| | f) | $\text{Co}^{2+} + 4\text{Cl}^- \rightarrow \text{CoCl}_4^{2-}$ | unidentate |
| | g) | $\text{Fe}^{2+} + 3\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2 \rightarrow \text{Fe}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3^{2+}$ | bidentate |
| | h) | $\text{Cr}^{3+} + 3\text{C}_2\text{O}_4^{2-} \rightarrow \text{Cr}(\text{C}_2\text{O}_4)_3^{3-}$ | bidentate |
| | i) | $\text{Cu}^{2+} + \text{edta}^{4-} \rightarrow \text{Cu}(\text{edta})^{2-}$ | hexadentate |
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|----|----|-----------------------------|
| 3. | a) | carries oxygen in the blood |
| | b) | anti-cancer drug |
| | c) | test for aldehydes |
| | d) | used in photography |
| | e) | used in electroplating |

5.4 Exercise 3

1.
 - a) Solution turns yellow when acidified
Due to formation of VO_2^+
Yellow solution turns blue then green then violet
as the vanadium is reduced from oxidation state +5 to +4 to +3 to +2
 - b) Solution turns orange when acidified
Due to formation of $\text{Cr}_2\text{O}_7^{2-}$
Orange solution turns dark green and then blue
As the chromium is reduced from oxidation state +6 to +3 to +2

2.
 - a) The pink solution becomes a blue precipitate of $\text{Co}(\text{OH})_2$
The blue precipitate turns brown when hydrogen peroxide is added
As the $\text{Co}(\text{OH})_2$ is oxidized to $\text{Co}(\text{OH})_3$
 - b) The dark green solution becomes a green solution of $\text{Cr}(\text{OH})_6^{3-}$
The green solution turns yellow when hydrogen peroxide is added
As the $\text{Cr}(\text{OH})_6^{3-}$ is oxidized to CrO_4^{2-}

3. The pink solution becomes straw coloured
due to the formation of the complex ion $\text{Co}(\text{NH}_3)_6^{2+}$
The straw colour darkens/turns brown on standing in air
Due to the oxidation of the complex ion to $\text{Co}(\text{NH}_3)_6^{3+}$

4. It can be determined by pipetting a 25 cm³ sample of the solution
 Adding dilute sulphuric acid
 Then either:
 Titrating against a solution of KMnO₄ until a permanent pink colour remains
 $\text{MnO}_4^- + 8\text{H}^+ + 5\text{Fe}^{2+} \rightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O} + 5\text{Fe}^{3+}$
 or:
 Titrating against a solution of K₂Cr₂O₇ using diphenylaminesulphonate indicator
 until a purple colour appears
 $\text{Cr}_2\text{O}_7^{2-} + 14\text{H}^+ + 6\text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O} + 6\text{Fe}^{3+}$
5. a) i) $2\text{SO}_2 + \text{O}_2 \rightleftharpoons 2\text{SO}_3$
 a step in the manufacture of sulphuric acid
 i) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$
 manufacture of ammonia
 iii) $\text{C}_2\text{H}_6 + \text{H}_2 \rightarrow \text{C}_2\text{H}_6$
 Hydrogenation of oils to form margarine
 iv) $2\text{CO} + 2\text{NO} \rightarrow \text{N}_2 + 2\text{CO}_2$
 removal of pollutants in car engines
- b) Fe in the Haber process is poisoned by S (an impurity in the Fe)
 Rh in catalytic converters is poisoned by Pb (added to petrol to slow down combustion)
- c) The catalyst is expensive and must be used in small quantities
 It needs to have a large surface area to maximize its effectiveness
 So it is spread thinly over an inert support
- d) W is a poor catalyst because it adsorbs too strongly and desorption is too slow
 Ag is a poor catalyst because it absorbs too weakly and desorption is too quick.
 Fe adsorbs strongly enough for the reaction to take place, but not so strongly that desorption is prevented.
6. using Fe²⁺:
 $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$
 $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$
 using Fe³⁺:
 $2\text{Fe}^{3+} + 2\text{I}^- \rightarrow 2\text{Fe}^{2+} + \text{I}_2$
 $\text{S}_2\text{O}_8^{2-} + 2\text{Fe}^{2+} \rightarrow 2\text{SO}_4^{2-} + 2\text{Fe}^{3+}$
 these steps are all fast because they involve a collision between oppositely charged ions, which attract each other
 The uncatalysed reaction involves a collision between two anions, which repel, making the reaction slow

7. a) $2\text{MnO}_4^- + 16\text{H}^+ + 5\text{C}_2\text{O}_4^{2-} \rightarrow 2\text{Mn}^{2+} + 8\text{H}_2\text{O} + 10\text{CO}_2$
b) Initially the reaction is slow because it requires a collision between two repelling anions
But after the reaction has started the Mn^{2+} produced can catalyse the reaction, so it proceeds faster towards the end-point. It is an example of autocatalysis

5.4 Exercise 4

1. $n = 12$ 2. $x = 7$ 3. 1.37 mol dm^{-3} 4. 99.8 % 5. $x = 2$ 6. +5