Chem Factsheet

January 2003 Number 47

Answering Questions on Transition Metals

To succeed in this topic you need to:
- Understand the principle of oxidation numbers;
- Understand the principle of redox reactions and the use of $E^\ominus$ values (Factsheets 37 and 45);
- Understand types of bonding and molecular shapes (Factsheets 04 and 06);
- Understand work so far on Transition metals (Factsheets 38 and 46).

After working through this Factsheet you will:
- Have more experience of questions based on transition metals;

Questions on transition metals are common in exams, as the examiners can use them as a theme to incorperate several different strands of chemistry in one question. To succeed candidates must have a solid understanding of topics such as electronic configuration, molecular shapes, redox reactions, standard electrode potentials, acid-base character and the work covered specifically on transition metals and their compounds and complexes.

1. Learn the definition

Ensure that you have learned the definition of transition metals, and that you can explain why scandium and zinc are d-block metals, but **not** transition metals.

> **Definition** - Transition metals are d-block elements, which can form one or more stable ions with partially filled d-orbitals.

2. Learn the properties

Properties of transition metals are commonly asked for, so learn:
(a) Exist in a variety of oxidation states.
(b) Form complex ions.
(c) Form coloured ions or compounds.
(d) Catalytic properties of elements and compounds.

Evidence of understanding may also be required.

3. Electronic configurations

You should be able to produce the electron configurations of the first row (period 4) of d-block elements and those of their common ions. Be sure to be confident in using arrows in boxes notation.

Example: Complete the electronic structure of the following.
When completing these remember that when electrons are removed from atoms (i.e. when forming cations) they are removed from the outermost orbital first. The 4s electrons are removed before the 3d electrons, despite the fact that when filling orbitals we fill the 4s before the 3d.

	3d					4s
Ni [Ar]						
Ni^{2+} [Ar]						
Sc^{3+} [Ar]						

Remember to use the periodic table, always available in exams, to check the atomic number and therefore the number of electrons in a neutral atom. So the answers will be:

	3d					4s
Ni [Ar]	↑↓	↑↓	↑↓	↑	↑	↑↓
Ni^{2+} [Ar]	↑↓	↑↓	↑↓	↑	↑	
Sc^{3+} [Ar]						

Understand the effect of the addition of ligands on electronic structure
Each ligand donates an electron pair into the outer orbitals of a transition metal as it forms dative covalent bonds.

Example: The electronic structure for the Cr^{3+} ion.

	3d					4s	4p		
Cr^{3+} [Ar]	↑	↑	↑						

Now the electronic structure of Cr^{3+} in the aqua complex $[Cr(H_2O)_6]^{3+}$:

	3d					4s	4p		
$[Cr(H_2O)_6]^{3+}$[Ar]	↑	↑	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

4. Names of transition metal complexes

Factsheet 38 gives the set of rules candidates must learn to be able to name complex ions. If given a formula or a structural diagram of a complex ion candidates should be able to give the name.

For example: $[Cu(H_2O)_6]^{2+}$ hexaaquacopper (II) ion

6 aqua ligands, hence "hexaaqua". Metal is copper, and overall charge of complex ion is positive, hence "copper". Oxidation state of metal is +2, hence "(II)".

$[Cu(CN)_6]^{4-}$ hexacyanocuprate (II) ion

6 nitrile, or cyano, ligands, hence "hexacyano". Metal is copper, overall charge on complex ion is negative, hence Latin "cuprate". Oxidation state of metal is +2, hence "(II)".

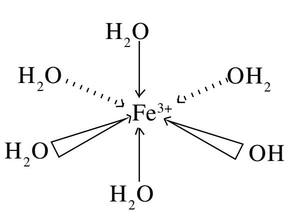
5. Shapes of transition metal complexes

Most complex ions have 6 ligands surrounding the central metal ion, so the most common shape is octahedral.

Some complexes have fewer ligand bonds, and therefore different shapes. Those complexes with 4 ligands will be tetrahedral or square planar, and those with just 2 ligands will be linear in shape.

Candidates should be able to represent the shapes of complex ions in 3-D where appropriate.

For example:



hexaaquairon(III) ions

6. Reactions of complex ions

Candidates should be aware that different ligands bind to transition metal ions with different strengths. Simple substitution reactions (ligand exchange reactions) will occur if a stronger binding ligand is introduced to a solution of metal ions surrounded by weaker bound ligands.

Candidates are expected to know the expected observations of the reactions of transition metal ions with aqueous sodium hydroxide and aqueous ammonia (Factsheet 46). Take time to learn about these tests, and be able to identify where deprotonation has taken place, and where ligand exchange has occurred.

7. The oxidation states of vanadium

Questions on the chemistry of vanadium are common. Already covered in Factsheet 46 are the reactions with zinc and potassium manganate (VII), which are able to display all of vanadium's common oxidation states and the associated colours.

Ion	VO_2^+	VO^{2+}	V^{3+}	V^{2+}
oxidation state	+5	+4	+3	+2
colour	yellow	blue	green	lavender

$$\xrightarrow{\text{reduction (zinc)}}$$

$$\xleftarrow{\text{oxidation (KMnO}_4\text{)}}$$

Other reducing or oxidising agents can be used, but depending on their strength may not reduce the +5 state all the way to +2, or oxidise +2 all the way to +5.

Given $E^\ominus$ data, candidates should be able to predict the effect of various chemicals on the different oxidation states of vanadium.

Reduction Half Equations

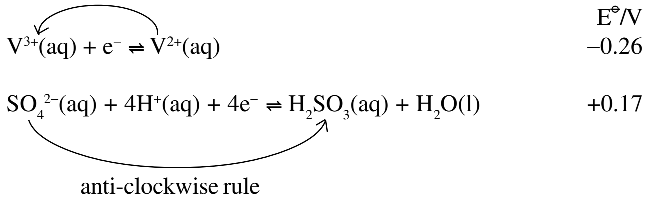
	$E^\ominus$/V
$Zn^{2+}(aq) + 2e^- \rightleftharpoons Zn(s)$	–0.76
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$SO_4^{2-}(aq) + 4H^+(aq) + 4e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17
$VO^{2+}(aq) + 2H^+(aq) + e^- \rightleftharpoons V^{3+}(aq) + H_2O(l)$	+0.34
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00
$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightleftharpoons 4H_2O(l) + Mn^{2+}$	+1.51

Candidates should be able to use the above data to predict equations, colour changes and so on.

Worked example of oxidation

Question: What effect would dilute sulphuric acid have on a solution of vanadium (II) ions?

Answer: The sulphate ions present in the dilute sulphuric acid are oxidising agents. By using the anti-clocwise rule it can be seen that they are powerful enough to oxidise the V^{2+} to V^{3+} ions.



	$E^\ominus$/V
$V^{3+}(aq) + e^- \rightleftharpoons V^{2+}(aq)$	–0.26
$SO_4^{2-}(aq) + 4H^+(aq) + 4e^- \rightleftharpoons H_2SO_3(aq) + H_2O(l)$	+0.17

On further examination of the $E^\ominus$ data, it can be seen that further oxidation of the V^{3+} ions is not possible with SO_4^{2-} ions.

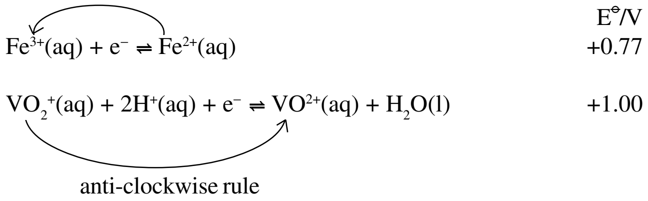
The colour change associated with this reaction will be the lavender of the V(+2) solution to the green of the V(+3) solution.

Eqn: $4V^{2+}(aq) + SO_4^{2-}(aq) + 4H^+(aq) \rightarrow 4V^{3+}(aq) + H_2SO_3(aq) + H_2O(l)$

Worked example of reduction

Question: What effect would a solution of iron (II) ions have on an acidified solution of sodium vanadate (V)?

Answer: Iron (II), Fe^{2+}, is a reducing agent. By using the anti-clockwise rule, it can be seen that it is powerful enough to reduce vanadate (V) ions to the +4 oxidation state:



	$E^\ominus$/V
$Fe^{3+}(aq) + e^- \rightleftharpoons Fe^{2+}(aq)$	+0.77
$VO_2^+(aq) + 2H^+(aq) + e^- \rightleftharpoons VO^{2+}(aq) + H_2O(l)$	+1.00

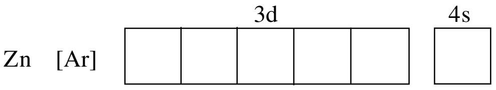
On further examination of the $E^\ominus$ data, it can be seen that further reduction of the VO^{2+} (oxidation state +4) is not possible with the Fe^{2+} ions.

Colour changes in this case may be difficult to observe, but candidates should recognise that the vanadium ions are going from yellow (+5) to blue (+4), whist Fe^{2+} (green) changes to Fe^{3+} (brown).

Eqn: $VO_2^+(aq) + 2H^+(aq) + Fe^{2+}(aq) \rightarrow VO^{2+}(aq) + H_2O(l) + Fe^{3+}(aq)$

Questions

1. Write out the electronic configuration of:
   (a) Cu atom.
   (b) Cu^{2+} ion.
2. Complete the following:



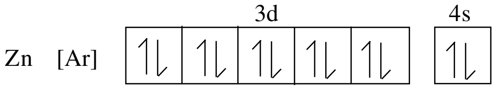
   Explain why zinc is not a transition metal despite its position in the d-block.
3. Name the following complex ions, and represent their shapes using 3-D diagrams:
   (a) $[Fe(H_2O)_6]^{2+}$
   (b) $[Cu(CN)_4]^{2-}$ (hint: not tetrahedral)
4. A few drops of dilute sodium hydroxide is added to a solution of hexaaquachromium (III) ions.
   (a) Describe the product.
   (b) Write the equation for this reaction.
   (c) What type of reaction has occured?
   (d) The product reacts further in excess NaOH(aq). Explain why.
5. A solution of hexaaquairon (III) ions reacts with the CN^- ions in a solution of potassium cyanide in a ligand exchange reaction.
   (a) Write an ionic equation for the reaction.
   (b) Why does this reaction take place?
6. Zinc metal is added to an acidified solution of vanadate (IV), VO^{2+}(aq), ions. Describe the colour changes in the subsequent reactions.

Answers

1. (a) [Ar] $3d^{10}4s^1$

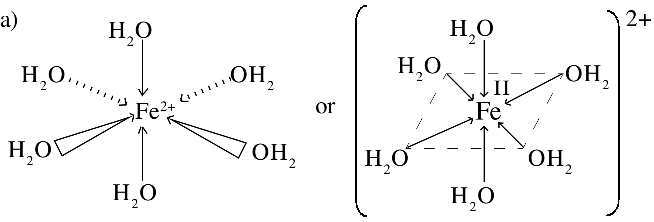
   (b) [Ar] $3d^9$

2.



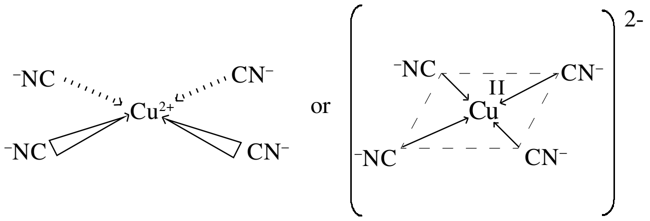
Zinc is not a transition metal because it does not form any stable ions which have an incomplete d-subshell of electrons.

3. (a)



hexaaquairon(II) ions

   (b)



tetracyanocuprate (II) ion

4. (a) Green precipitate.

   (b) $[Cr(H_2O)_6]^{3+}(aq) + 3OH^-(aq) \rightarrow Cr(OH)_3(s) + 6H_2O(l)$

   (c) Deprotonation

   (d) Chromium hydroxide is amphoteric in nature, so reacts with a base.

5. (a) $[Fe(H_2O)_6]^{3+}(aq) + 6CN^-(aq) \rightarrow [Fe(CN)_6]^{3-}(aq) + 6H_2O(l)$

   (b) The cyano ligand is a stronger binding ligand than the aqua ligand.

6. Zinc reduces the blue VO^{2+} ions (V+4) to green V^{3+} ions (V+3) and then to lavender V^{2+} ions (V+2).

Acknowledgements:
This Factsheet was researched and written by Kieron Heath
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