

DEPARTMENT OF CHEMISTRY
FOURAH BAY COLLEGE
UNIVERSITY OF SIERRA LEONE

CHEM 122

Unit 1

Introduction to Group Chemistry

CREDIT HOURS	2.0
MINIMUM REQUIREMENTS	C6 in WASSCE Chemistry or equivalent Pass in CHEM 111 and CHEM 112 <i>To be taken alongside CHEM 124</i>
REQUIRED FOR	CHEM 213

CHEM 122 UNIT 1 – GROUP CHEMISTRY

COURSE OUTLINE

How do the properties of atoms change across and down the Periodic Table? How do these properties influence the structure and bonding in the different elements of the Periodic Table? How do these properties influence the structure and bonding in different compounds? Why are some elements metallic and others non-metallic? Why are some compounds ionic and others covalent?

How do physical and chemical properties vary within the elements of the s-block? How do the different s-block elements react with oxygen, halogens, nitrogen, hydrogen and carbon? What are the main characteristics of the different compounds formed? How do the different s-block elements react with water, acids and alkalis? To what extent do the s-block form complex ions? How are lithium and beryllium different from the other elements in their respective groups?

What are the main physical and chemical properties of the halogens and their halides? How does reactivity vary down the group? How does the oxidising power of the halogens change down the group and why? How does the reducing power of the halides change down the group and why?

CONTENTS

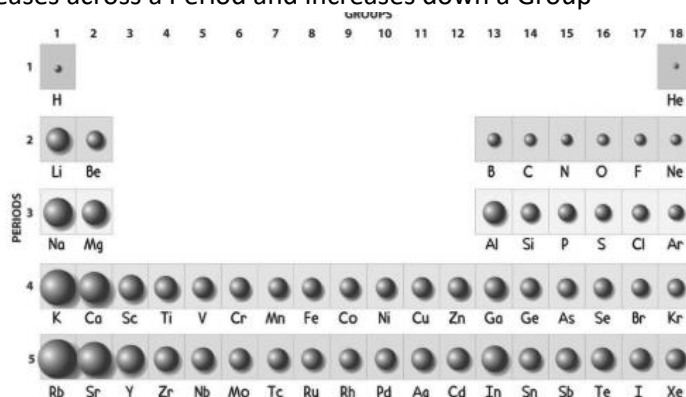
1.	<i>Trends in the Periodic Table I: properties of atoms, structure and bonding in elements</i>
2.	Trends in the Periodic Table II: structure and bonding in compounds
3.	<i>The Chemistry of the s-block I: trends in reactivity with water, acids and non-metals</i>
4.	The Chemistry of the s-block II: chemical properties of s-block compounds
5.	<i>The Chemistry of the Halogens I: Physical and Chemical Properties</i>
6.	<i>The Chemistry of the Halogens II: Redox Reactions</i>
7.	
8.	
9.	
10.	

items in italics are covered at senior secondary level

Lessons 1 and 2 - The Periodic Table: An Overview

a) Properties of Atoms in the Periodic Table

- The ionisation energies of atoms increase across a Period (with some exceptions) and decrease down a Group
- The electron affinities of atoms increase across a Period (with some exceptions) and decrease down a Group
- The size of atoms decreases across a Period and increases down a Group



- Explanation:
 - nuclear charge increases across a Period which increases the attraction between the nucleus and the outer electrons
 - electrons are shielded from the nuclear pull by electrons in inner shells; the number of shells does not change across a Period, so the shielding also stays the same
 - the nuclear charge increases down a group, but the number of shells also increases so the shielding increases; the effect of extra shielding outweighs the effect of extra nuclear charge
 - the exceptions to the trends of increasing ionisation energy and electron affinity across a Period are due to
 - the presence of sub-shells; p-electrons are slightly shielded by the s-electrons in the same shell; this means that they are slightly easier to remove and harder to add than s-electrons
 - electron pairing in p-orbitals; electrons in the same p-orbital repel each other and so are easier to remove and harder to add than unpaired p-electrons
 - when the effect of ionisation energy and electron affinity are combined, the trend is consistent; it becomes easier to lose electrons and harder to add electrons as you move from left to right across a Period

b) Chemical Bonding and Structure of Elements in the Periodic Table

- The ability of an atom to attract bonding electrons is known as electronegativity; electronegativity increases across a Period and decreases down a Group; atoms with high electronegativity are **electronegative** and atoms with low electronegativity are **electropositive**
- Atoms on the left-hand side and at the bottom of the Periodic Table (ie electropositive atoms) do not hold on to bonding electrons strongly; these atoms can give up their valence electrons; when bonding with each other, the valence electrons will become delocalised and there will be an attraction between the lattice of cations and the delocalised electrons; this is known as **metallic bonding**; elements which contain atoms bonded together by metallic bonding are known as **metals**; metals have **giant metallic** structures

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- Atoms on the right-hand side and at the top of the Periodic Table (ie electronegative atoms) hold on to bonding electrons strongly; these atoms are not able to lose their valence electrons and will tend to gain or share electrons; when bonding with each other, the valence electrons will become shared and **covalent bonds** will be formed; elements which contain atoms bonded together by covalent bonding are known as **non-metals**; non-metals can have **giant covalent** or **simple molecular** structures; noble gases form no bonds at all with each other and exist as free atoms; they are also classified as non-metals and their structure is described as **simple atomic**
- In some elements, the bonding between the atoms is covalent at low temperatures but becomes increasingly metallic at high temperatures; these elements have properties in between those of metals and non-metals and are known as **metalloids** or **semi-metals** (B, Si, Ge, As, Sb, Te)

c) Chemical Bonding and Structures of Compounds

- Electropositive atoms (ie atoms of metals) will form **ionic bonds** with electronegative atoms (ie atoms of non-metals); these compounds will have **giant ionic structures**
- Electronegative atoms tend to form **covalent bonds** with other electronegative atoms; covalent bonding is possible between metal atoms and non-metal atoms if the electronegativity difference is not large; the resulting compounds will have **giant covalent** or **simple molecular structures**
- Electropositive atoms tend form **metallic bonds** with other electropositive atoms; the resulting substances have **giant metallic structures** and are called **alloys**; these substances have no fixed composition and so are mixtures and not compounds
- All bonds except those between the same atoms have some ionic character and some covalent character; we describe them as “ionic” or “covalent” depending on which of these two extremes the bonding resembles more closely:
 - If all bonds are considered covalent, the ionic character of the bond can be estimated based on the difference in electronegativity between the two atoms; the greater the difference in electronegativity, the greater the ionic character in the bond
 - If all bonds are considered ionic, the covalent character the bond can be estimated based on the polarizing power of the cation and the polarizability of the anion; the more polarizing the cation and the more polarizable the anion, the greater the covalent character in the bond

d) Physical Properties of Elements and Compounds (melting point and boiling point only)

- The melting point of metals and alloys depends on the strength of the metallic bonding; the greater the charge on the cations, and the smaller the size of the cations, the stronger the metallic bonding and the higher the melting point
- The melting point of giant covalent structures depends on the strength of the covalent bonding and the number of covalent bonds per atom; the smaller the size of the atoms in the covalent bond, the stronger the covalent bonds and the higher the melting point
- The melting point of simple molecular and simple atomic structures depends on the strength of the intermolecular forces; the larger and more polar the molecule, the stronger the intermolecular forces and the higher the melting point

Lessons 3 and 4 – The Chemistry of the S-block

(a) Group 1 – The Alkali Metals

- The alkali metals are all reactive metals, which show typical Group trends:
 - Reactivity increases down the group from Li to Cs (as the outer shell electrons are more shielded, so more easily lost)
 - The metals become softer and their melting point decreases down the group (metallic bonding becomes weaker as the cation size becomes larger)

All of the Group I metals are reactive, soft and have low melting points; all except Li can be easily cut with a knife

(i) Reaction with non-metals

- alkali metals react rapidly with oxygen and are quickly tarnished when exposed to air; they are therefore stored under oil or petroleum jelly
- lithium burns in oxygen to give lithium oxide (Li_2O); sodium burns in oxygen to give a mixture of sodium oxide (Na_2O) and sodium peroxide (Na_2O_2); potassium burns in oxygen to give a mixture of potassium oxide (K_2O), potassium peroxide (K_2O_2) and potassium superoxide (KO_2); rubidium and caesium react in a similar way to potassium; peroxides contain the O_2^{2-} ion and superoxides contain the O_2^- ion; metal peroxides react with water to give hydrogen peroxide
- all of the alkali metals react with halogens to make halides
- all of the alkali metals react with hydrogen to make hydrides
- some of the alkali metals react with carbon to make carbides (eg Na_2C_2)
- lithium reacts with nitrogen to make Li_3N

(ii) Reaction with water, acids and alkalis

- Water contains H^+ and OH^- ions in small quantities; the H^+ ion (found in acids) can oxidise metals to their cations, and be reduced to hydrogen in the process
- All of the alkali metals react rapidly with cold water to make the metal hydroxide and hydrogen:

$$2\text{Na}(s) + 2\text{H}_2\text{O}(l) \rightarrow 2\text{NaOH}(aq) + \text{H}_2(g)$$
- Alkali metals also give typical reactions with acids to make salts, but these reactions are highly explosive
- Cations of alkali metals do not react with OH^- so alkali metals react with alkalis in the same way as they react with water

(iii) Reactions of alkali metal compounds

- The oxides and hydroxides of alkali metals are strongly basic, the oxides dissolve in water to give the metal hydroxide: $\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$
- The halides of alkali metals are completely ionic and are neutral (the cations have low polarising power)

(iv) Extraction

- Alkali metals cannot be chemically isolated; they are extracted by electrolysis of their molten chlorides; alkali metals are usually found in nature as chlorides

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(v) Complex ion formation

- Lithium ions are smaller and have a higher polarising power than the other alkali metal ions; it is the only Group 1 metal which forms complex ions; its empty 2s and 2p orbitals can accept electron pairs from ligands: eg $[\text{Li}(\text{H}_2\text{O})_4]^+$

(b) Group 2 – The Alkali Earth Metals

- The alkali earth metals are all reactive metals and they show typical Group trends:
 - Reactivity increases down the group from Be to Ba (as the outer shell electrons are more shielded, so more easily lost)
 - The metals become softer and their melting point decreases down the group (metallic bonding becomes weaker as the cation size becomes larger); the exception from Mg to Ca is due to a change in crystal structure
- The Group 2 metals are less reactive than the Group 1 metals; the metallic bonding is stronger and the ionisation energies are higher; they are also harder than Group 1 metals and have higher melting points; Be is very hard and Mg cannot be cut with a knife

(i) Reaction with non-metals

- alkali earth metals react with oxygen and are gradually tarnished when exposed to air; the reactions are slower than those of the alkali metals and the elements do not generally need to be stored under oil
- alkali earth metals burn in oxygen to give the oxide (eg MgO); barium burns in oxygen to give a mixture of sodium oxide (Ba_2O) and sodium peroxide (Ba_2O_2)
- alkali earth metals also react with nitrogen in the air to form nitrides (eg Mg_3N_2) (only Li in Group 1 does this)
- all of the alkali earth metals react with halogens to make halides
- all of the alkali earth metals react with hydrogen to make hydrides
- Ca, Sr and Ba react with carbon to make acetylide carbides (eg CaC_2) but Be and Mg react with carbon to make methanide carbides (eg Mg_2C)

(ii) Reaction with water, acids and alkalis

- Ca, Sr and Ba react with cold water to make the metal hydroxide and hydrogen:
 $\text{Ca}(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Ca}(\text{OH})_2(\text{aq}) + \text{H}_2(\text{g})$
With Ca, the solution becomes cloudy due to the limited solubility of the $\text{Ca}(\text{OH})_2$
- Be and Mg do not react with cold water; partly due to the stronger metallic bonding and higher ionisation energies, but also due to the low solubility of the oxides and hydroxides; Be and Mg will react with steam to give the oxide and hydrogen: eg $\text{Be} + \text{H}_2\text{O} \rightarrow \text{BeO} + \text{H}_2$
- All of the Group 2 metals react with acids to make salts (Be needs to be powdered)
- $\text{Be}(\text{OH})_2$ is amphoteric and soluble in excess alkali to give $\text{Be}(\text{OH})_4^{2-}$; this allows Be to be oxidised by water in alkaline conditions: $\text{Be} + 2\text{H}_2\text{O} + 2\text{OH}^- \rightarrow \text{Be}(\text{OH})_4^{2-} + \text{H}_2$

(iii) Reactions of Group 2 compounds

- The oxides and hydroxides of alkali metals have limited solubility in water and are therefore only weakly basic
- The halides of alkali metals are neutral, with the exception of BeCl_2 , which is covalent and rapidly hydrolysed in water: $\text{BeCl}_2(\text{s}) + 2\text{H}_2\text{O}(\text{l}) \rightarrow \text{Be}(\text{OH})_2(\text{s}) + 2\text{HCl}(\text{g})$

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(iv) Extraction

- Be is extracted by converting its ore into a fluoride and reducing with magnesium
- Mg - Ba can be extracted by electrolysis of their chlorides, but they can also be reduced by reactive metals (MgO can react with Si and CaO – BaO can react with Al)

(v) Complex ion formation

- Group 2 ions have a stronger tendency to form complex ions than Group 1 ions; the tendency to form complex ions decreases down the group (Sr and Ba have limited tendency to form complex ions)
- Be can only use its 2s and 2p electrons so can only form 4-coordinate complex ions eg $\text{Be}(\text{OH})_4^{2-}$; Mg and Ca can use available d orbitals and can therefore form 6-coordinate complex ions (eg MgF_6^{4-})

(vi) Solubility of Ionic Compounds

- All compounds of Group 1 are soluble
 - The chlorides and nitrates of Group 2 are soluble
 - The carbonates of Group 2 are insoluble
 - The solubility of the hydroxides and sulphates vary down Group 2: the solubility of hydroxides increases down Group 2 ($\text{Mg}(\text{OH})_2$ is insoluble but $\text{Ba}(\text{OH})_2$ is soluble) but the solubility of sulphates decreases down Group 2 (MgSO_4 is soluble but BaSO_4 is insoluble)
- The solubility of an ionic compound in water depends on the relative magnitude of the lattice enthalpies and the hydration enthalpies; both decrease down the group as the size of the cation increases; however the lattice enthalpy is also influenced by the relative size of the cation and anion; if they are similar, the lattice enthalpy is slightly larger than expected and if they are very different, the lattice enthalpy is smaller than expected
 - Sulphate ions are large and so the lattice enthalpies with larger ions such as Ba^{2+} are larger than expected; this causes the solubility of these compounds to decrease
 - Hydroxide ions are small and so the lattice enthalpies with smaller ions such as Mg^{2+} are larger than expected; this causes the solubility of these compounds to decrease

Lessons 5 and 6 – The Chemistry of Group 7

- The **halogens** are the collective name given to the elements in group VII of the Periodic Table; there are five halogens: fluorine, chlorine, bromine, iodine and astatine; astatine is very radioactive and cannot exist for more than a few microseconds before decaying; we will thus be concerned with the chemistry of fluorine, chlorine, bromine and iodine
- All these elements are most commonly found in the -1 oxidation state, as X^- ions. These are known as **halide** ions

a) Structure and Physical Properties

- Since each atom in this group has seven valence electrons, they tend to form diatomic molecules, eg F_2 , Cl_2 , Br_2 and I_2 ; they are thus simple molecular, with weak intermolecular forces between the molecules.
- Halogens have characteristic colours, which vary depending on which form the halogen is in:

Halogen	In pure form	In non-polar solvents	In water
Fluorine	Pale yellow gas	- (Reacts with solvents)	- (Reacts with water)
Chlorine	Pale green gas	Pale green solution	Pale green solution
Bromine	Dark red liquid	Orange solution	Orange solution
Iodine	Grey solid	Purple solution	- (Insoluble) but forms a brown solution if excess KI is present

- The halogens are usually used in the laboratory in aqueous solution; although iodine is insoluble in water, it is soluble if iodide ions are present (the iodine reacts with iodide ions to form triiodide ions as follows: $I_2(aq) + I^-(aq) \rightarrow I_3^-(aq)$; the triiodide ions give the solution its brown colour
- The melting and boiling points of the halogens increase steadily down the group:

Halogen	Melting point /°C	Boiling point /°C
Fluorine	-220	-188
Chlorine	-101	-35
Bromine	-7	59
Iodine	114	184

- This is due to the increase in strength of the Van Der Waal's forces between the molecules, which results from the increasing number of electrons in the molecule and the increasing surface area of the molecule

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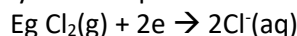
b) Chemical Properties

- The electronegativity of the halogen atoms decreases down a group:

Halogen	Electronegativity
F	4.0
Cl	3.0
Br	2.8
I	2.5

- As the number of shells increases, the shielding increases and the electrons in the covalent bond are further from (and more shielded from) the nucleus; therefore they are less strongly attracted to the nucleus and the electronegativity decreases

- The halogens are oxidising agents, as they can accept electrons and get reduced:



- Fluorine is the best oxidising agent, followed by chlorine; iodine is a mild oxidising agent; the fewer the number of shells in the atom, the closer the electrons can get to the nucleus and the less shielded the electrons are from the nucleus; the attraction of the electrons to the nucleus is thus stronger and the atom is more likely to accept electrons; thus the oxidising power of the halogens decreases down a group:

Fluorine	Chlorine	Bromine	Iodine
Very strong oxidising agent	Strong oxidising agent	Fairly strong oxidising agent	Mild oxidising agent

- The halide ions are reducing agents, as they can lose electrons and get oxidised:

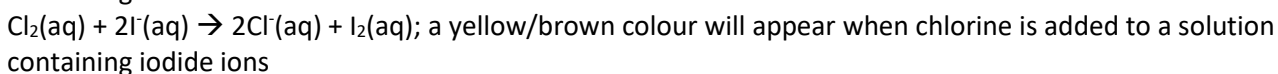
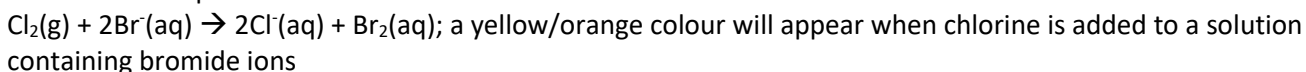


- Iodide ions are the most reducing, followed by bromide ions; fluoride ions have no significant reducing properties; as the number of shells in the ion increases, there is more shielding of the nucleus and the outer electrons become less strongly held; these electrons are thus lost more easily and the halide ion is more readily oxidised; thus the reducing power of the halides increases down a group:

Fluoride	chloride	Bromide	Iodide
Very poor reducing agent	Poor reducing agent	Fairly poor reducing agent	Fairly good reducing agent

- The displacement reactions of halogens with halide ions provides a clear illustration of the trends in oxidizing properties of the halogens and the trends in reducing properties of the halide ions in aqueous solution; the more reactive halogens (ie the strongest oxidising agents) will displace the more reactive halides (ie the strongest reducing agents) from solutions of their ions:

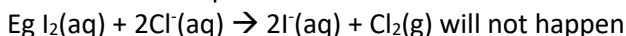
- Chlorine will displace bromide and iodide ions from solution:



- Bromine will displace iodide ions from solution, but not chloride ions:

- $\text{Br}_2(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Br}^-(\text{aq}) + \text{I}_2(\text{aq}); \text{ a yellow/brown colour will appear when bromine is added to a solution containing iodide ions}$

- Iodine cannot displace either bromide or chloride ions from solution:



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- The variation in reducing strength of the halides can be clearly seen in the reaction of the sodium halides with concentrated sulphuric acid
 - concentrated sulphuric acid is a strong acid and can convert the sodium salts of the halides into the hydrogen halides: $\text{H}_2\text{SO}_4(\text{l}) + \text{NaX}(\text{s}) \rightarrow \text{NaHSO}_4(\text{s}) + \text{HX}(\text{g})$ or $\text{H}_2\text{SO}_4(\text{l}) + \text{X}^- \rightarrow \text{HSO}_4^- + \text{HX}(\text{g})$; the halide ions are not oxidised in this reaction - they are behaving as bases
 - Concentrated sulphuric acid is also an oxidising agent; it can be reduced either to SO_2 , to S or to H_2S :
 - $\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{SO}_2 + 2\text{H}_2\text{O}$ (S reduced from +6 to +4)
 - $\text{H}_2\text{SO}_4 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{S} + 4\text{H}_2\text{O}$ (S reduced from +6 to 0)
 - $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O}$ (S reduced from +6 to -2)
 - Cl^- is not a strong reducing agent so is not oxidised by H_2SO_4 ; only the acid-base reaction takes place and HCl gas is formed: $\text{H}_2\text{SO}_4 + \text{Cl}^- \rightarrow \text{HSO}_4^- + \text{HCl}$ (acid-base reaction); white fumes of HCl will be seen; the fumes will turn blue litmus paper red
 - Br^- is a better reducing agent and is oxidised, but the sulphur in the H_2SO_4 is only reduced from +6 to +4 (SO_2); the acid-base reaction may also take place to an extent: $\text{H}_2\text{SO}_4 + \text{Br}^- \rightarrow \text{HSO}_4^- + \text{HBr}$ (acid-base reaction); $\text{H}_2\text{SO}_4 + 2\text{H}^+ + 2\text{Br}^- \rightarrow \text{SO}_2 + \text{Br}_2 + 2\text{H}_2\text{O}$ (redox reaction); white fumes of HBr will be seen which turn blue litmus paper red; the red/orange colour of bromine will also be seen
 - I^- is a good reducing agent and is oxidised, reducing the sulphur in the H_2SO_4 from +6 to +4 (SO_2), to 0 (S) or to -2 (H_2S); the acid-base reaction may also take place to an extent: $\text{H}_2\text{SO}_4 + \text{I}^- \rightarrow \text{HSO}_4^- + \text{HI}$ (acid-base reaction); $\text{H}_2\text{SO}_4 + 6\text{H}^+ + 6\text{I}^- \rightarrow \text{S} + 3\text{I}_2 + 4\text{H}_2\text{O}$ (redox reaction); $\text{H}_2\text{SO}_4 + 8\text{H}^+ + 8\text{I}^- \rightarrow \text{H}_2\text{S} + 4\text{I}_2 + 4\text{H}_2\text{O}$ (redox reaction); white fumes of HI will be seen which turn blue litmus paper red; the purple colour of iodine vapour will also be seen and there will be a smell of rotten eggs due to the presence of H_2S
 - The products of the reaction between the sodium halides and concentrated sulphuric acid can be summarized in the following table:

Salt	Products of reaction with concentrated sulphuric acid	Types of reaction occurring
NaCl	HCl, NaHSO ₄	Acid-base
NaBr	Br ₂ , H ₂ O, SO ₂ , NaHSO ₄	Acid-base and redox
NaI	I ₂ , H ₂ O, S, H ₂ S, NaHSO ₄	Acid-base and redox

- The silver (I) ion, Ag^+ , forms insoluble precipitates with the chloride, bromide and iodide ions; each has its characteristic colour and these precipitation reactions can thus be used as chemical tests for these ions:
 - If **silver nitrate** solution, and a little nitric acid, is added to an aqueous solution containing a halide ion, the following reactions take place:
 - $\text{Ag}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \rightarrow \text{AgCl}(\text{s})$ white precipitate
 - $\text{Ag}^+(\text{aq}) + \text{Br}^-(\text{aq}) \rightarrow \text{AgBr}(\text{s})$ cream precipitate
 - $\text{Ag}^+(\text{aq}) + \text{I}^-(\text{aq}) \rightarrow \text{AgI}(\text{s})$ yellow precipitate
 - the **nitric acid** is added to ensure that any carbonate or hydroxide ions, often found as impurities with halide ions, are removed as CO_2 or water and so do not interfere with the precipitate
 - the three precipitates are similar in colour and thus it is not always easy to tell them apart; a further test should thus be used to distinguish between them and concentrated or dilute ammonia can be added to the precipitate: if dilute or concentrated ammonia is added to $\text{AgCl}(\text{s})$, the precipitate dissolves; if dilute ammonia is added to $\text{AgBr}(\text{s})$, there is no reaction but if concentrated ammonia is added then the precipitate dissolves; silver iodide does not dissolve either in dilute or in concentrated ammonia; the precipitates dissolve because Ag^+ ions form a complex ion with NH_3 : $[\text{Ag}(\text{NH}_3)_2]^+$

Halide ion	Colour of silver halide precipitate	Solubility of precipitate in dilute NH_3	Solubility of precipitate in concentrated NH_3
Chloride	White	Soluble	Soluble
Bromide	Cream	Insoluble	Soluble
Iodide	Yellow	Insoluble	Insoluble

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Questions

- 1.1**
- (a) Explain why a sodium atom is larger than a chlorine atom
 - (b) Explain why a potassium atom is larger than a sodium atom
 - (c) Explain why aluminium is more electronegative than magnesium
 - (d) Explain why aluminium is more electropositive than boron
- 1.2**
- (a) Explain why tin is a metal but silicon is not
 - (b) Explain why beryllium is a metal but boron is not
 - (c) Explain the meaning of the term metalloid and give one example
- 1.3**
- (a) Explain (using electronegativity) why the bonding in magnesium chloride is ionic but the bonding in aluminium chloride is covalent
 - (b) Explain (using polarization) why the bonding in boron trifluoride is covalent but the bonding in aluminium fluoride is ionic
 - (c) Explain why the bonding in aluminium fluoride is ionic but the bonding in aluminium chloride is covalent
- 1.4**
- (a) Explain why magnesium has a higher melting point than sodium
 - (b) Explain why potassium has a lower melting point than sodium
 - (c) Explain why diamond has a higher melting point than silicon
 - (d) Explain why chlorine has a higher melting point than fluorine
- 1.5**
- (a) Explain why magnesium chloride has a higher melting point than sodium chloride
 - (b) Explain why potassium chloride has a lower melting point than sodium chloride
 - (c) Explain why potassium chloride has a lower melting point than potassium fluoride
- 2.1**
- (a) Write equations to show the reaction of an alkali metal with oxygen to form:
 - (i) an oxide
 - (ii) a peroxide
 - (iii) a superoxide
 - (b) Describe the structure of a peroxide ion and a superoxide ion and state the oxidation number of oxygen in each. Explain why lithium does not form peroxides or superoxides.
- 2.2** Using equations where appropriate, and explaining any differences, compare the reactions of sodium and magnesium with:
- (a) Oxygen
 - (b) Water
 - (c) Nitrogen
 - (d) Carbon
- 2.3** Explain why the Group 1 and Group 2 metals become more reactive on descending the group
- 2.4** Give two examples of the anomalous behaviour of lithium
- 2.5** Give two examples of the anomalous behaviour of beryllium
- 2.6** Describe and explain any differences in the solubilities of the hydroxides and sulphates of Group 2

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- 3.1** State and explain the trend in electronegativity of the Group 7 elements
- 3.2** State and explain the trend in boiling point of the Group 7 elements
- 3.3** Explain why the halogens are all oxidizing agents and state and explain the trend in oxidizing ability of the halogens
- 3.4** Explain why the halides are all reducing agents and state and explain the trend in reducing ability of the halides
- 3.5** Predict whether or not a reaction would take place between the following pairs of solutions. If a reaction does take place, state what you would observe and write an ionic equation for the reaction taking place:
- (a) Sodium chloride and iodine
 - (b) Sodium iodide and chlorine
 - (c) Sodium bromide and iodine
 - (d) Sodium iodide and bromine
 - (e) Potassium chloride and bromine
 - (f) Potassium bromide and chlorine
- 3.6**
- (a) Write equations for the following half-reactions:
 - (i) I^- to I_2
 - (ii) Br^- to Br_2
 - (iii) H_2SO_4 to SO_2
 - (iv) H_2SO_4 to H_2S
 - (b) "Chloride ions cannot reduce concentrated sulphuric acid; bromide ions reduce concentrated sulphuric acid to sulphur dioxide and iodide ions reduce concentrated sulphuric acid to hydrogen sulphide"
Explain these observations in terms of the relative reducing ability of the halides and write equations to show the reactions between:
 - (i) Iodide ions and concentrated sulphuric acid
 - (ii) Bromide ions and concentrated sulphuric acid
 - (c) Chloride ions react with concentrated sulphuric acid to give hydrogen chloride gas; write an equation for this reaction and show that it is not a redox reaction

Lessons 7 – 10: The Chemistry of the d-block

(a) Atomic Structure

- A d-block element is an element which has at least one s-electron and at least one d-electron but no p-electrons in its outer shell

(i) Atoms

- The outer electronic configuration of elements in the first row of the d-block is as follows:

		4s	3d					
Sc	[Ar]	↑↓	↑					
Ti	[Ar]	↑↓	↑	↑				
V	[Ar]	↑↓	↑	↑	↑			
Cr	[Ar]	↑	↑	↑	↑	↑	↑	↑
Mn	[Ar]	↑↓	↑	↑	↑	↑	↑	↑
Fe	[Ar]	↑↓	↑↓	↑	↑	↑	↑	↑
Co	[Ar]	↑↓	↑↓	↑↓	↑	↑	↑	↑
Ni	[Ar]	↑↓	↑↓	↑↓	↑↓	↑	↑	↑
Cu	[Ar]	↑	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓
Zn	[Ar]	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓	↑↓

- Note the unusual structures of chromium and copper; the 4s and 3d subshells are very similar in energy and therefore it is easy to promote electrons from the 4s into the 3d orbitals
- In chromium the $4s^1 3d^5$ structure is adopted because the repulsion between two paired electrons in the 4s orbital is more than the energy difference between the 4s and 3d subshells; it is thus more stable to have unpaired electrons in the higher energy 3d orbital than paired electrons in the lower energy 4s orbital
- In copper and zinc the 3d subshell is actually lower in energy than the 4s subshell; the 3d orbitals are thus filled before the 4s orbital; thus copper adopts a $4s^1 3d^{10}$ configuration

(ii) Ions

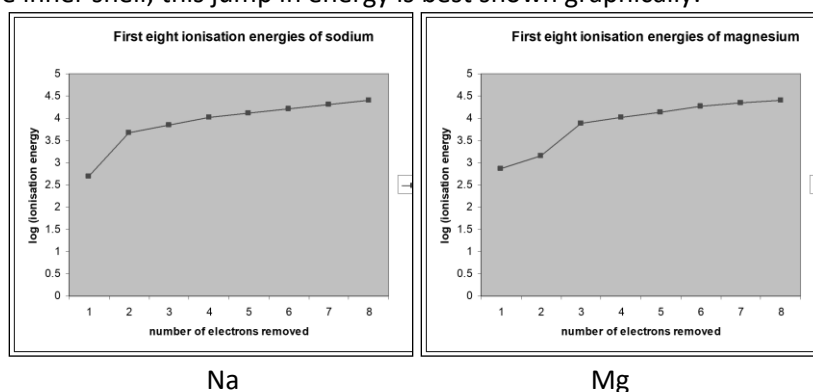
- In all ions of d-block elements, the 3d subshell is lower in energy than the 4s subshell so the 4s electrons are always removed first; 3d electrons are only removed after all 4s electrons have been removed; some examples of electronic configurations of transition metal ions are shown below:

		4s	3d					
V^{2+}	[Ar]		↑	↑	↑			
Cr^{3+}	[Ar]		↑	↑	↑			
Mn^{2+}	[Ar]		↑	↑	↑	↑	↑	

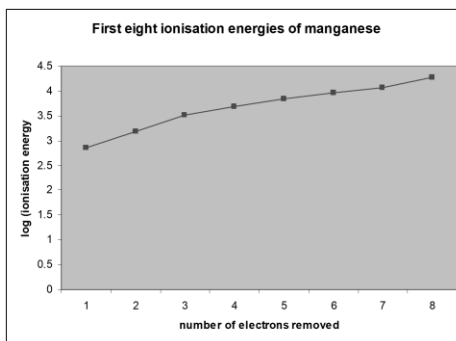
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(b) Oxidation states

- the oxidation state formed by an element in its compounds is determined by the maximum number of electrons it can lose without requiring so much energy to remove the electrons that the energy cannot be recovered in bonding
- s-block elements only form one stable oxidation state in their compounds; they lose all their valence electrons easily but cannot lose any more electrons since there is a large amount of energy required to remove the electrons from the inner shell; this jump in energy is best shown graphically:



- Na always adopts the +1 oxidation state in its compounds because there is a large jump between the first and the second ionisation energies
- Mg always adopts the +2 oxidation state in its compounds because there is a small jump between the first and the second ionisation energies but a very large jump between the second and third ionisation energies
- In the d-block elements, however, there are often a large number of valence electrons and removing them all would require more energy than can be recovered in bonding; it is usually only possible to remove some of the valence electrons; d-block elements can give up their 4s electrons fairly easily but the d-electrons are harder to remove; since the successive ionisation energies of d-electrons increase steadily, it is difficult to predict how many can be lost; this effect can be shown graphically by considering the successive ionisation energies of an element such as manganese:



- The ionisation energies increase steadily after the removal of the 4s electrons
- the energy required to remove the 3d electrons is sometimes recovered in bonding, but not always
- the number of 3d electrons removed thus varies from compound to compound
- d-block metals are thus able to adopt a variety of different oxidation states in their compounds**

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- The oxidation states most commonly formed by the first-row d-block elements are as follows:
Sc: +3 only (d^0); Ti: +3 (d^1), +4 (d^0); V: +2 (d^3), +3 (d^2), +4 (d^1), +5 (d^0); Cr: +3 (d^3), +6 (d^0); Mn: +2 (d^5), +3 (d^4), +4 (d^3), +6 (d^1), +7 (d^0); Fe: +2 (d^6), +3 (d^5); Co: +2 (d^7), +3 (d^6); Ni: +2 (d^8); Cu: +1 (d^{10}), +2 (d^9); Zn: +2 only (d^{10})
- All the first row transition metals except Sc and Zn form at least one stable ion with partially filled d-orbitals, and it is this property which defines a transition metal; a **transition metal is a metal which forms at least one stable ion with partially filled d-orbitals**; zinc and scandium do not share this property and are not transition metals

(c) Complex ions

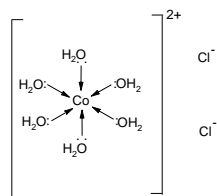
(i) definition

- A complex ion is an ion comprising one or more ligands attached to a central metal cation by means of a dative covalent bond
- A ligand is a species which can use its lone pair of electrons to form a dative covalent bond with a transition metal; examples of ligands are H_2O , NH_3 , Cl^- , OH^- , CN^-
- Cations which form complex ions must have two features:
 - they must have a high charge density, and thus be able to attract electrons from ligands
 - they must have empty orbitals of low energy, so that they can accept the lone pair of electrons from the ligands
 - cations of d-block metals are small, have a high charge and have available empty 3d and 4s orbitals of low energy. They thus form complex ions readily
 - most metals form complex ions; exceptions are Na – Ca in Group 1 and Ca – Ba in group 2
- The number of lone pairs of electrons which a cation can accept is known as the **coordination number** of the cation; it depends on the size and electronic configuration of that cation, and also on the size and charge of the ligand; 6 is the most common coordination number, although 4 and 2 are also known
- Examples of complex ions are $[Fe(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$, $[Cu(NH_3)_4(H_2O)_2]^{2+}$; note that the formula of the ion is always written inside square brackets with the overall charge written outside the brackets
- Some ligands are capable of forming more than one dative covalent bond per ligand. These are known as **multidentate** ligands or **chelates**; examples are ethanedioate ($C_2O_4^{2-}$) and 1,2-diaminoethane ($H_2NCH_2CH_2NH_2$), both of which donate 2 lone pairs per ligand and are said to be bidentate; $edta^{4-}$ can form 6 dative covalent bonds per ligand and is thus said to be hexadentate; ligands such as H_2O , Cl^- and CN^- form only one dative covalent bond per ligand and are said to be monodentate; complexes involving polydentate ligands usually have a coordination number of 6, but because each ligand provides more than one lone pair, fewer ligands are required: eg $[Fe(C_2O_4)_3]^{3-}$; $[Cr(H_2NCH_2CH_2NH_2)_3]^{3+}$; $[Cu(edta)]^{2-}$
- When metal ions are in solution, they are usually represented as the simple ion, such as $Fe^{2+}(aq)$, $Co^{2+}(aq)$, $Cr^{3+}(aq)$ or $Fe^{2+}(aq)$; this is, however, a simplified representation as all d-block cations and many other cations with high polarising power exist as the hexaaqua complex, eg $[Fe(H_2O)_6]^{2+}$
 - Eg $FeSO_4(aq)$ consists of $[Fe(H_2O)_6]^{2+}$ and SO_4^{2-} ions
 - Eg $Fe_2(SO_4)_3(aq)$ consists of $[Fe(H_2O)_6]^{3+}$ and SO_4^{2-} ions
 - Eg $CuCl_2(aq)$ consists of $[Cu(H_2O)_6]^{2+}$ and Cl^- ions

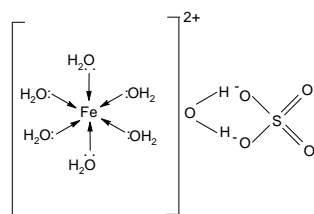
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- Many complex ions exist in the solid state; in these cases the ligands are often written after the rest of the compound, separated by a dot: Eg $[\text{Co}(\text{H}_2\text{O})_6]\text{Cl}_2(\text{s})$ is often represented as $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$

The six water molecules are behaving as ligands:

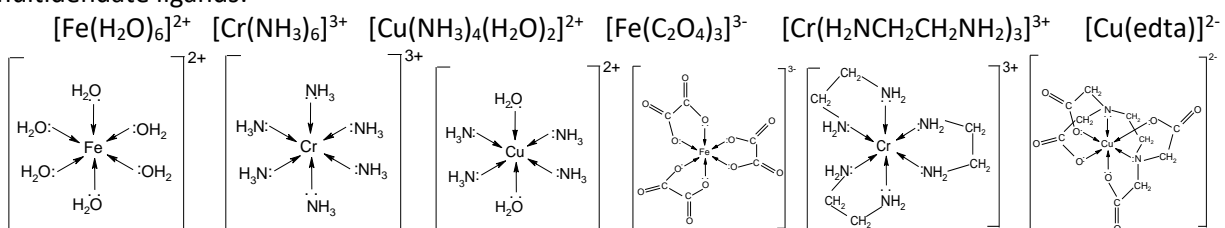


- the dot does not always, however, mean that there are ligands present; some salts contain water of crystallisation, where the water is not a ligand but a link between the ions
- Eg in $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$, the water molecules are not behaving as ligands, but as water molecules of crystallisation
- Eg in $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, six of the water molecules are behaving as ligands, and the seventh is a water of crystallisation. It helps link the cation to the anion:

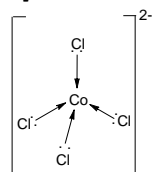


(ii) shape

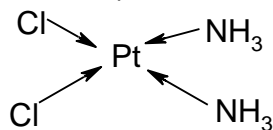
- 6-coordinate complexes are all octahedral; they are formed with small ligands such as H_2O and NH_3 and with multidentate ligands:



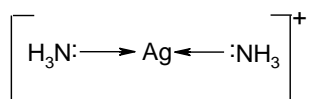
- 4-coordinate complexes are generally tetrahedral and are formed with larger ligands such as Cl^- ; larger ligands cannot fit around the transition metal so easily and hence form smaller complexes. They can be drawn as follows: Eg $[\text{CoCl}_4]^{2-}$:



- Some 4-coordinated complexes however, especially if they involve Pt, are square planar: Eg $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$



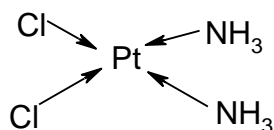
- 2-coordinate complexes are in general linear, and are formed with Ag^+ ions; eg $[\text{Ag}(\text{NH}_3)_2]^+$



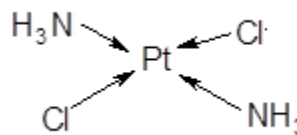
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(iii) isomerism

- Complex ions can show types of isomerism similar to organic compounds:
 - square planar complexes in which the ligands are not all identical can display a form of E-Z isomerism (isomers different due to restricted rotation) known as cis-trans isomerism; the most common example of this is in complexes which contain two each of two different types of ligand – for example $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$; the identical ligands can either be adjacent to each other or opposite each other:

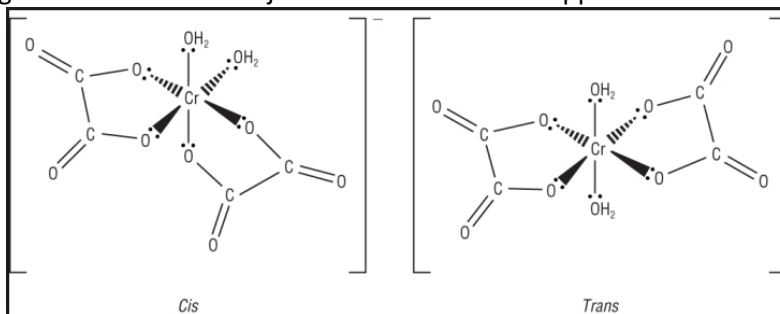


Z or cis isomer (cisplatin)

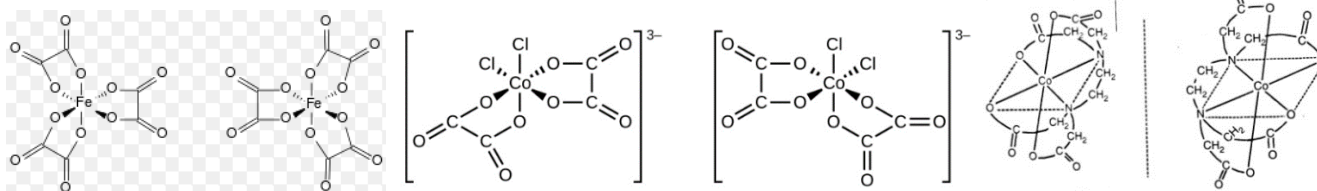


E or trans isomer (transplatin)

- octahedral complexes also show cis-trans isomerism when they contain four ligands (or two bidentate ligands) of one type and two ligands of another type - for example $[\text{Cr}(\text{Cl}_2)(\text{H}_2\text{O})_4]^+$ or $[\text{Cr}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2]^+$; the two minority ligands can either be adjacent to each other or opposite each other:

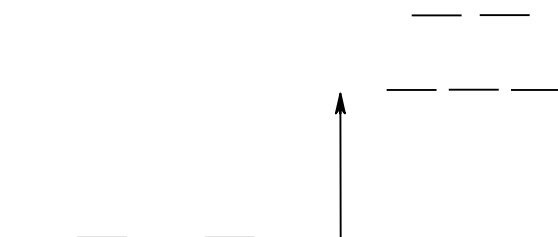


- Octahedral complexes can display optical isomerism (non-superimposable mirror images) when they contain one of the following combinations:; three bidentate ligands, eg $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$; two bidentate ligands and two monodentate ligands (cis isomer only), eg $[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$ or one hexadentate ligand, eg $[\text{Co}(\text{edta})]^{2-}$



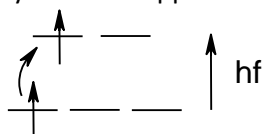
(iv) colour

- When a cation forms a complex ion, the incoming ligands repel the electrons in the atom, and thus they are raised in energy; some of the d-orbitals are repelled more than others and the result is that the d-orbitals are split into 2 groups of orbitals, with three orbitals being slightly lower in energy than the other two:



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- The difference in energy between these groups of orbitals is similar to the energy of visible light; if these d-orbitals are partially filled, some of the electrons in the lower energy orbitals are excited into the higher energy orbitals, and in doing so absorb the light that corresponds to that frequency; the resultant light is deficient in the light of that frequency and thus appears coloured

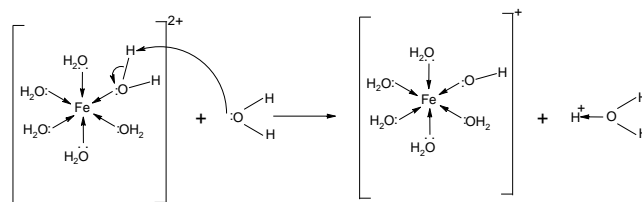


- Note that two criteria must be satisfied if the ion is to be coloured:
 - there must be a splitting of the d-orbitals; this only happens in the presence of ligands and thus only complex ions are coloured; anhydrous ions do not have split d-orbitals and so cannot absorb light in the visible spectrum and are white; eg anhydrous CuSO_4 (d^9) is white but hydrated $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue
 - the d-orbitals must be partially filled; if the d-orbitals are empty (Eg Sc^{3+} , Al^{3+}) then there are no electrons which can be excited into the higher energy d-orbitals and the ions will be colourless; if the d-orbitals are full (Eg Cu^+ , Zn^{2+}) then there are no empty orbitals into which the electrons can be excited and the ions will be colourless

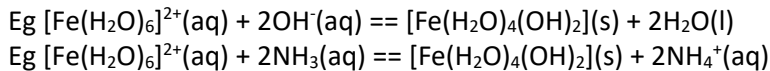
(d) Chemical Reactions

(i) acid-base reactions (deprotonation)

- Most metal cations exist as the hexaqua complex in solution; if the charge density of the cation is particularly high, the electron density in the aqua ligand moves even closer to the cation and the bonds in the water are weakened; in such cases the hydrogen in the water ligand can be lost as a proton
Eg $[\text{Fe}(\text{H}_2\text{O})_6]^{2+} \rightleftharpoons [\text{Fe}(\text{H}_2\text{O})_5\text{OH}]^+ + \text{H}^+$



- This process is known as **deprotonation**; it is an example of salt hydrolysis; deprotonation is caused by the high charge density on the central cation, which weakens the O-H bonds in the water ligands, and enables the H^+ (the proton) to leave; hydroxide ions and ammonia will remove more than one proton to become a hydroxide:

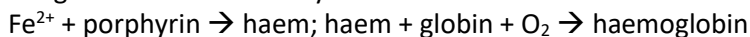


(ii) ligand exchange reactions

- Ligand exchange is the replacement of one ligand by another in a complex; many ligands are capable of replacing water in transition metal complexes:
 - Eg $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{NH}_3(\text{aq}) \rightarrow [\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$ (pale blue solution - dark blue solution)
 - $[\text{Co}(\text{H}_2\text{O})_6]^{2+}(\text{aq}) + 4\text{Cl}^-(\text{aq}) \rightleftharpoons [\text{CoCl}_4]^{2-}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$ (pink solution – blue solution)
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}(\text{aq}) + 3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2(\text{aq}) \rightleftharpoons [\text{Fe}(\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2)_3]^{3+}(\text{aq}) + 6\text{H}_2\text{O}(\text{l})$
- The replacement of monodentate ligands by multidentate ligands in a complex ion is energetically favourable due to the increase in entropy of the system; this is known as **the chelate effect**

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- Another important complex ion involving multidentate ligands is **haemoglobin**; **haem** is a complex ion consisting Fe^{2+} and a complex tetradentate ligand called porphyrin; the complex is generally found with a protein called globin, which provides the fifth coordinate bond, and a molecule of oxygen which forms the sixth bond; the complete six coordinate complex is called haemoglobin; this structure is responsible for carrying oxygen in the blood throughout the human body:



Carbon monoxide is a similar size and shape to oxygen and forms a much stronger bond with the iron; it thus displaces the oxygen from the complex and reduces the blood's ability to carry oxygen; it is thus a very poisonous gas

(iii) redox reactions

- Since transition metals show a variety of transition states in their compounds, much of their chemistry is dominated by movement between these transition states
- Iron exists in two common oxidation states, +2 (Fe^{2+}) and +3 (Fe^{3+}); in aqueous solution, the Fe is readily oxidised from Fe^{2+} to Fe^{3+} : $\text{Fe}^{2+}(\text{aq}) \rightarrow \text{Fe}^{3+}(\text{aq}) + \text{e}^-$; Fe^{2+} is a reducing agent and Fe^{3+} ion is an oxidising agent
- Manganese can exist in a number of oxidation states, but is most stable in an oxidation state of +2, +4 or +7; in the +7 oxidation state it exists as the intense purple ion MnO_4^- ; this can be reduced to the colourless Mn^{2+} in acidic solution: $\text{MnO}_4^-(\text{aq}) + 8\text{H}^+(\text{aq}) + 5\text{e}^- \rightarrow \text{Mn}^{2+}(\text{aq}) + 4\text{H}_2\text{O}(\text{l})$; this is the basis for manganate titrations
- Chromium is most stable in oxidation states of +3, +6; the orange $\text{Cr}_2\text{O}_7^{2-}$ can be readily reduced in acidic solution to the green Cr^{3+} ion: $\text{Cr}_2\text{O}_7^{2-}(\text{aq}) + 14\text{H}^+(\text{aq}) + 6\text{e}^- \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 7\text{H}_2\text{O}(\text{l})$; this reaction is used in organic chemistry as a test for reducing organic compounds such as primary alcohols and aldehydes

(e) Catalytic properties

- The ability of transition metals to form more than one stable oxidation state means that they can accept and lose electrons easily; this enables them to catalyse certain redox reactions; they can be readily oxidised and reduced again, or reduced and then oxidised again, as a consequence of having a number of different oxidation states of similar stability; they can behave either as homogeneous catalysts or as heterogeneous catalysts
- A homogeneous catalyst is a catalyst in the same phase as the reactants; homogeneous catalysis involves aqueous transition metal ions catalysing reactions, often between two anions; the cation reacts with each anion in turn, thus avoiding the need for a direct collision between two anions (this is difficult since they repel each other): eg $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + \text{I}_2(\text{aq})$ can be catalysed by Fe^{2+} or Fe^{3+} ions:
With Fe^{2+} : $\text{S}_2\text{O}_8^{2-}(\text{aq}) + 2\text{Fe}^{2+}(\text{aq}) \rightarrow 2\text{SO}_4^{2-}(\text{aq}) + 2\text{Fe}^{3+}(\text{aq})$, $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$
With Fe^{3+} : $2\text{Fe}^{3+}(\text{aq}) + 2\text{I}^-(\text{aq}) \rightarrow 2\text{Fe}^{2+}(\text{aq}) + \text{I}_2(\text{aq})$, $2\text{Fe}^{2+}(\text{aq}) + \text{S}_2\text{O}_8^{2-}(\text{aq}) \rightarrow 2\text{Fe}^{3+}(\text{aq}) + 2\text{SO}_4^{2-}(\text{aq})$
- A heterogeneous catalyst is a catalyst in a different phase from the reactants; in most cases, the catalyst is a solid and the reactants are liquids or gases; the reaction occurs at active sites on the catalyst surface; the catalyst therefore needs to have a large surface area to be effective, which in turn means it needs to be very thinly spread out in order to reduce its cost, and might need a special support
- Examples of heterogeneous catalysts are; Fe in the production of ammonia, V_2O_5 in the contact process or Pt and Rh in a catalytic converter; in the Contact process, V_2O_5 oxidises SO_2 to SO_3 , itself getting reduced: $\text{SO}_2 + \text{V}_2\text{O}_5 \rightarrow \text{SO}_3 + \text{V}_2\text{O}_4$; V_2O_4 then uses the O_2 to get oxidised back to V_2O_5 : $\text{V}_2\text{O}_4 + 1/2\text{O}_2 \rightarrow \text{V}_2\text{O}_5$

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- 4.1**
- Give the electronic configuration of the following atoms: V, Cr, Co, Cu, Zn
 - Give the electronic configuration of the following ions: Co^{2+} , Cu^+ , V^{3+} , Cr^{2+} , Fe^{3+}
 - Explain why Sc and Zn are not classified as transition metals
- 4.2**
- Explain why many metals, including all transition metals, can form complex ions. Name two metals which cannot form complex ions
 - Explain why transition metal complex ions are often coloured.
 - Explain why Cu^+ complex ions are not coloured.
- 4.3**
- Explain the meaning of the terms “complex ion”, “ligand” and “coordination number”.
 - Write the formulae of the complex ion most likely to be formed by:
 - Fe^{2+} and H_2O
 - Fe^{2+} and CN^-
 - Ag^+ and $\text{S}_2\text{O}_3^{2-}$
 - Co^{2+} and Cl^-
 - Fe^{2+} and $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$
 - Cu^{2+} and edta^{4-}
 - Draw the two isomers of $\text{Pt}(\text{NH}_3)_2\text{Cl}_2$ and state the type of isomerism shown
 - Draw the two isomers of $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and state the type of isomerism shown
 - Draw the three isomers of $[\text{Co}(\text{C}_2\text{O}_4)_2\text{Cl}_2]^{3-}$ and state the type of isomerism shown
- 4.4** Write equations for the reactions taking place during the following laboratory observations:
- If aqueous sodium hydroxide solution is added to a solution of iron (II) chloride, a dirty green precipitate appears.
 - If aqueous sodium hydroxide solution is added to a solution of aluminium (III) sulphate, a white precipitate appears which dissolves in excess sodium hydroxide to give a colourless solution.
 - If aqueous ammonia is added to a solution of copper (II) sulphate, a pale blue precipitate appears which dissolves in excess ammonia to give a deep blue solution.
 - If concentrated hydrochloric acid is added to an aqueous solution of cobalt (II) nitrate, the solution turns blue. If the mixture is then diluted, it reverts to its original pink colour.
- 4.5**
- Explain why a 1.0 mol dm^{-3} solution of iron (II) nitrate has a higher pH than a 1.0 mol dm^{-3} solution of iron (III) nitrate.
 - Explain why the reaction between $[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$ and edta^{4-} ions is thermodynamically favoured.
- 4.6**
- Explain why transition metals and their compounds are often effective catalysts.
 - Explain the difference between homogeneous and heterogeneous catalysis.
 - Explain how the following reaction can be catalysed by Fe^{2+} ions: $\text{S}_2\text{O}_8^{2-} + 2\text{I}^- \rightarrow 2\text{SO}_4^{2-} + \text{I}_2$
 - Explain how the Contact process is catalysed by V_2O_5