

## Periodicity

### 3.4 Periodic trends in period 3 (Na to Ar) -

**13.1.1. Explain the physical properties of the chlorides and oxides of the elements in the third period (Na → Ar) in terms of their bonding and structure. Limit the explanation to the physical states of the compounds under standard conditions and electrical conductivity in the molten state only.**

**13.1.2. Describe the chemical trends for the chlorides and oxides referred to in 13.1.1. Include relevant equations.**

*Limit this to acid-base properties of the oxides and the reactions of the chlorides and oxides with water.*

The position of elements within the periodic table affects the type of chemical bonding in their compounds and consequently the formulae and properties of their compounds.

Na, Mg and Al are metals and form ionic bonds with oxygen and chlorine.

Elements after aluminum are nonmetals and form covalent bonds with oxygen and chlorine. Aluminum oxide is a semiconductor. Silicon has a giant covalent network and consequently no conductivity.

### Period 3 chlorides

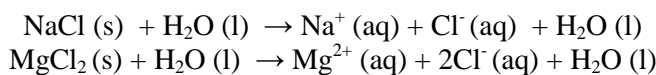
Valency electrons increase, therefore number of chlorine atoms bonded increases.

NaCl (s)	MgCl <sub>2</sub> (s)	AlCl <sub>3</sub> (s)	SiCl <sub>4</sub> (l)	PCl <sub>5</sub> (s)/PCl <sub>3</sub> (l)
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*Note: sulfur chloride is not required*

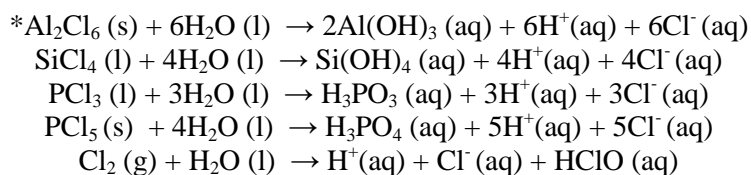
#### Metal chlorides (NaCl and MgCl<sub>2</sub>)

- Ionic, crystalline
- High melting points
- Dissolve without chemical reaction
- Solutions conduct electricity
- 



#### Nonmetal chlorides

- Molecular covalent structures
- Weak forces between molecules
- Low melting and boiling points SiCl<sub>4</sub> (b.p.58.6°C), PCl<sub>5</sub> (m.p. 180°C), PCl<sub>3</sub> (b.p.76°C)
- Hydrolyze when added to water forming an acidic solution containing hydrogen and chloride ions and the oxide or oxyacid of the element:



H<sub>3</sub>PO<sub>3</sub> = Phosphorous Acid, H<sub>3</sub>PO<sub>4</sub> = Orthophosphorus Acid, HClO = Chloric(I) acid (Hypochlorous acid).

\*The behavior of many aluminium compounds is more typical of nonmetals – a consequence of the small size and high charge of the aluminium ion.

Aluminium chloride, although a solid, sublimates at 178°C.

Anhydrous AlCl<sub>3</sub> hydrolyses when added to water!

### Period 3 oxides

The most noticeable trend across the period is the change from basic to acidic character.

The non-metals form acidic oxides, aluminum is amphoteric (can be both basic and acidic), and the metal oxides are all basic.

One extra oxygen atom for each successive element:

$\text{Na}_2\text{O(s)}$	$\text{MgO(s)}$	$\text{Al}_2\text{O}_3\text{(s)}$	$\text{SiO}_2\text{(s)}$	$\text{P}_4\text{O}_6\text{(s)}/\text{P}_4\text{O}_{10}\text{(s)}$	$\text{SO}_2\text{(g)}/\text{SO}_3\text{(g)}$	$\text{Cl}_2\text{O(l)}/\text{Cl}_2\text{O}_7\text{(l)}$
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Sodium and magnesium oxides are ionic solids and react with water to form an alkaline solution of the hydroxide. Sodium and magnesium oxides are reasonable conductors in the molten state because they are ionic

Aluminium and silicon oxides have a giant covalent structure (extended lattice) and are virtually insoluble. Aluminium oxide is amphoteric (react with both acids and bases).

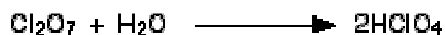
Silicon dioxide is weakly acidic and will form silicates with hot concentrated alkalis.

Other nonmetal oxides (P, S, Cl) are covalent molecular solids, liquids or gases that react with water to form acids that then dissociate.

Dichlorine monoxide (Chlorine(I) oxide):  $\text{Cl}_2\text{O}$  (b.p.  $20^\circ\text{C}$ ) is far less acidic than chlorine(VII) oxide. It reacts with water to some extent to give chloric(I) acid,  $\text{HOCl}$  - also known as hypochlorous acid.



Dichlorine heptoxide (Chlorine(VII) oxide):  $\text{Cl}_2\text{O}_7$  (b.p.  $82^\circ\text{C}$ ) reacts with water to give the very strong acid, chloric(VII) acid - also known as perchloric acid. The pH of typical solutions will, like sulphuric acid, be around 0.



	$\text{Na}_2\text{O}$	$\text{MgO}$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{P}_4\text{O}_{10}$ (or $\text{P}_4\text{O}_6$ )	$\text{SO}_3$ (or $\text{SO}_2$ )	$\text{Cl}_2\text{O}_7$ $\text{Cl}_2\text{O}$
Adding $\text{H}_2\text{O}$	$\text{Na}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{NaOH}$	$\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2$	Insoluble	Insoluble	$\text{P}_4\text{O}_{10} + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_4$ $\text{P}_4\text{O}_6 + 6\text{H}_2\text{O} \rightarrow 4\text{H}_3\text{PO}_3$	$\text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_4$ $\text{SO}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{SO}_3$	$\text{Cl}_2\text{O}_7 + \text{H}_2\text{O} \rightarrow 2\text{HClO}_4$ $\text{Cl}_2\text{O} + \text{H}_2\text{O} \rightarrow 2\text{HOCl}$

### 3.5 The d-block elements Scandium to Zinc - page 103

#### 13.2.1. List the characteristic properties of transition elements.

Restrict this to variable oxidation states, complex ion formation, coloured compounds and catalytic properties.

The transition elements (d-block elements) have similar characteristics such as variable oxidation states, complex ion formation, some catalytic properties, and colored compounds.

#### 13.2.2. Identify which elements are considered to be typical of the d-block elements.

Sc and Zn are not typical.

#### 13.2.3. Describe the existence of variable oxidation states in d-block elements.

The 4s and 3d sub-levels are close in energy. Students should know that all d-block elements can show an oxidation state of +2. In addition, they should be familiar with the oxidation states of the following: Cr (+3, +6), Mn (+4, +7), Fe (+3) and Cu (+1).

Symbol	Name	Atomic Number	Electronic Configuration
Sc	Scandium	21	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
Ti	Titanium	22	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
V	Vanadium	23	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
Cr	Chromium	24	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^5$
Mn	Manganese	25	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
Fe	Iron	26	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
Co	Cobalt	27	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
Ni	Nickel	28	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
Cu	Copper	29	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1, 3d^{10}$
Zn	Zinc	30	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$

The first rule of thumb is that transition elements can lose the 2 valence electrons in the 4s orbital of the higher energy level (remember that the 4s energy level is actually at a lower energy state than the 3d) to form +2 cations. However, Chromium can also form a +3 or a +6 cation.

When chromium forms the +3 cation it loses the 4s electron as well as two d-block electrons.

When it forms the +6 cation, it can lose all of the 3d electrons and the 4s electron.

Know the other possible oxidation states: Cr (+3, +6), Mn (+4, +7), Fe (+3) and Cu (+1). Generally speaking, as you move farther to right, the possible oxidation level get lower because the nucleus of the atom is becoming more positive and thus the electrons are more attracted to the nucleus, and are harder to remove.

### Transition metals:

- Occur in the central block of the periodic table.
- d-subshell is being filled.
- The transition metals are those which have a partially filled d-electron shell in at least one common oxidation state.
- All are dense, hard metallic elements.
- Cr and Cu electronic structures associated with the additional stability of a half-filled and completely filled d-orbital.
- Ionization energy required to remove 4s electrons remarkably constant due to shielding by 3d electrons.
- Similar physical and chemical characteristics.
- Properties shared by transition metals (except Scandium and Zinc)
  - Variety of stable oxidation states
  - Ability to form complex ions
  - Formation of colored ions -  $\text{Cu}^+$  and  $\text{Zn}^{2+}$  are not colored as the 3d subshell is full
  - Catalytic ability

### Variable oxidation states

No large increase in successive ionization energies as 3d and 4s electrons have similar energies.

Most commonly found oxidation state in +2 (the two 4s electrons).

Second most common oxidation state corresponds to the loss of all 3d and 4s valence electrons (+3 for scandium, +4 for titanium).

Highest oxidation state occurs as oxoanions:  $\text{Cr}_2\text{O}_7^{2-}$  Dichromate,  $\text{MnO}_4^-$  permanganate.

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Oxidation numbers that occurs in compounds					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	

13.2.4. Define the term ligand.

Adapted from: <http://en.wikipedia.org/wiki/Ligand>

13.2.5. Describe how complexes of d-block elements are formed.

Suitable examples are:  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ ,  $[\text{Fe}(\text{CN})_6]^{3-}$ ,  $[\text{CuCl}_4]^{2-}$ ,  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ ,  $[\text{Ag}(\text{NH}_3)_2]^+$ . Only monodentate ligands are required.

### Formation of complex ions

Low energy unfilled d-orbitals can accept lone pairs of electrons from some species known as ligands to form dative bonds. Species which contain ligands bonded to a central metal ion are known as complex ions e.g.  $[\text{Cu}(\text{NH}_3)_4]^{2+}$

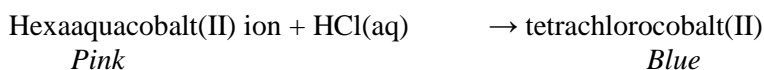
In chemistry, a **ligand** is an atom, ion, or molecule (see also: functional group) that generally donates its electrons through a coordinate covalent bond to, or shares its electrons through a covalent bond with one or more central atoms or ions.

The most common examples of ligands are: water, ammonia and the chloride ion.

Six ligands arranged octahedrally (water and ammonia) – coordination number of 6

Four ligands arranged tetrahedrally (chloride ions) – coordination number of 4

Complex ion formation can stabilize certain oxidation states and affect color and solubility.



Complex ions also exhibit isomerism analogous to those found with organic compounds.

Most commonly the central atom is a metal or metalloid in inorganic chemistry, but also in organic chemistry ligands are used, e.g.  $\text{BH}_3$

The molecule resulting from the coordination of a ligand (or an array of ligands) to a central atom is termed a complex.

Factors that characterize the ligands are their charge, size (bulk), and of course the nature of the constituent atoms.

The ligands in a complex:

- stabilise the central atom, and
- dictate the reactivity of the central atom.

The most common ligands in complexes are:

1. Water: most ions form hydrated ions in solution. For example:

$[\text{Cu}(\text{H}_2\text{O})_6]^{2+}$  hexaqua copper (II) ion

2. Ammonia: the co-ordinate bond is formed between the nitrogen atom and the metal ion, the nitrogen atom donating the lone pair of electrons. For example:

$[\text{Co}(\text{NH}_3)_6]^{3+}$  hexaammine cobalt (III) ion.

3. The Cyanide ion: the lone pair of carbon atoms is used to form co-ordinate bonds. For example:

$[\text{Fe}(\text{CN})_6]^{4-}$  hexacyano ferrate (II) ion

4. The Halide ion: the halide provides the lone pair of electrons. For example:  
 $[\text{CuCl}_4]^{3-}$  tetrachloro cuprate (II) ion

Naming complex ions

1. Number ligands using mono-, di, tri, tetra, penta, hexa-

2. Identify ligands using names ending in -o for anions.

F- fluoro, CN- cyano, Cl- chloro, OH- hydroxo ( $\text{H}_2\text{O}$  is aqua,  $\text{NH}_3$  is ammine).

3. Name the cation using English name in +ve complex but latinized name in -ve complex with suffix -ate. aluminate, plumbate, cuprate, ferrate, zincate, nickelate.

4. Indicate oxidation number of central cation using I, II, III etc.

### **13.2.6. Explain why some complexes of d-block elements are colored.**

*Students need only know that in complexes the d orbitals are split into two sets at different energy levels and the electronic transitions that take place between them are responsible for their colors.*

#### **Colored ions**

An isolated atom/ion has d-orbitals with the same energy. However, if surrounded by ions or polar molecules the orbitals may be split into two groups.

With octahedral ligands three orbitals will be at a lower energy than the remaining two.

The frequency of light corresponding to this difference in energy is in the visible region. Consequently, transition metal compounds appear colored due to absorption of some frequencies and the promotion of an electron to one of the higher energy orbitals. Transmitted light is the complimentary color of the absorbed light.

Copper(II) compounds absorb red and yellow and appear blue-green.

If there are no d-electrons that can move ( $\text{Sc}^{3+}$  and  $\text{Ti}^{4+}$ ), or the d-orbitals are full ( $\text{Zn}^{2+}$ ), then the compounds are colorless.

### **13.2.7. Outline the catalytic behavior of d-block elements and their compounds.**

*Limit this to:*

- *$\text{MnO}_2$  in the decomposition of hydrogen peroxide.*
- *$\text{V}_2\text{O}_5$  in the Contact process.*
- *Fe in the Haber process.*
- *Ni in the conversion of alkenes to alkanes.*

*The mechanisms of action are not required.*

#### **Catalytic activity**

- Ability to form complex ions with species that can donate a lone pair results in close contact between different ligands/metal and ligands.
- Wide variety of stable oxidation states mean they can readily participate in redox reactions.
- Catalysis can be heterogeneous or homogeneous
  - Heterogeneous e.g.  $\text{MnO}_2$  and  $\text{H}_2\text{O}_2$
  - Homogeneous e.g. The role of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  with acidified  $\text{H}_2\text{O}_2$  and I
- Many enzymes involved in redox reactions also contain a transition metal ion near the active site