1.3 Transition Metals

Electronic Configuration of Transition Metals

- d-block transition metals have an incomplete d-subshell in at least one of their *ions*.
- 4s electrons are lost *before* 3d electrons during ionisation to positive ions
- filling of d-orbitals follows the Aufbau Principle

Element	Electronic Configuration	
	Spectroscopic Notation	Orbital Box Notation (d-block only)
Scandium	[Ar] $3d^1\ 4s^2$	[↑][ ][ ][ ][ ]
Titanium	[Ar] $3d^2\ 4s^2$	[↑][↑][ ][ ][ ]
Vanadium	[Ar] $3d^3\ 4s^2$	[↑][↑][↑][ ][ ]
Chromium	[Ar] $3d^5\ 4s^1$	[↑][↑][↑][↑][↑]
Manganese	[Ar] $3d^5\ 4s^2$	[↑][↑][↑][↑][↑]
Iron	[Ar] $3d^6\ 4s^2$	[↑↓][↑][↑][↑][↑]
Cobalt	[Ar] $3d^7\ 4s^2$	[↑↓][↑↓][↑][↑][↑]
Nickel	[Ar] $3d^8\ 4s^2$	[↑↓][↑↓][↑↓][↑][↑]
Copper	[Ar] $3d^{10}\ 4s^1$	[↑↓][↑↓][↑↓][↑↓][↑↓]
Zinc	[Ar] $3d^{10}\ 4s^2$	[↑↓][↑↓][↑↓][↑↓][↑↓]

- Cr and Cu are exceptions
  - Cr [Ar] $3d^5\ 4s^1$
  - Cu [Ar] $3d^{10}\ 4s^1$

$\}$ Electron borrowed from 4s to achieve half-filled or completely-filled d-subshell

Questions

1. Write down the electronic configurations in both spectroscopic and orbital box notations for the following atoms and ions
   a) Cu
   b) Mn^{2+}
   c) Ti^{3+}
   d) Co
   e) Co^{2+}
   f) Co^{3+}
   g) Ni^{9+}
   h) Cu^{+}
   i) Fe^{3+}
2. Zinc usually forms the Zn^{2+} ion and the only ion of Scandium is the Sc^{3+} ion. Using spectroscopic notation, write down the electronic configurations for both these ions and use them to explain why zinc and scandium are often not regarded as transition metals.

Oxidation States

- Fe^{2+} ions have an oxidation state of +2
- Fe^{3+} ions have an oxidation state of +3

But what is the oxidation state of Mn in the MnO_4^- ?

Rules for Oxidation States

1. Oxidation number in a free or uncombined element in zero
   e.g. Mg(s) and Cl in Cl_2 gas
2. For single atoms ions, the oxidation number is the same as the charge on the ion
   e.g. Cl^- has oxidation number= –1
   O^{2-} has oxidation number= –2
   Al^{3+} has oxidation number= +3
3. In *most* compounds oxidation number of
   1. hydrogen is +1 [except hydrides where H is –1]
   2. oxygen is –2 [except peroxides where O is –1]
4. The algebraic sum of all the oxidation numbers in a molecule must be zero
5. The algebraic sum of all the oxidation numbers in a polyatomic ion must be equal to the charge on the ion
   e.g. S in SO_4^{2-} S has oxidation number = +6

Question

1. Use the Rules on Oxidation States to calculate the oxidation states of
   a) Mn in MnF_2
   b) S in SO_2
   c) S in SO_3
   d) C in CO_3^{2-}
   e) Mn in MnO_2
   f) S in SO_4^{2-}
   g) Mn in MnO_4^{2-}
   h) Mn in MnO_4^-
   i) Cu in $CuCl_4^{2-}$

- Oxidation numbers can be used to work out if oxidation or reduction has taken place
    - increase in oxidation number - oxidation has occurred
    - decrease in oxidation number - reduction has occurred

e.g. $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

oxid^n no.=+7 $\xrightarrow{\text{reduction}}$ oxid^n no.=+2

- compounds containing metals with high oxidation numbers tend to be oxidising agents
    - agents are reduced themselves to lower oxidation number

- compounds containing metals with low oxidation numbers tend to be reducing agents
    - agents are oxidised themselves to increase oxidation number

- Transition metals exhibit various oxidation states of differing stability
    - It is very common to have an oxidation state of +2 as the $4s^2$ electrons are lost before 3d electrons
    - Subsequent loss of 3d electrons by transition metals forms further oxidation states

- Changing from one oxidation state to another is important in transition metal chemistry
    - It is often characterised by a change in colour

Ion	Oxidation State of Transition Metal	Colour
VO_3^-	+5	Yellow
VO^{2+}	+4	Blue
V^{3+}	+3	Green
V^{2+}	+2	Violet

Questions

1. Write an ion-electron equation for Fe^{2+} acting as
    - i. an oxidising agent
    - ii. a reducing agent
2. Work out the oxidation number of Cr on $Cr_2O_7^{2-}$
    - i. Is the conversion of $Cr_2O_7^{2-}$ to Cr^{3+} is oxidation or reduction?
    - ii. Write an ion-electron equation for this reaction.
    - iii. Is $Cr_2O_7^{2-}$ acting as an oxidising agent or a reducing agent?
3. Orange $Cr_2O_7^{2-}$ ions can be converted to yellow CrO_4^{2-} ions.
    - i. What is the oxidation number of Cr in $Cr_2O_7^{2-}$?
    - ii. What is the oxidation number of Cr in CrO_4^{2-} ?
    - iii. Is the conversion of $Cr_2O_7^{2-}$ ions to CrO_4^{2-}ions an example of oxidation or reduction?
4. The most common oxidation states of iron ions are +2 and +3.
    - i. Using orbital box notation, draw the electronic configurations of both iron ions.
    - ii. Which of the two ions is most stable?

Transition Metal Complexes

- A complex consists of a central metal ion surrounded by ligands

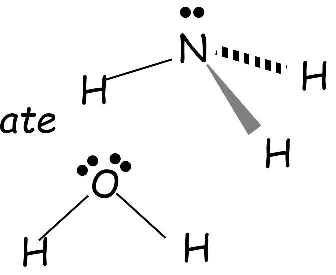
- A ligand is a molecule or ion electron donor which bonds to the metal ion by the donation of one or more electron pairs to unfilled metal ion orbitals

    - Water is a common neutral ligand with 2 lone electron pairs

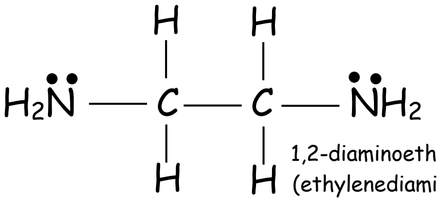
    - Ammonia NH_3 is neutral ligand with one lone pair

    - There are negative ions which are ligands

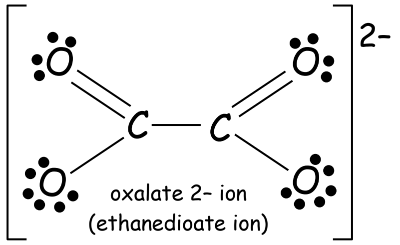
        - cyanide ion CN^-
        - halide ions: F^-, Cl^-, Br^-, I^-
        - nitrite ion NO_2^-
        - hydroxide ion OH^-



- Ligands which donate 1 pair of electrons are *monodentate*
    - Dentate comes from Latin for tooth
    - H_2O and NH_3 are monodentate



1,2-diaminoethane (ethylenediamine)

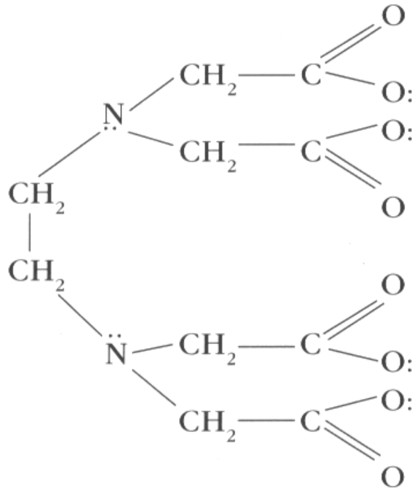


oxalate 2– ion (ethanedioate ion)

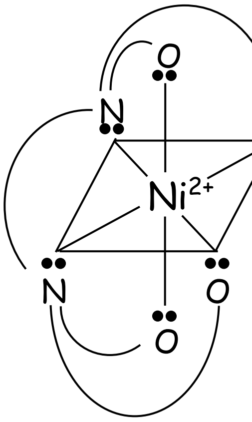
- Ligands which donate 2 pairs of electrons are *bidentate*
    - The 2 pairs of electrons must be on different parts of the molecule, not the same atom
    - Oxalate ions and 1,2-diaminoethane are both *bidentate*

- polydentate means that a ligand has more than one pair of electrons is donated to the central metal ion

- ligands are called chelating agents (chelate: from the Greek for claw)
- **E**thylene**d**iamine**t**etra**a**cetic acid (**EDTA**) is a common hexadentate ligand used in volumetric analysis and complexes with metal ions in a ratio of 1:1



E.D.T.A.



Hexadentate EDTA complexing with Ni^{2+} ion

Co-ordination Number

- The number of bonds of the ligand(s) to the central ion is called the co-ordination number
    - EDTA has a co-ordination number of 6
    - $[Cu(H_2O)_6]^{2+}$ has a co-ordination number of 6 as the central Cu^{2+} ion is surrounded by 6 water molecules
    - $[CuCl_4]^{2-}$ has a co-ordination number of 4 as the central Cu^{2+} ion is surrounded by 4 negative chloride ions

Naming Complexes

a) Writing the Formula of Complexes

- standardised set of rules (IUPAC)
- Formula of complex ions are written in square brackets
- Metal symbol comes first
- Negative ligands come next
- Neutral ligands come next
- Overall charge written after square brackets
  e.g. $[CuCl_4]^{2-}$, $[Cu(H_2O)_6]^{2+}$

b) Writing the Name of Complexes

- Ligands should be named first (alphabetically) followed by the name of the central metal ion

- If the ligand is a negative ion
  - ***ide*** ending becomes –id**o**
    e.g. chloride ions become chlorido
    cyanide ions become cyanido
  - ***ate*** ending become –at**o**
    e.g. nitrate NO_3^- ions become nitrato
  - ***ite*** ending becomes –it**o**
    e.g. nitrite NO_2^- ions become nitrito

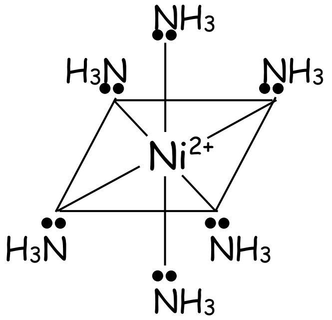
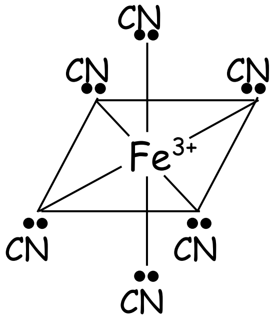
- If ligand is neutral
  - If ligand is water aqua
  - If ligand is ammonia ammine
  - If ligand is CO carbonyl

- Mono, di, tri, tetra, penta, hexa, etc prefixes are used for multiple ligands of the same type

- If complex ion is overall a negative ion (anion), the suffix –ate is added to the metal
  - nickel becomes nickelate (II)
  - iron becomes ferrate (III) [not ironate]
  - copper becomes cuprate (II) [not copperate]

- If complex ion is overall a positive ion (cation), the metal does not have the suffix –ate

- The oxidation state of the metal is written after the metal (roman numerals in brackets) e.g.

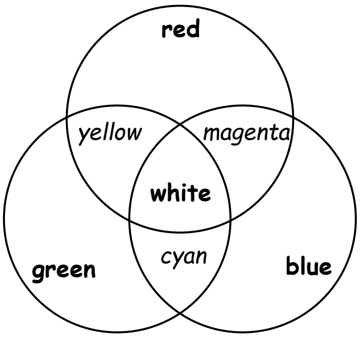
Complex Diagram	Formula of Complex	Name of Complex
	$[Ni(NH_3)_6]^{2+}$	Hexaamminenickel(II)
	$[Fe(CN)_6]^{3-}$	Hexacyanidoferrate(III)

Question

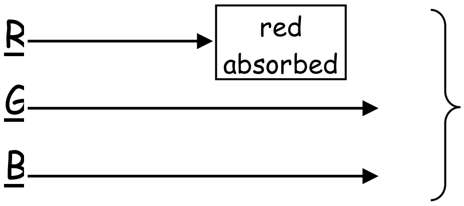
1. Name the following complexes
   a) $[CoCl_4]^{2-}$
   b) $[Ni(H_2O)_6]^{2+}$
   c) $[Fe(CN)_6]^{4-}$
   d) $[Ti(NH_3)_6]^{3+}$
   e) $[Ni(CN)_6]^{4-}$
   f) MnO_4^-
   g) $[PtCl_6]^{2-}$
   h) $Ni(CO)_4$
   i) $[Cu(NH_3)_4]^{2+}$

Colours and Complex Ions

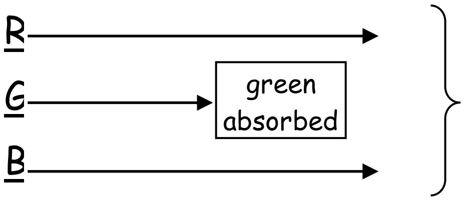
Transition metals ions (simple or complex) are often coloured



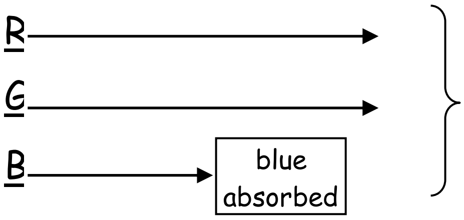
- ion absorbs light in certain parts of the visible spectrum
- remaining wavelengths are transmitted
- colour seen is complementary to colour absorbed



G + B transmitted
cyan (green/blue) observed



R + B transmitted
magenta (red/blue) observed



R + G transmitted
yellow (red/green) observed

In a free ion, all five 3d-orbitals are degenerate (of equal energy)

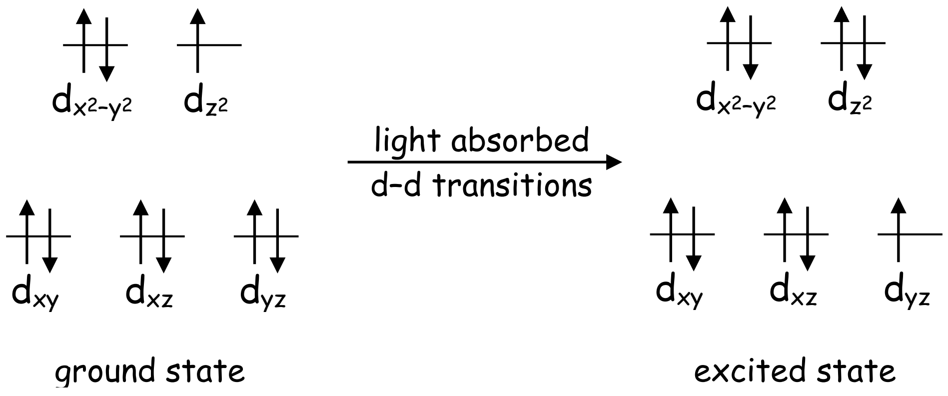
- 3d orbitals are labelled d_{xy}, d_{xz}, d_{yz}, $d_{x^2-y^2}$, d_{z^2}
- $d_{x^2-y^2}$ and d_{z^2} orbitals are raised to a higher energy level due to electrostatic repulsion from the ligands in the complex
- energy difference between the split in the d-orbitals depends on the ligand involved. Ligands are listed in the Spectrochemical Series

$$I^- < Br^- < Cl^- < F^- < H_2O < NH_3 < CN^-$$

Transition metals can absorb light because photons (at a particular energy and therefore particular wavelength) excite electrons in the lower d-orbitals (ground state) up to a higher energy d-orbital (excited state)

- this absorbed energy dissipates as heat energy and does not remerge as light energy

e.g. Cu^{2+} ion with electron arrangement [Ar] $3d^9$



- For Cu^{2+}, blue green is transmitted as red light is absorbed to excite a d-orbital electron.

<u>However</u>

- MnO_4^- ions have Mn in Oxidation State = 7
- Mn has electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$ in this state
- Mn has no electrons in 3d orbital in this state
- Purple colour is caused by different kind of electron transition

UV and Visible Absorption Spectroscopy

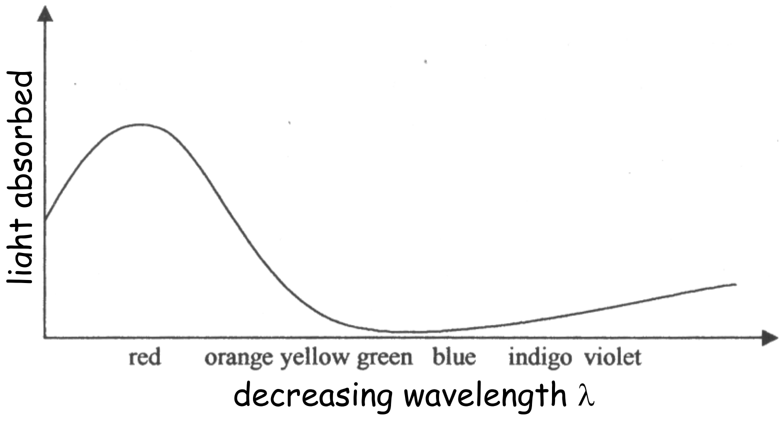
- Effect of d-d transitions can be studied using UV and visible spectroscopy

- UV and visible absorption spectroscopy involves the energy difference between and electron's ground and excited states being supplied by particular wavelengths in the UV and visible regions of the EM spectrum

  - UV λ = 200 – 400 nm
  - Visible λ = 400 – 700 nm

- The particular wavelengths used to promoted (excite) electrons are removed from the light passing through the sample and appear as dark lines in the transmitted light spectrum

- The spectrophotometer compares the reduced intensity of particular wavelengths from the sample against the original intensity of the light passing though the sample



Transition Metal Catalysis

- Transition metals often act as catalysts in a wide selection of chemical reactions

Process	Reaction	Catalyst Used
Haber	$N_2 + 3H_2 \rightarrow 2NH_3$	Fe granules
Contact	$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$	V_2O_5
Ostwald	$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O$	Pt gauze
Catalytic Converter in car exhaust	$4CO + 2NO_2 \rightarrow 4CO_2 + N_2$	Platinum Pt, Palladium Pd and Rhodium Rh
Preparation of Methanol	$CO + 2H_2 \rightarrow CH_3OH$	Copper
Preparation of Margarine	$C_{17}H_{33}COOH + H_2 \rightarrow C_{17}H_{35}COOH$	Nickel
Polymerisation of Alkenes	$n\ C_2H_4 \rightarrow (C_2H_4)_n$	Titanium compounds

- Transition metals can form a variable number of bonds due to the availability of unoccupied and half-filled d-orbitals

- This allows the easier formation of intermediate complexes

- This provides reaction pathways of lower energy to proceed

- The variability of oxidation state of transition metals is another important factor. The transition metal reverts to original oxidation state once the reaction is complete