Chem Factsheet

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Revision Summary: Trends in the Periodic Table 2

Before working through this Factsheet you should:
- Be familiar with the organisation, layout and information available from the Periodic Table;
- Be familiar with the trends in properties such as atomic radius, ionisation energy etc (covered in Factsheet 68).

After working through this Factsheet you will have revised:
- Trends in the chemical properties of Period 3 and Groups 1, 2 and 7, together with their explanations.

Note that the chemical reactions depend on the trends on physical properties (Factsheet 69) so you should revise these first before attempting to learn the material covered here.

Reactions of Period 3 elements with oxygen, chlorine and water

Element	Reaction with oxygen	Reaction with water	Reaction with chlorine
Sodium	Burns to form mixture of peroxide and oxide $2Na + O_2 \rightarrow Na_2O_2$ and $4Na + O_2 \rightarrow 2Na_2O$	Reacts very vigorously to form the hydroxide $2Na + 2H_2O \rightarrow 2NaOH + H_2$	Reacts vigorously $2Na + Cl_2 \rightarrow 2NaCl$
Magnesium	Burns in air $2Mg + O_2 \rightarrow 2MgO$	Reacts with steam to form the oxide (or hydroxide with excess steam) $Mg + H_2O \rightarrow MgO + H_2$ $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$	Reacts readily $Mg + Cl_2 \rightarrow MgCl_2$
Aluminium	Does not normally react readily with air, due to surface layer of oxide. Burns in oxygen $4Al + 3O_2 \rightarrow 2Al_2O_3$	Reacts with steam to form the oxide $2Al + 3H_2O(g) \rightarrow Al_2O_3 + 3H_2$	Reacts readily $2Al + 3Cl_2 \rightarrow 2AlCl_3$
Silicon	Thin oxide coating prevents reaction with air unless very high temperatures used. $Si + O_2 \rightarrow SiO_2$	No reaction	Reacts vigorously $Si + 2Cl_2 \rightarrow SiCl_4$
Phosphorus	White phosphorus spontaenously ignites in air, $P_4 + 5O_2 \rightarrow P_4O_{10}$	No reaction	Reacts vigorously $2P + 3Cl_2 \rightarrow 2PCl_3$
Sulphur	Burns in air . $S_8 + 8O_2 \rightarrow 8SO_3$	No reaction	Reacts on heating $S_8 + 4Cl_2 \rightarrow 4S_2Cl_2$
Chlorine	Does not react with oxygen (although oxides do exist)	Reacts with water to form chlorate (I) ions $Cl_2(g) + H_2O(l) \rightleftharpoons OCl^-(aq) + 2H^+(aq) + Cl^-(aq)$	N/A
Argon	No reaction	No reaction	No reaction
	Oxides - key points The enthalpy of formation of the oxides is usually **negative**, so the oxides are generally very **stable.** This is due to the high **electronegativity** of oxygen. Moving across the period, electronegativity increases - so the electronegativity difference with oxygen decreases. This results in reduced stability and increasing covalent character. We also see a change from **basic** to **acidic** oxides.	**Reactions with water - key points** When **metals** react, the products are **basic.** Most **non-metals** do not react, but those that do form **acidic** products.	**Chlorides - key points** As with oxygen, we see a decline in stability going across the period; again, this is due to the decreasing electronegativity difference. Likewise, the bonding becomes increasingly covalent.

Exam Hint: *You need to be able to quote both the reactions and the balanced equations for them. Many of the equations and products are easy to remember; concentrate on learning the "unusual" ones, such as* S_2Cl_2

Aside from the reactions of the period 3 elements themselves, you also need to know the characteristics and trends in the reactions of their oxides and chlorides. The following tables give summaries of these reactions.

Period 3 oxides

Oxide	Structure/Bonding	Acidic/Basic character	Reaction with water
sodium oxide Na_2O	giant ionic	basic	Reacts to form a strong alkali $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$
magnesium oxide MgO	giant ionic, polarised	basic, but less so than Na_2O	Reacts to form a weak alkali $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2(aq)$
aluminium oxide Al_2O_3	ionic, some covalent character	amphoteric - reacts with both H^+ and OH^- ions $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(1)$ $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(1) \rightarrow 2Al(OH)_4^-(aq)$	No reaction
silicon(IV) oxide SiO_2	giant covalent	acidic - reacts with OH^- ions $SiO_2(s) + 2OH^-(aq) \rightarrow SiO_3^{2-}(aq) + H_2O(l)$	No reaction
phosphorus(V) oxide P_4O_{10}	molecular covalent solid	acidic	Reacts to form phosphoric (V) acid $P_4O_{10}(s) + 6H_2O(l) \rightarrow H_3PO_4(aq)$
sulphur(IV) oxide (or dioxide) SO_2 sulphur(VI) oxide (or trioxide) SO_3	molecular covalent gas	acidic	React to form sulphuric (IV) and sulphuric (VI) acids: $SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$ $SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
chlorine oxide(Cl_2O)	molecular covalent gas	acidic	Reacts to form hypochlorous acid $Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$

Period 3 chlorides

Chloride	Structure/ Bonding	Reaction with water
sodium chloride NaCl	Giant ionic	Dissolves to give a neutral solution
magnesium chloride $MgCl_2$	Giant ionic	Dissolves to give a weakly acid solution
aluminium chloride $AlCl_3$	When anhydrous, covalent solid which exists as dimers Al_2Cl_6 The hydrated form is an ionic solid	Anhydrous form reacts to produce hydrochloric acid $AlCl_3(s) + 3H_2O(l) \rightarrow Al(OH)_3(s) + 3HCl(aq)$ Hydrated form is hydrolysed in water, forming acidic solution $[Al(H_2O)_6]^{3+}(aq) + H_2O(l) \rightarrow Al[(H_2O)_5(OH)]^{2+}(aq) + H_3O^+(aq)$
silicon chloride $SiCl_4$	molecular covalent liquid	Reacts to produce hydrochloric acid $SiCl_4(1) + 2H_2O(1) \rightarrow SiO_2(s) + 4HCl(aq)$
phosphorus chlorides PCl_3 and PCl_5	molecular covalent liquid	Reacts to form phosphoric and hydrochloric acids $PCl_3(1) + 3H_2O(1) \rightarrow H_3PO_4(aq) + 3HCl(aq)$
sulphur chlorides S_2Cl_2, SCl_2 and SCl_4	molecular covalent liquid	Reacts to form hydrochloric acid $2S_2Cl_2(1) + 2H_2O(1) \rightarrow 3S(s) + SO_2(aq) + 4HCl(aq)$

Practice questions on trends across the period

1. One of the period 3 elements forms an amphoteric oxide. Use equations to illustrate the amphoteric nature of the compound.

2. Explain why the heat evolved in the formation of the period 3 chlorides decreases as we move across the period.

3. If an oxide of an element can react with water, it will form either a hydroxide or an oxyacid depending on the nature of the element concerned. Using examples from period 3,

   (a) Give an example of an oxide which forms a hydroxide with water and state the nature of the oxide. Write a balanced chemical equation for the reaction which occurs.

   (b) Give an example of an oxide which forms an oxyacid with water and state the nature of the oxide. Write a balanced chemical equation for the reaction which occurs.

Answers

1. Aluminium oxide is amphoteric.
   As a base: $Al_2O_3(s) + 6H^+(aq) \rightarrow 2Al^{3+}(aq) + 3H_2O(l)$
   As an acid: $Al_2O_3(s) + 2OH^-(aq) + 3H_2O(l) \rightarrow 2Al(OH)_4^-(aq)$

2. s-block metals are very electropositive, so form strong ionic bonds with electronegative chlorine, releasing a great deal of energy. As we move across the period, bonds formed become more covalent in character and the heat released on formation decreases.

3 (a) Oxide: Na_2O / MgO Nature: Basic
$Na_2O(s)+H_2O(l) \rightarrow 2NaOH(aq)$
$MgO(s)+H_2O(l) \rightarrow Mg(OH)_2(aq)$

(b) Oxide: SO_2, SO_2, P_4O_{10} or Cl_2O Nature: Acidic
$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$
$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq)$
$P_4O_{10}(s) + 6H_2O(l) \rightarrow H_3PO_4(aq)$
$Cl_2O(g) + H_2O(l) \rightarrow 2HOCl(aq)$

Trends within groups of the Periodic Table

Elements within the same group on the Periodic Table tend to show similar chemical and physical properties due to similarities in electronic configuration.

Groups 1 and 2

Members of groups 1 and 2 are all metals. The trends in groups 1 and 2 are generally similar.

Reactivity	thermal stability of nitrates	thermal stability of carbonates
↓ Increases	↓ Increases	↓ Increases

Exam Hints:

*1. Check whether your specification requires you to know the **explanations** for the trends, or just what they are.*

2. When quoting trends, you need to be able to quote appropriate examples - for example, what evidence is there that reactivity increases down Group 1 ?

Notes

The reactivity increases down the group due to the decrease in 1st ionisation energy - which is due to the increasing distance of the outer electrons from the nucleus, and the increased shielding.

There are two ways of looking at the thermal stability - arguments are given for carbonates, but nitrates work the same way. First note that the carbonates decompose to give the oxide and carbon dioxide.

1. **Lattice enthalpy.** The comparative sizes of the lattice enthalpy for the carbonate and oxide indicate how much energy must be supplied to force the carbonate to decompose.
Both lattice enthalpies decrease down the group due to the increasing size of the metal ions - and so the increasing distance between the positive and negative ions. However, the percentage decrease in the oxide lattice enthalpy is greater. This is because the oxide ion is small, so the increasing size of the metal ions has a large % impact on the distance between ions: the carbonate ion is much bigger, so the proportional impact of the metal ions is much less.

2. **Polarising ability.** The carbonate ion has a system of delocalised electrons. In an ionic compound, it tends to be polarised so that the oxygen adjacent to the cation acquires a greater share of the negative charge. This tendency makes it easier for the carbon and other two oxygens to break away on heating to form carbon dioxide. The smaller cations at the top of the groups have a greater polarising ability, because of their greater charge density - so it requires less heat to decompose their carbonates.

Group 2 Only Trends

- Solubility of **hydroxides increases** as group is descended.
- Solubility of **sulphates decreases** as group is descended.

Both of these trends are due to the changes in **lattice enthalpy** and **hydration enthalpy** as the group is descended.
The lattice enthalpy falls going down the group - the distance between cations and anions increase as the cations become larger. The hydration enthalpy also falls - the water molecules are less strongly attracted to the larger ions. So the issue is which of them falls faster - if the lattice enthalpy falls faster, then dissolving becomes more exothermic and compounds become more soluble, whereas if the hydration enthalpy falls faster, dissolving becomes more endothermic and solubility decreases.

As explained above, the percentage decrease in lattice enthalpy is greater if the anion is small, since the size of the cation then contributes more significantly to the distance between the ions. Hydroxide ions are smaller than sulphate ions - so the lattice enthalpy for hydroxides decreases faster than that for sulphates. For hydroxides, the lattice enthalpy decreases faster than the hydration enthalpy - they become soluble. For sulphates, the hydration enthalpy decreases faster than the lattice enthalpy - they become less soluble.

Products of reactions of Group 1 and 2 metals

The table shows the reactions of groups 1 and 2 with oxygen, water and chlorine.

Element	**Products of reaction with:**		
	Oxygen	**Water**	**Chlorine**
Li	Li_2O	$LiOH + H_2$	LiCl
Na	Na_2, NaO_2	$NaOH + H_2$	NaCl
K	K_2O, K_2O_2, KO_2	$KOH + H_2$	KCl
Rb	Rb_2O, Rb_2O_2, RBO_2	$RbOH + H_2$	RbCl
Cs	Cs_2O, Cs_2O_2, CsO_2	$CsOH + H_2$	CsCl
Be	BeO	No reaction	$BeCl_2$
Mg	MgO	$Mg(OH)_2 + H_2$	$MgCl_2$
Ca	CaO	$Ca(OH)_2 + H_2$	$CaCl_2$
Sr	SrO	$Sr(OH)_2 + H_2$	$SrCl_2$
Ba	BaO	$Ba(OH)_2 + H_2$	$BaCl_2$

Points to note

- Group 1 generally form oxides, peroxides and superoxides; however lithium forms only the oxide and sodium only the oxide and peroxide. This is due to the relatively small size of lithium and sodium cations
- Beryllium is anomalous in its lack of reaction with water
- Beryllium chloride is covalent and polymerise via dative bonds

Group 7 trends

Group 7, the halogens, are the most reactive group of non-metals. They are strong oxidising agents as they require only one electron to gain the electronic configuration of noble gases

solubility	reactivity	oxidising ability	acidity of HX
Decreases ↓	Decreases ↓	Decreases ↓	Increases ↓

Notes

Fluorine is the most reactive - and the strongest oxidising agent - because of its high electronegativity. When the halogens act as oxidising agents, they are attracting an electron; as the atoms increase in size, this becomes less exothermic as the electron is at an increasing distance from the nucleus, with increased shielding - hence they become less effective oxidising agents. (*Though note that the first electron affinity for fluorine is actually smaller than that of chlorine)*

The increasing acidity of the hydrogen halides is due to the decreasing bond strength (the H - X bond becomes longer as we go down the group). Note that HF is a weak acid, unlike HCl, HBr and HI.

Practice questions on group trends

1. State and explain the trend in reactivity as group 2 is descended.

2. (a) Under what conditions does water react rapidly with magnesium? Write a balanced chemical equation for the reaction, giving the states of matter for all reactants and products.

   (b) State the conditions and write a similar chemical equation for the reaction of barium powder with water.

   (c) State and explain two ways in which the reactions in a) and b) differ from each other.

3. (a) State the trend in thermal stability of nitrates within group 2.

   (b) Write an equation for the thermal decomposition of calcium nitrate

4. State the trends in solubility of group 2 hydroxides and sulphates

5. (a) (i) Chlorine appears to dissolve in water to form a solution commonly called 'chlorine water'. Write a balanced chemical equation for this reversible reaction.

   (ii) Explain why the solution is yellowish-green in colour and smells of chlorine.

   (iii) Using the chemical equation from a) (i) above, predict the effect on the odour of chlorine water when acid is added to it.

   (b) Fluorine, by contrast, reacts violently with water. White, steamy fumes are produced together with another gas, which will rekindle a glowing splint. Write a balanced chemical equation for this reaction.

   (c) What type of chemical reaction occurs in each case?

   (d) What conclusion can you draw concerning the relative oxidising powers of chlorine and fluorine?

6. (a) Write a balanced chemical equation, including state symbols, for the reactions that occurs on heating magnesium carbonate with a Bunsen burner.

   (b) How would you test for the presence of one of the products of the thermal decomposition of magnesium carbonate?

   (c) Magnesium carbonate undergoes thermal decomposition rapidly at around 700 °C. Would the thermal decomposition of barium carbonate require a higher or lower temperature?

Answers

1. Elements become more reactive as group 2 is descended
   Due to reactions involving the loss of electrons (oxidation) and ionisation energies decrease down group as there is increased distance between nucleus and outer shell electrons, and increased shielding.

2. (a) Pass steam over heated magnesium
   $Mg(s) + H_2O(g) \rightarrow MgO(s) + H_2(g)$

   .

   (b) Add barium to cold water in a large trough
   $Ba(s) + 2H_2O(l) \rightarrow Ba(OH)_2(aq) + H_2(g)$

   (c) Reaction with Ba is easier / more rapid / occurs at a lower temperature. Ba is a stronger reducing agent than Mg / the standard electrode potential of Ba is of greater magnitude

   Reaction with Mg gives the oxide / reaction with Ba gives the hydroxide. At the high temperature needed for Mg to react, $Mg(OH)_2$ decomposes into MgO (1)

3. (a) Increases
   (b) $2Ca(NO_3)_2 \rightarrow 2CaO + 4NO_2 + O_2$

4. hydroxides become more soluble down the group; sulphates become less soluble down the group

5. (a) (i) $Cl (aq) + H_2O(l) \rightleftharpoons HCl(aq) + HOCl(aq)$

   (ii) A dynamic equilibrium exists / reaction does not proceed to completion. So free chlorine is present, which is yellow-green and very volatile (½)

   (iii) The odour of chlorine increases. By Le Chatelier's principle the system responds to counteract the increased [H+] by shifting the position of equilibrium to the left hand side

   (b) $2F_2(aq) + 2H_2O(l) \rightarrow 4HF(aq) + O_2(g)$

   (c) Chlorine with water: Disproportionation
   Fluorine with water: Redox / oxidation-reduction

   (d) Fluorine is a more powerful oxidising agent than chlorine (1)

6. (a) $MgCO_3(s) \rightarrow MgO(s) + CO_2(g)$

   (b) Bubble through limewater - the limewater goes cloudy

   (c) Higher

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