RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Lecture Notes 22 – The Periodic Table (II)

A Content

The similarities and trends in the physical and chemical properties of Group 2 and Group 17 elements, and their compounds.

B Learning outcomes

For elements in Group 2 (magnesium to barium) and Group 17 (chlorine to iodine), candidates should be able to:

(a) recognise variation in the electronic configurations down a Group

(b) describe and explain qualitatively the general trends and variations in atomic radius, ionic radius, first ionisation energy and electronegativity down a Group in terms of increasing number of electronic shells, shielding and nuclear charge

(c) describe and explain the trend in volatility of the Group 17 elements in terms of instantaneous dipole-induced dipole attraction

(d) describe and deduce from $E^\ominus$ values the relative reactivity of elements of:
  (i) Group 2 as reducing agents
  (ii) Group 17 as oxidising agents

(e) describe and explain the trend in thermal stability of:
  (i) Group 2 carbonates in terms of the charge density of the cation and the polarisability of the large anion
  (ii) Group 17 hydrides in terms of bond energies

(f) predict the characteristic properties of an element in a given Group by using knowledge of chemical periodicity

(g) deduce the nature, possible position in the Periodic Table, and identity of unknown elements from given information of physical and chemical properties

C Lecture Outline

Group 2

1 Introduction
2 Physical Properties
3 Chemical Properties
4 Thermal Stability of Group 2 Carbonates

Group 17

1 Introduction
2 Physical Properties
3 Chemical Properties
4 Physical Properties of Hydrogen Halides
5 Applications in Experimental Chemistry

D References

1 Chemistry in Context by Graham Hill and John Holman
2 Chemistry in Action by Michael Freemantle
3 Chemistry by Raymond Chang
4 Concise Inorganic Chemistry by J. D. Lee
5 Understanding Advanced Physical Inorganic Chemistry by J. Tan and K.S. Chan
6 A-Level Chemistry by Ramsden
7 Chemistry – The Molecular Nature of Matter and Change by Silberberg
8 Website: www.chemguide.co.uk

Group 2

1 INTRODUCTION

- The Group 2 elements are: Be, Mg, Ca, Sr, Ba and Ra.
- They are commonly called **alkaline earth metals.** This is because their **oxides** give **basic (alkaline) solutions** and **melt** at such **high temperatures** that they remained as solids ("earths") in the alchemists' fires.
- Other general characteristics of Group 2 elements:
  - ➲ They have higher melting points than the corresponding Group 1 elements (alkali metals) but lower melting points than the transition elements
  - ➲ They are very reactive and are powerful reducing agents
  - ➲ They are able to reduce water to hydrogen (except Be)

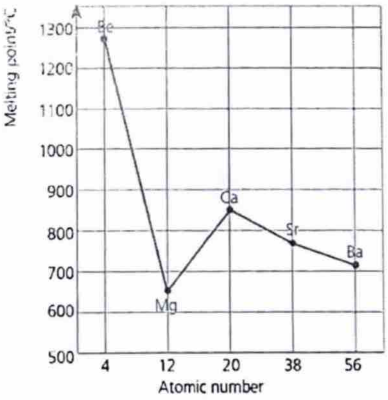
Group 2

2 PHYSICAL PROPERTIES

2.1 Summary of physical properties

Group 2 Element	**beryllium**	**magnesium**	**calcium**	**strontium**	**barium**
symbol	Be	Mg	Ca	Sr	Ba
atomic number	4	12	20	38	56
electronic configuration	$[He]2s^2$	$[Ne]3s^2$	$[Ar]4s^2$	$[Kr]5s^2$	$[Xe]6s^2$
atomic radius, M / nm	0.112	0.160	0.197	0.215	0.217
ionic radius, M^{2+} / nm	0.031	0.065	0.099	0.113	0.135
1st ionisation energy / kJ mol^{-1}	900	736	590	548	502
2nd ionisation energy / kJ mol^{-1}	1760	1450	1150	1060	966
3rd ionisation energy / kJ mol^{-1}	14800	7740	4940	4120	3390
principal oxidation state	+2	+2	+2	+2	+2
Electronegativity	more electronegative → less electronegative				
melting point / °C	1278	649	839	769	725
boiling point / °C	2770	1107	1484	1384	1643
density / g cm^{-3}	1.85	1.74	1.55	2.6	3.5

- The trends of some physical properties of the Group 2 elements are explained in the table below. *(also refer to lecture notes on Atomic Structure)*

	Physical Property	**Trend down Group 2**	**Explanation / Remarks**
1	atomic radius & ionic radius	increases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **increase** in the size of the electron cloud. Hence atomic and ionic radii increase down a group.
2	first ionisation energy	decreases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in a **decrease** in the energy required to remove the valence electron from an atom. Hence first ionisation decreases.
3	electronegativity	decreases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the bonding electrons **decreases**. Hence electronegativity decreases.
4	melting point	no clear trend	• The metals adopt different crystal structures. • The type of structure and packing of the metal lattice affects the melting point of the metal.  Hence melting points do not vary regularly

3 CHEMICAL PROPERTIES

3.1 Reactivity of Group 2 elements

- The reactivity of Group 2 elements **increases** down the group. Why is this so?

> This is because the ease of Group 2 elements losing electrons increases down the group.

(a) Ease of losing electrons based on ionisation energies

- When a Group 2 element participates in a reaction, it acts as a reducing agent and undergoes oxidation, with each atom losing 2 valence electrons to form a M^{2+} ion (+2 oxidation state).

Example: Reaction with oxygen	$Mg(s) + \frac{1}{2}O_2(g) \longrightarrow MgO(s)$ $Ca(s) + \frac{1}{2}O_2(g) \longrightarrow CaO(s)$ $Sr(s) + \frac{1}{2}O_2(g) \longrightarrow SrO(s)$ $Ba(s) + \frac{1}{2}O_2(g) \longrightarrow BaO(s)$

- The reactivity of Group 2 elements increases down the group essentially because the sum of the first and second ionisation energies of the Group 2 elements decreases down the group, resulting in increasing ease of losing the 2 valence electrons down the group.

Element	**1st I.E. / kJ mol^{-1}** $M(g) \rightarrow M^+(g) + e^-$	**2nd I.E. / kJ mol^{-1}** $M^+(g) \rightarrow M^{2+}(g) + e^-$	**Sum of 1st and 2nd I.E. / kJ mol^{-1}** $M(g) \rightarrow M^{2+}(g) + 2e^-$
Be	900	1760	2660
Mg	736	1450	2186
Ca	590	1150	1740
Sr	548	1060	1608
Ba	502	966	1468

Down a group,
- the **number of electronic shells increases**
- distance between the nucleus and the valence electrons **increases**
- shielding experienced by valence electrons **increases**

Despite the increasing nuclear charge,
- electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in a **decrease** in the energy required to remove a valence electron.

Hence,
- ionisation energy decreases
- **sum of 1st and 2nd ionisation energies decreases**
- ease of atoms losing valence electrons to form cations (M^{2+}) increases

hence reactivity of Group 2 element increases

(Since metals lose electrons (oxidation) when they react to form compounds and it is ***easier*** *to lose electrons down Group 2, reactivity of the metals* ***increases*** *down Group 2.)*

(b) Relation between ease of losing electrons and standard electrode potential ($E^\ominus$) values

- The reactions of Group 2 elements involve them undergoing oxidation to the +2 oxidation state.
- By undergoing oxidation, the Group 2 elements also act as reducing agents.

Example: Reaction with dilute hydrochloric acid	$M(s) + 2HCl(aq) \longrightarrow MCl_2(aq) + H_2(g)$ where M = Mg, Ca, Sr or Ba

Recall:
- A reducing agent is oxidised in a redox reaction. The **more likely** the Group 2 element is **oxidised**, the **stronger its reducing power**.

- The **reducing power (and hence reactivity)** of the Group 2 elements increases down the group. This is reflected by the $E^\ominus$ value being **more negative** down the group.

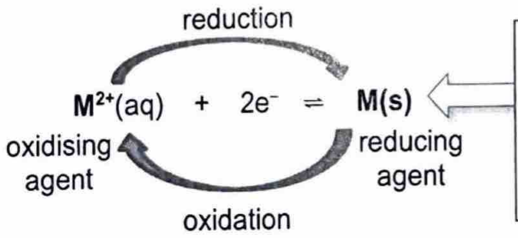
Recall Standard Electrode Potential, $E^\ominus$?
(refer to Electrochemistry lecture notes)

- The standard electrode potential, $E^\ominus$, is a measure of the tendency of reduction (i.e. gaining electrons) occurring.

  The more positive the value of $E^\ominus$, the more *likely* reduction is to occur.

- $E^\ominus$ values also give an indication of the position of equilibrium of a reaction.
  A more positive $E^\ominus$ value indicates that the position of equilibrium lies to the right.
  A more negative $E^\ominus$ value indicates that the position of equilibrium lies to the left.

A more positive $E^\ominus$ value means:	A more negative the $E^\ominus$ value means:
⇒ the forward reaction is more favoured,	⇒ the backward reaction is more favoured,
⇒ the more likely reduction occurs,	⇒ the more likely oxidation occurs,
⇒ the higher the tendency to gain e⁻,	⇒ the higher the tendency to lose e⁻,
⇒ the stronger the oxidising agent.	⇒ the stronger the reducing agent.



- Group 2 elements undergo oxidation and act as reducing agents in redox reactions.
- Hence, when comparing the reducing power of Group 2 elements, we need to compare how favoured the backward reaction is.

Reduction half-equations (M^{2+}/M)	
$Be^{2+}(aq) + 2e^- \rightleftharpoons$ **Be(s)**	$E^\ominus = -1.85$ V
$Mg^{2+}(aq) + 2e^- \rightleftharpoons$ **Mg(s)**	$E^\ominus = -2.38$ V
$Ca^{2+}(aq) + 2e^- \rightleftharpoons$ **Ca(s)**	$E^\ominus = -2.87$ V
$Sr^{2+}(aq) + 2e^- \rightleftharpoons$ **Sr(s)**	$E^\ominus = -2.89$ V
$Ba^{2+}(aq) + 2e^- \rightleftharpoons$ **Ba(s)**	$E^\ominus = -2.90$ V

Down the group,
- $E^\ominus$ value becomes more negative
- tendency of backward reaction occurring increases
- tendency of **metal** losing electrons increases
- **reducing power of metal increases**
- **reactivity of the metal increases**

4.1 Thermal decomposition of Group 2 carbonates

- Group 2 carbonates undergo thermal decomposition to give the metal oxide and carbon dioxide gas.

$$MCO_3(s) \xrightarrow{\text{heat}} MO(s) + CO_2(g)$$

4.2 Driving force for the thermal decomposition reaction

- Consider the thermal decomposition of calcium carbonate. Why does the reaction occur?

$\Delta H_{decomposition} > 0$	$\Delta S_{decomposition} > 0$
• For more details, refer to http://www.chemguide.co.uk/inorganic/group2/thermstab.html	• CO_2 gas is produced in the reaction, resulting in the products being more disordered than the reactants.

$$\Delta G = \Delta H - T\Delta S$$

- Since $\Delta H_{decomposition} > 0$ and $-T\Delta S_{decomposition} < 0$, $\Delta G < 0$ only at large values of T.
- At high T, the negative $-T\Delta S$ outweighs the positive ΔH, and hence $\Delta G < 0$
- The thermal decomposition reaction is said to be entropy-driven.

4.3 Trend in the thermal decomposition of Group 2 carbonates

Polarising power of cation

- refers to the ability of the cation to distort the electron cloud of an anion.
- dependent on the **charge density** of the cation. The greater the charge density of the cation, the stronger is its polarising power.

polarising power $\propto$ charge density

$$\left(\text{charge density} \propto \frac{\text{charge}}{\text{ionic radius}}\right)$$

- A small and highly charged cation has strong polarising power.

Ion	Radius / nm
Be^{2+}	0.031
Mg^{2+}	0.065
Ca^{2+}	0.099
Sr^{2+}	0.113
Ba^{2+}	0.135

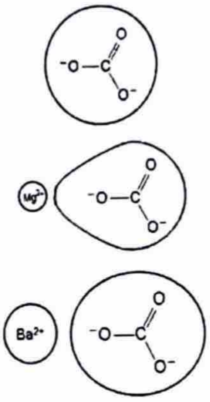
Down Group 2,

- cationic radius increases
- charge density decreases
- **polarising power decreases**
- ability of cation to distort the electron cloud of the anion decreases

Polarisability of anion

- the ease with which its electron cloud gets distorted.
- A large and highly charged anion has high polarisability since its electron cloud is more easily distorted.

- **Polarisation** is the distortion of the electron cloud of an anion by a cation.



Down the group,

- **decomposition temperatures** increase
- increasingly more difficult to decompose the carbonate
- **thermal stability <u>increases</u>**

(i.e. thermal stability of $MgCO_3 < CaCO_3 < SrCO_3 < BaCO_3$)

	Thermal decomposition temperatures /°C
$MgCO_3$	400
$CaCO_3$	900
$SrCO_3$	1280
$BaCO_3$	1360

Trend	**Thermal stability <u>increases</u> down the group**	
Why?	Down the group, • Cationic radius increases, resulting in a lower charge density and weaker polarising power of the cations. • Consequently, there is decreasing extent of distortion of the electron cloud of the CO_3^{2-} anion and hence decreasing extent of weakening of covalent bonds within the CO_3^{2-} anion. • More heat energy is required to break the covalent bonds within the CO_3^{2-} anion, causing the decomposition temperature to increase. Hence, thermal stability of the Group 2 carbonates increases.	**<u>Key Points:</u>** ✓ larger ionic radius of cation ✓ lower charge density ✓ weaker polarising power ✓ smaller distortion of the electron cloud of the CO_3^{2-} anion ✓ decreasing extent of weakening of the covalent bonds within the CO_3^{2-} anion ✓ more heat required for decomposition ✓ higher decomposition temperature

Group 17

1 INTRODUCTION

- The elements in Group 17 (F, C*l*, Br, I and At) are known as **halogens.**
- Halogens are salt producers. In Greek, *hals* means 'salt' and *gen* means 'producing'.
- Halogens exist as **diatomic molecules, X_2** (i.e. F_2, Cl_2, Br_2 and I_2), which are **non-polar** and have **simple molecular structures.**

Group 17

2 PHYSICAL PROPERTIES

2.1 Summary of Physical Properties

Group 17 Element	Fluorine	Chlorine	Bromine	Iodine
Atomic number	9	17	35	53
Stable isotopes	^{19}F	^{35}Cl, ^{37}Cl	^{79}Br, ^{81}Br	^{127}I
Electronic configuration	$[He]2s^{2}2p^{5}$	$[Ne]3s^{2}3p^{5}$	$[Ar]3d^{10}4s^{2}4p^{5}$	$[Kr]4d^{10}5s^{2}5p^{5}$
Atomic radii / nm	0.072	0.099	0.114	0.133
Ionic radii	0.136	0.181	0.195	0.216
1st Ionisation energy/ kJ mol^{-1}	1680	1260	1140	1010
Electronegativity	most electronegative ⟶ least electronegative			
Bond length / nm	0.143	0.199	0.228	0.266
Bond dissociation energy/ kJ mol^{-1}	+158	+244	+193	+151
Type of bonding and structure	covalent bonding within the molecules; simple molecular structure (non-polar diatomic molecules) with instantaneous dipole–induced dipole interactions			
Melting point / °C	–220	–101	–7	114 (sublimes)
Boiling point / °C	–188	–35	59	183
Physical state and colour at rtp	pale yellow gas	greenish yellow gas	reddish brown liquid	black solid
Colour in aqueous solution		pale yellow	orange	brown
Colour in hexane		pale yellow	orange-red	purple

(can be found in *Data Booklet*, section 9(b) – Colour of halogens)

- The trends of some physical properties of the Group 17 elements are explained in the table below. *(also refer to lecture notes on Atomic Structure)*

	Physical Property	**Trend down Group 17**	**Explanation / Remarks**
1	atomic radius & ionic radius	increases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in an **increase** in the size of the electron cloud. Hence atomic and ionic radii increase down a group.
2	first ionisation energy	decreases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the valence electrons **increases** • shielding experienced by valence electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the valence electrons **decreases**, resulting in a **decrease** in the energy required to remove a valence electron. Hence first ionisation decreases.
3	electronegativity	decreases	Down the group, • the **number of electronic shells increases**, • distance between the nucleus and the bonding electrons **increases**, • shielding experienced by bonding electrons **increases** Despite the increasing nuclear charge, • electrostatic attraction between the nucleus and the bonding electrons **decreases**. Hence electronegativity decreases.
4	bond dissociation energy	decreases **(Exception: F_2)**	Down the group, • there is **less effective orbital overlap** between the bonding orbitals (as atomic size increases and valence orbitals become more diffuse) hence, the halogen–halogen bond becomes **weaker** when moving down Group 17 from C*l* to I. **Note:** The F–F bond is **not as strong as expected**. Due to the **small atomic size** of the fluorine atom, there is great **repulsion** between the lone pairs of electrons on the two fluorine atoms in each F_2 molecule, hence weakening the F–F bond.
5	volatility	decreases	Down the group, • the number of electrons per molecule **increases** / size of electron cloud **increases** • electron cloud becomes **more easily distorted / polarisable** • instantaneous dipole-induced dipole interactions become **stronger** • **more energy is required** to break the intermolecular forces of attraction hence, boiling point increases in the order: $F_2 < Cl_2 < Br_2 < I_2$ volatility decreases in the order: $F_2 > Cl_2 > Br_2 > I_2$

3 CHEMICAL PROPERTIES

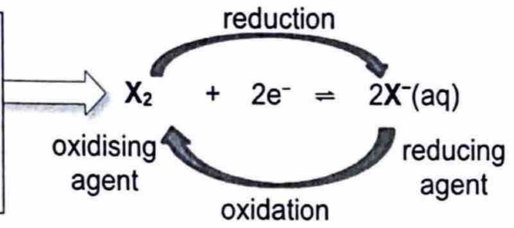
3.1 Relative Oxidising Power and Standard Electrode Potentials ($E^\ominus$)

The halogens are so reactive that they are rarely found in their elemental states in nature. Their **reactivity is linked to their oxidising power**, which depends partly on their bond dissociation energies and electron affinities.

Recall:

- An oxidising agent is reduced in a redox reaction. The **more likely** a halogen is **reduced**, the **stronger its oxidising power**.
- A **more positive** $E^\ominus$ value suggests that the forward reaction is favoured, and the **position of equilibrium lies to the right**. *(refer to section 3.1(b), pg 5)*

- Halogens undergo <u>reduction</u> and act as <u>oxidising agents</u> in redox reactions.
- Hence, when comparing the oxidising power of halogens, we need to compare how favoured is the <u>forward</u> reaction.



Reduction half-equations (X_2/X^-)		Down the group,
F_2(g) + $2e^- \rightleftharpoons 2F^-$(aq)	$E^\ominus = +2.87$ V	• $E^\ominus$ value becomes less positive • tendency of forward reaction occurring decreases • tendency of **halogen** gaining electrons decreases • **oxidising power of halogen <u>decreases</u>** • **reactivity of the halogens <u>decreases</u>**
Cl_2(g) + $2e^- \rightleftharpoons 2Cl^-$(aq)	$E^\ominus = +1.36$ V	
Br_2(l) + $2e^- \rightleftharpoons 2Br^-$(aq)	$E^\ominus = +1.07$ V	
I_2(s) + $2e^- \rightleftharpoons 2I^-$(aq)	$E^\ominus = +0.54$ V	

3.2 Reactions of Halogens as Oxidising Agents

- The halogens generally undergo similar reactions, although under varying conditions, as these depend on their oxidising strengths.

- The decrease in oxidising power of halogens down the Group can be observed in their
  (a) displacement reactions
  (b) reaction with thiosulfate
  (c) reaction with iron

- For these redox reactions, we will be using the sign of standard cell potential, $E^\ominus_{cell}$, to predict the spontaneity of the reaction.

Relationship between $\Delta G^\ominus$; $E^\ominus_{cell}$ and spontaneity

$\Delta G^\ominus$	$E^\ominus_{cell}$	Spontaneity
< 0	> 0	reaction is thermodynamically feasible and spontaneous
$= 0$	$= 0$	reaction is at equilibrium
> 0	< 0	reaction is not thermodynamically feasible and not spontaneous

(recall from Electrochemistry lectures notes for $E^\ominus_{cell}$ calculations)

a) Displacement reactions

- A **more reactive/oxidising** halogen **displaces** a **less reactive/oxidising** halogen from its compound.
- Each halide ion can be **oxidised** by the halogen **above** it in the group.

	Halide		
Halogen	**Chloride, Cl^-**	**Bromide, Br^-**	**Iodide, I^-**
Chlorine, Cl_2		Chlorine **can displace** bromine from aq solution of bromide $Cl_2 + 2Br^- \longrightarrow Br_2 + 2Cl^-$ ($E^{\ominus}_{cell} = +0.29V$) **Observations:** Orange solution of $Br_2(aq)$ is formed.	Chlorine **can displace** iodine from aq solution of iodide $Cl_2 + 2I^- \longrightarrow I_2 + 2Cl^-$ ($E^{\ominus}_{cell} = +0.82$ V) **Observations:** Brown solution of $I_2(aq)$ is formed.
Bromine, Br_2	**No reaction** ($E^{\ominus}_{cell} = -0.29V$)		Bromine **can displace** iodine from aq. solution of iodide $Br_2 + 2I^- \longrightarrow I_2 + 2Br^-$ ($E^{\ominus}_{cell} = +0.53$ V) **Observations:** Brown solution of $I_2(aq)$ is formed.
Iodine, I_2	**No reaction** ($E^{\ominus}_{cell} = -0.82$ V)	**No reaction** ($E^{\ominus}_{cell} = -0.53V$)	

Application of Displacement Reactions

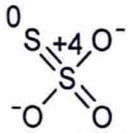
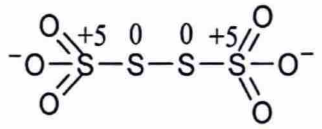
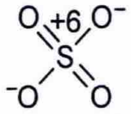
Aqueous Cl_2 can be used to **detect the presence of Br^- and I^-** in solution.

Test	Step 1: Add $Cl_2(aq)$ to the unknown solution and shake. Step 2: Add organic solvent (e.g. hexane, CCl_4) and shake.
Observations	If an **orange aq. layer** and an **orange–red organic layer** are formed ⇒ Br_2 is formed via displacement reaction ⇒ shows that **Br^-** is present in the unknown sample If a **brown aq. layer** and a **purple organic layer** are formed ⇒ I_2 is formed via displacement reaction ⇒ shows I^- is present in the unknown sample

b) Reactions with Thiosulfate

The reactions of chlorine and iodine with aqueous sodium thiosulfate ($S_2O_3^{2-}$) reflect that **Cl_2 is a stronger oxidising agent than I_2.**

Halogen	Reaction of thiosulfate with halogen
Chlorine	$S_2O_3^{2-}(aq) + 4Cl_2(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 8Cl^-(aq) + 10H^+(aq)$ The **average oxidation state of S** increases from **+2 to +6**. *(The central S atom in $S_2O_3^{2-}$ increases in oxidation state from +4 to +6 in SO_4^{2-} ;* *the other S atom in $S_2O_3^{2-}$ increases in oxidation state from 0 to +6 in SO_4^{2-})*
Bromine	$S_2O_3^{2-}(aq) + 4Br_2(aq) + 5H_2O(l) \longrightarrow 2SO_4^{2-}(aq) + 8Br^-(aq) + 10H^+(aq)$ The **average oxidation state of S** increases from **+2 to +6**. *(The central S atom in $S_2O_3^{2-}$ increases in oxidation state from +4 to +6 in SO_4^{2-} ;* *the other S atom in $S_2O_3^{2-}$ increases in oxidation state from 0 to +6 in SO_4^{2-})*
Iodine	$2S_2O_3^{2-}(aq) + I_2(aq) \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$ The **average oxidation state of S** increases from **+2 to +2.5**. *(Only the central S atom in $S_2O_3^{2-}$ increases in oxidation state from +4 to +5 in $S_4O_6^{2-}$)*

Species	**$S_2O_3^{2-}$**	**$S_4O_6^{2-}$**	**SO_4^{2-}**
Structure			
Oxidation state(s) of sulfur	0, +4 (average oxidation state: +2)	0, +5 (average oxidation state: +2.5)	+6

c) Reactions with Iron

The extent of oxidation of iron in the reactions between the iron and the halogens shows that **Cl_2** and **Br_2** are **stronger oxidising agents than I_2**.

As seen from the tables below,

- both **Cl_2** and **Br_2** are able to oxidise Fe to Fe^{3+} (i.e. from Fe to Fe^{2+}, and then from Fe^{2+} to Fe^{3+}).
- **I_2**, being a weaker oxidizing agent, can only oxidize Fe to Fe^{2+}.

Fe with Cl_2	Fe with Br_2	Fe with I_2
$Cl_2 + Fe \longrightarrow 2Cl^- + Fe^{2+}$ $E^\ominus_{cell} = +1.80\text{ V} > 0$ Hence, reaction of Fe with Cl_2 to form Fe^{2+} and Cl^- is spontaneous.	$Br_2 + Fe \longrightarrow 2Br^- + Fe^{2+}$ $E^\ominus_{cell} = +1.51\text{ V} > 0$ Hence, reaction of Fe with Br_2 to form Fe^{2+} and Br^- is spontaneous.	$I_2 + Fe \longrightarrow 2I^- + Fe^{2+}$ $E^\ominus_{cell} = +0.98\text{ V} > 0$ Hence, reaction of Fe with I_2 to form Fe^{2+} and I^- is spontaneous.

Fe^{2+} with Cl_2	Fe^{2+} with Br_2	Fe^{2+} with I_2
$Cl_2 + Fe^{2+} \longrightarrow 2Cl^- + Fe^{3+}$ $E^\ominus_{cell} = +0.59\text{ V} > 0$ Hence, reaction of Fe^{2+} with Cl_2 to form Fe^{3+} and Cl^- is spontaneous. $FeCl_3$ is formed.	$Br_2 + Fe^{2+} \longrightarrow 2Br^- + Fe^{3+}$ $E^\ominus_{cell} = +0.30\text{ V} > 0$ Hence, reaction of Fe^{2+} with Br_2 to form Fe^{3+} and Br^- is spontaneous. $FeBr_3$ is formed.	$I_2 + Fe^{2+} \longrightarrow 2I^- + Fe^{3+}$ $E^\ominus_{cell} = -0.23\text{ V} < 0$ Hence, reaction of Fe^{2+} with I_2 to form Fe^{3+} and I^- is **not** spontaneous. FeI_2 is formed.

4.1 Thermal Stability of Hydrogen Halides

Hydrogen Halide	Bond dissociation energy / kJ mol^{-1}	Decomposition Reaction	Comment
HF	+562	–	stable to heat; does not decompose
HC*l*	+431	–	stable to heat; does not decompose
HBr	+366	$2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$	decomposes slightly when heated; reddish brown vapour of Br_2 observed
HI	+299	$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$	decomposes readily when heated; purple fumes of I_2 formed

Trend

Thermal stability **decreases** in the order: **HF > HC*l* > HBr > HI**

Explanation

- Thermal stability of the hydrogen halides (HX) is related to the **H–X bond strength**.
- **More endothermic** bond dissociation energy suggests that the **H–X bond is stronger** and that HX is **more thermally stable.**
- Since **bond dissociation energy** of H–X bond decreases in the order:

  H–F > H–C*l* > H–Br > H–I

  thermal stability thus decreases in the order:

  H–F > H–C*l* > H–Br > H–I

Why does H–X bond strength decrease down Group 17?

Down Group 17,

- there is **less effective orbital overlap** between the 1s orbital of hydrogen and the valence p orbital of the halogen (as the size of the halogens gets bigger and the valence orbital used for bonding is more diffuse).
- also, electronegativity difference between hydrogen and the halogen decrease, resulting in a **decrease in bond polarity**.
- hence, H–X bond strength decreases

5 APPLICATIONS IN EXPERIMENTAL CHEMISTRY

5.1 Solubility of iodine in KI

Iodine becomes **more soluble in water** when aqueous **potassium iodide** is added.

$$I_2(s) \rightleftharpoons I_2(aq) \text{ ------- } (1)$$

$$I_2(aq) + I^-(aq) \rightleftharpoons I_3^-(aq) \text{ -------}(2)$$

- Upon addition of I^-, the formation of the **soluble brown triiodide complex ion, I_3^-**, causes **$[I_2(aq)]$ to decrease**.
- By Le Chatelier's principle, the position of equilibrium **(1)** will shift to the **right**, causing iodine to be **more soluble** in water.

Note:
I_3^- is soluble in water due to the favourable **ion-dipole interactions** between I_3^- and water molecules.

5.2 Reactions of Halide ions with Ag^+ followed by aqueous NH_3

- The reaction between halides and $AgNO_3(aq)$ forms the basis of **qualitative analysis** of halides (Cl^-, Br^- and I^-).
- To identify the halide ion:
  - ① React the halide with $AgNO_3(aq) \Rightarrow$ silver halide ppt will be formed.
  - ② Examine the **colour** of the silver halide ppt AND its **solubility in NH_3** (dilute or concentrated).

Note:
Testing of the solubility of the silver halide ppt in NH_3 (dilute or concentrated) is required as the silver halide ppt may sometimes appear to be similar in colour.

	$Cl^-(aq)$	$Br^-(aq)$	$I^-(aq)$
Step 1 Add $AgNO_3(aq)$	white ppt of $AgCl$	pale cream ppt of $AgBr$	yellow ppt of AgI
Step 2 Add excess $NH_3(aq)$	ppt soluble	ppt partially soluble	ppt insoluble
Add conc. NH_3	ppt soluble	ppt soluble	ppt insoluble
Effect of sunlight on AgX	AgX undergoes decomposition to form Ag and X_2.		

(recall difference in solubility of AgX in $NH_3(aq)$ from Solubility Equilibria lecture notes)

RAFFLES INSTITUTION
YEAR 6 H2 CHEMISTRY 2023
Tutorial 22 – The Periodic Table (II)

Self-Check Questions

Group 2

1 **(a)** Magnesium carbonate and barium carbonate decompose similarly on heating. Write a balanced equation for the decomposition of magnesium carbonate.

(b) There is a noticeable difference in the temperature for decomposition of these two carbonates. Which of these carbonates decomposes at a lower temperature? Explain your answer.

(c) Explain the relative numerical values of the lattice energies of magnesium carbonate and barium carbonate.

2 **(a)** A 4.50 g sample of a carbonate of a Group 2 metal (known to be either calcium or strontium) lost 1.34 g in mass when heated strongly.

Identify the metal, showing clearly your working.

(b) The mineral dolomite is a double carbonate of magnesium and calcium, with the formula $CaMg(CO_3)_2$. When 1.000 g of an impure sample of dolomite was completely dissolved in an excess of hydrochloric acid, 0.450 g of carbon dioxide was given off.

Write a balanced equation for the reaction and calculate the purity of the dolomite.

(c) Calcium sulfate occurs naturally as the dihydrate gypsum, $CaSO_4.2H_2O$. When heated to 160 °C, gypsum loses some of its water to give plaster of Paris, which is used for making fine plaster casts and for setting broken limbs. During the heating process, 100 g of gypsum loses 15.7 g of water.

Determine the formula of plaster of Paris.

(d) The calcium salt **E** has the formula CaC_xO_y. When 1.00 g of **E** was heated strongly, 374 cm^3 of a mixture of two gases (measured at r.t.p.) was produced, and 0.438 g of a white solid remained. The addition of an excess of NaOH(aq) to the gaseous mixture caused its volume to decrease by 187 cm^3.

(i) Calculate the average M_r of the gaseous mixture.

(ii) Suggest the identity of the gas that reacted with NaOH(aq).

(iii) Hence calculate the M_r of the other gas in the gaseous mixture and suggest its identity.

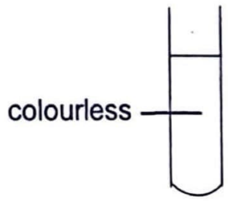
(iv) Suggest the formula of **E** and write a balanced equation for its thermal decomposition.

Group 17

3 State the physical states of chlorine, bromine and iodine at room temperature, and explain the observed trend in their volatilities.

4 Aqueous chlorine is added to aqueous sodium bromide and the mixture is shaken with an equal volume of 1,1,1–trichloroethane. Which observation would be made?

A



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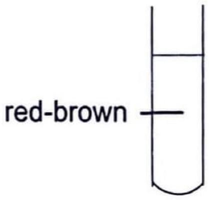

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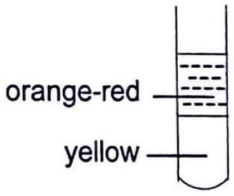

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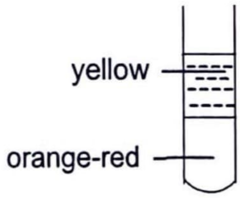


5 Astatine, the element below iodine in Group 17, is produced in trace amounts only. Using your knowledge of the halogens, predict what you might observe in the following experiments. Write balanced equations, with state symbols, for the reactions which occur.

(a) Aqueous bromine is added into aqueous sodium astatide.

(b) Aqueous silver nitrate is added into aqueous sodium astatide, followed by excess aqueous ammonia.

6 A mixture of iodine and chlorine was reacted with excess sodium thiosulfate solution. The resulting mixture was then treated with excess aqueous barium nitrate. Precipitate **T** formed was filtered off and washed with distilled water. The filtrate was treated with excess aqueous silver nitrate. The precipitate formed was filtered off and washed with excess aqueous ammonia. The mixture was once again filtered leaving behind precipitate **U**.

Which anion was present in each of the precipitates respectively?

	Precipitate **T**	Precipitate **U**
A	Cl^-	I^-
B	I^-	SO_4^{2-}
C	SO_4^{2-}	I^-
D	SO_4^{2-}	Cl^-

7 If an organic halogeno-compound is heated with sodium, any halogen present in the compound is converted into the corresponding sodium halide.

$CH_2ClCHICO_2H$ is heated with sodium and the resultant residue dissolved in dilute nitric acid. Aqueous silver nitrate is then added to the mixture and finally concentrated ammonia is added dropwise, until present in excess.

Which observation is made when the ammonia is added?

A All the precipitate dissolves.
B All the precipitate remains.
C The precipitate appears less yellow.
D The precipitate appears more yellow.

Practice Questions

Group 2

8 Zinc carbonate and magnesium carbonate decompose when heated to give similar products.

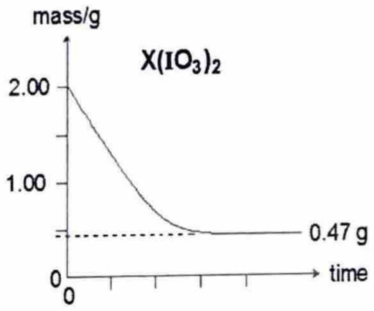
(a) Suggest an equation for the thermal decomposition of zinc carbonate.

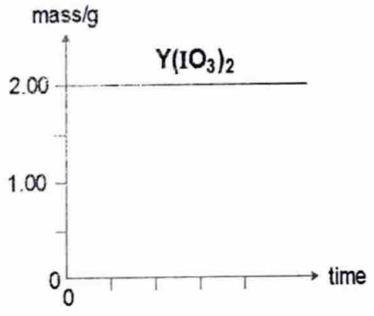
(b) The radius of Zn^{2+} cation is 0.074 nm. Use the *Data Booklet* to deduce whether zinc carbonate will decompose at a higher or lower temperature than magnesium carbonate. Explain your answer.

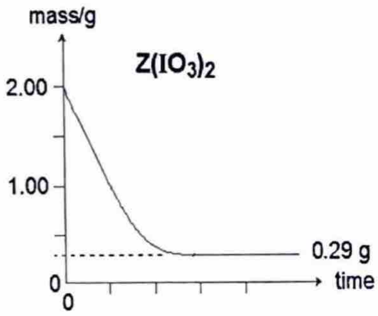
9 **X**, **Y** and **Z** are Group 2 metals (Mg to Ba, not necessarily in that order). **X**$(IO_3)_2$, **Y**$(IO_3)_2$ and **Z**$(IO_3)_2$ are Group 2 iodates(V). Upon heating, each of these iodates(V) decomposes to yield a metal oxide, a purple gas and a colourless gas which relights a glowing splint.

(a) Write a balanced equation for the decomposition of $Mg(IO_3)_2$.

(b) The three graphs given below show the change in mass when 2.00 g each of **X**$(IO_3)_2$, **Y**$(IO_3)_2$ and **Z**$(IO_3)_2$ were heated separately at a temperature T °C.







With the aid of information from the graphs, identify the three iodates(V). Explain your answer.

10 **[RI 2015 Prelim P3 Q1c]**
When 2.0 g of calcium ethanoate, $Ca(CH_3CO_2)_2$, was heated to 450 °C, only propanone and a white solid, **M**, were produced.

(a) Write a balanced equation for the thermal decomposition of calcium ethanoate and state the identity of the white solid **M.** [1]

(b) On further heating, partial decomposition of solid **M** occurs to give off carbon dioxide and a white residue. The white residue contains 70% by mass of solid **M**.
Calculate the mass of carbon dioxide evolved from the partial decomposition.
[M_r of $Ca(CH_3CO_2)_2 = 158.1$; $CO_2 = 44.0$] [3]

(c) Predict whether barium ethanoate, $Ba(CH_3CO_2)_2$, decomposes at a higher or lower temperature than $Ca(CH_3CO_2)_2$. Explain your answer. [1]

Group 17

11 **[N13/3/1(a),(b)]**

(a) Use the *Data Booklet* to describe the relative reactivity of the halogens as oxidising agents, and relate this reactivity to relevant $E^\ominus$ values. [2]

(b) Some hydrogen halides are unstable to heat.

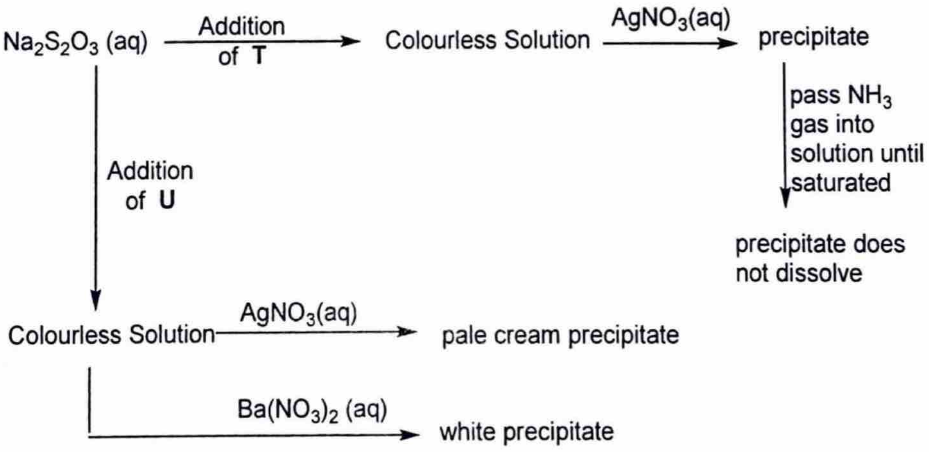
(i) Write an equation for the reaction undergone on heating a hydrogen halide.

(ii) Describe and explain how the thermal stabilities of the hydrogen halides vary down the Group. [3]

12 **[N2010/P1/17]**
Use of the Data Booklet is relevant to this question.
If iron is heated separately with chlorine, bromine and iodine, what are the likely products?

	chlorine	bromine	iodine
A	$FeCl_2$	$FeBr_2$	FeI_2
B	$FeCl_3$	$FeBr_2$	FeI_2
C	$FeCl_3$	$FeBr_3$	FeI_2
D	$FeCl_3$	$FeBr_3$	FeI_3

13 Consider the following reaction scheme undergone by sodium thiosulfate with halogens **T** and **U**.



(a) Suggest a suitable identity each for **T** and **U**.

(b) Use relevant data from the *Data Booklet* to explain the different reactions of halogens **T** and **U** with sodium thiosulfate.

14 Describe and explain what happens in each of the following experiments and write balanced equations for the reactions that occur.

(a) Chlorine is passed into aqueous iron(II) sulfate and aqueous sodium hydroxide is added to the resulting solution.

(b) Solid iodine is shaken with aqueous potassium iodide and aqueous sodium thiosulfate is then added.

(c) When aqueous silver nitrate is added to aqueous potassium chloride, a white precipitate is formed which dissolves in an excess of aqueous ammonia. The subsequent addition of aqueous sodium bromide causes the precipitation of a pale cream solid. The pale cream precipitate dissolves when aqueous sodium cyanide is added.