Chem Factsheet

September 2002 **Number 38**

Transition Metals 1: Definitions and Properties

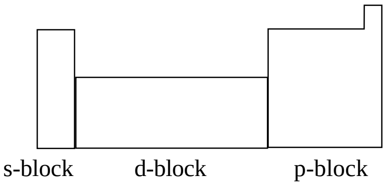
To succeed in this topic you need to:
- Be able to produce full electronic configurations for atoms and ions;
- Understand the principle of oxidation numbers;
- Understand types of bonding and molecular shapes;
- Have an understanding of atomic structure.

After working through this Factsheet you will:
- Be able to produce full electronic configurations for d-block atoms and common ions;
- Know the definition of 'transition metal';
- Know the common properties of the transition metals;
- Be able to write the formulae and represent the shapes of complex ions;
- Have an understanding of why many transition metal compounds are coloured;
- Know some common uses of transition metals in industry.

Definition and electronic configurations

The transition metals are d-block elements, which can form one or more stable ions with partially filled d-orbitals.

The d-block elements are situated between the s-block and p-block elements on the periodic table.



You need to be able to produce the electron configuration of d-block atoms. You will always be given the atomic number (on the periodic table!) and should use the standard procedure for working out electron configuration (see Factsheet 01 - Atomic Structure). The configurations are given below.

Element	s p d configuration	Electrons in boxes configuration	3d					4s
Sc	[Ar] 3d^1 4s^2	Ar	↑					↑↓
Ti	[Ar] 3d^2 4s^2	Ar	↑	↑				↑↓
V	[Ar] 3d^3 4s^2	Ar	↑	↑	↑			↑↓
Cr*	[Ar] 3d^5 4s^1	Ar	↑	↑	↑	↑	↑	↑
Mn	[Ar] 3d^5 4s^2	Ar	↑	↑	↑	↑	↑	↑↓
Fe	[Ar] 3d^6 4s^2	Ar	↑↓	↑	↑	↑	↑	↑↓
Co	[Ar] 3d^7 4s^2	Ar	↑↓	↑↓	↑	↑	↑	↑↓
Ni	[Ar] 3d^8 4s^2	Ar	↑↓	↑↓	↑↓	↑	↑	↑↓
Cu*	[Ar] 3d^{10} 4s^1	Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑
Zn	[Ar] 3d^{10} 4s^2	Ar	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

Note that the configurations for chromium and copper appear slightly anomolous:
- for chromium the 3d orbital has half shell stability, so this electron configuration is preferable.
- for copper, the 3d orbital enjoys full shell stability, hence the given electron configuration is more favourable.

The change in chemistry cross the d-block series is very slight, as all have two electrons in their outermost shell (except for chromium and copper).

The atomic radius and ionisation energies also vary little across the series as increased nuclear charge is offset by increased shielding of the outer electrons.

Ions of d-block elements

In ion formation, 4s electrons are lost before 3d electrons even though 4s fills before 3d when assigning electrons. This is because when the 3d orbital does start to fill, the 4s electrons are repelled further away from the nucleus.

Some electron configurations of d-block metal ions and oxidation states.

Ion/Oxidation State	s p d configuration
Sc^{3+}	[Ar]
Ti^{2+}	[Ar] 3d^2
Ti^{3+}	[Ar] 3d^1
V^{2+}	[Ar] 3d^3
V^{3+}	[Ar] 3d^2
Cr^{2+}	[Ar] 3d^4
Cr^{3+}	[Ar] 3d^3
Cr(VI)	[Ar]
Mn^{2+}	[Ar] 3d^5
Mn^{3+}	[Ar] 3d^4
Mn (VII)	[Ar]
Fe^{2+}	[Ar] 3d^6
Fe^{3+}	[Ar] 3d^5
Cu^{2+}	[Ar] 3d^9
Zn^{2+}	[Ar] 3d^{10}

The ions of scandium and zinc do not have partially filled d-orbitals
- *Sc^{3+} has no electrons in the d-orbital*
- *Zn^{2+} contains a full d-orbital*

Therefore, ***scandium and zinc are NOT transition metals***

Exam Hint: - *Assuming that all d-block elements are transition metals is a common mistake. Learn the definition and recall that scandium and zinc are not transition metals.*

Properties of Transition Metals.

Transition metals have the following four properties:-

1. *Exist in a variety of oxidation states.*
2. *Form complex ions.*
3. *Form coloured ions.*
4. *Display catalytic properties.*

1. Existence in a variety of oxidation states.

Transition metals have electrons of similar energy in their 3d and 4s subshells. Electrons from both subshells can be removed to form a variety of oxidation states.

All transition metals (so Sc and Zn not included) exhibit two or more oxidation states, so have 'variable valency'. The possible oxidation states for the d-block elements are shown below; the more common (stable) states are shown in ***bold italic***.

				7					
			6	6	6				
		5	5	5	5	5			
	4	4	4	***4***	4	4	4		
3	***3***	***3***	***3***	3	***3***	***3***	3	3	
	2	2	2	***2***	***2***	***2***	***2***	***2***	***2***
	1	1	1	1	1	1	1	***1***	
Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn

Exam Hint: - *Candidates need to be able to write out the full electronic configuration of the stable transition metal ions.*

2. Complex ion formation.

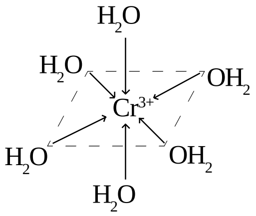
Ions (and sometimes atoms) of the transition metals can be surrounded and bonded to a number of molecules or ions called **ligands**.

- Ligands must have a lone pair of electrons - they are 'electron rich' and therefore anions or neutral.
- Dative covalent (coordinate) bonds are formed, binding the ligands to the transition metal.
- The complexes formed owe their stability to the energy released on formation of the dative bonds.

Common ligands include:

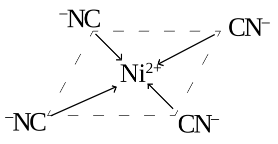
Halides	F^-, Cl^-
Sulphide	S^{2-}
Cyanide	CN^-
Hydroxide	OH^-
Water	H_2O
Ammonia	NH_3

There are commonly six ligands and six coordinate bonds arranged in an octahedral shape in a complex ion - eg hexa aquachromium (III) ion $[Cr(H_2O)_6]^{3+}$

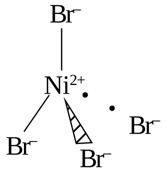


*The **coordination number** of a complex is the number of surrounding ligands (i.e. usually 6 in octahedral complexes).*

Some complexes have coordination number 4 (e.g. those of Ni^{2+}).



$[Ni(CN)_4]^{2-}$ square planar



$[NiBr_4]^{2-}$ tetrahedral

Some complexes have coordination number 2 (e.g. Ag^+) and are linear in shape.

$$^-NC \longrightarrow Ag^+ \longleftarrow CN^-$$

$[Ag(CN)_2]^-$

Naming complexes.
This is the procedure for naming complexes

I State the number of coordinating ligands
(2 = di-, 4 = tetra-, 6 = hexa-).

II Identify the ligands.
Anion names end in -o, neutral ligand names do not.

e.g.		
	H_2O	'aqua'
	NH_3	'ammine'
	Cl^-	'chloro'
	CN^-	'cyano'

III Name the transition metal.
Use the english name for a positively charged complex.
Use the latin name and the suffix '-ate' for a negatively charged complex.

IV Indicate the oxidation number of the transition metal using roman numerals.

Examples:

$[Cu(NH_3)_4]^{2+}$	tetraamminecopper (II) ion
$[Cu(CN)_4]^{2-}$	tetracyanocuprate (II) ion
$[Fe(CN)_6]^{4-}$	hexacyanoferrate (II) ion
$[Ag(NH_3)_2]^+$	diamminesilver (I) ion

Ligand binding strength.
Some ligands bond more strongly than others. When a transition metal compound is dissolved in water the 'aqua' ligands will bind to the transition metal ion, but H_2O is quite a weak ligand.

If a stronger ligand (or its compound) is added to the aqueous solution a ligand substitution (or 'ligand exchange') will occur.

E.g. $[Fe(H_2O)_6]^{2+} + 6CN^- \rightarrow [Fe(CN)_6]^{4-} + 6H_2O$

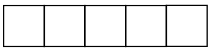
Some ligands in order of binding strength:

H_2O OH^- NH_3 Cl^- $NH_2CH_2CH_2NH_2$ EDTA

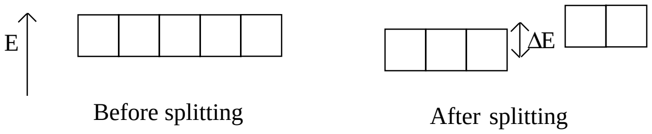
$$\xrightarrow[\text{increasing strength}]{\hspace{6em}}$$

3. Coloured Complex Ions.

By definition transition metals have incomplete d-subshells. The d-subshell contains 5 electron orbitals, each of which can contain 2 electrons.



- When a complex is formed ligands donate electrons (they form **dative** bonds) into vacant higher orbitals.
- Because each of the d-orbitals points in a different direction in space, they interact with the ligand electrons to varying extents.
- This causes a splitting of the d-orbitals into 2 higher energy and 3 slightly lower energy orbitals.



- When white light is shone on the substance a d-electron is moved from the lower to the higher energy level.

- The frequency of light that causes this ‘jump’ is in the visible range. This frequency is absorbed (removed) from the white light, so the complex appears coloured.

- The colour depends on the size of the energy gap ΔE which varies with the metal ion and ligand type - hence each complex has a different colour.

4. Catalytic Properties.

A catalyst increases the rate of a chemical reaction, but it is not consumed in the process. They work by providing an alternative reaction route or mechanism which has a lower activation energy.

The catalytic properties of transition metals are often associated with the variable oxidation states of the elements and available space in electron orbitals.

Examples:

Haber Process - the production of ammonia.

$3H_2\,(g) + N_2\,(g) \qquad 2NH_3\,(g)$

Fe catalyst, 400 atm, 350°C.

Hydrogenation of alkenes.

$RCH{=}CHR' + H_2 \qquad RCH_2{-}CH_2R'$

Ni catalyst, 150°C.

Contact Process - manufacture of sulphuric acid.

$2SO_2\,(g) + O_2(g) \qquad 2SO_3(g)$

V_2O_5 (vanadium (V) oxide) catalyst, 1.5 atm, 400°C.

Questions.

1. Write full electron configurations for the following species:
    (a) Mn
    (b) Cu
    (c) V^{3+}
    (d) Fe^{2+}

2. List three common properties of transition metals.

3. Draw the shapes of the following complex ions:
    (a) $[Cu(H_2O)_6]^{2+}$
    (b) $[Ag(H_2O)_2]^+$

4. Name the following complex ions:
    (a) $[Cu(H_2O)_6]^{2+}$
    (b) $[Ag(H_2O)_2]^+$
    (c) $[Fe(NH_3)_6]^{3+}$
    (d) $(Fe(CN)_6]^{4-}$

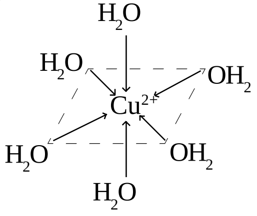
5. Name the catalysts used in:
    (a) The Haber process.
    (b) The Contact process.

Answers.

1. (a) [Ar] $3d^54s^2$
    (b) [Ar] $3d^{10}4s^1$
    (c) [Ar] $3d^2$
    (d) [Ar] $3d^6$

2. Three from:
    Existence in a variety of oxidation states
    Form complex ions
    Form coloured ions or compounds
    Catalytic properties
    Paramagnetism.

3. (a) octahedral



(b) linear

$H_2O \longrightarrow Ag^+ \longleftarrow OH_2$

4. (a) hexaaquacopper (II) ion (b) diaquasilver (I) ion
    (c) hexaaquairon (III) ion (c) hexacyanoferrate (II) ion

5. (a) Iron.
    (b) Vanadium (V) oxide.

Acknowledgements:
This Factsheet was researched and written by Kieron Heath
Curriculum Press, Unit 305B, The Big Peg, 120 Vyse Street, Birmingham, B18 6NF

ISSN 1351-5136