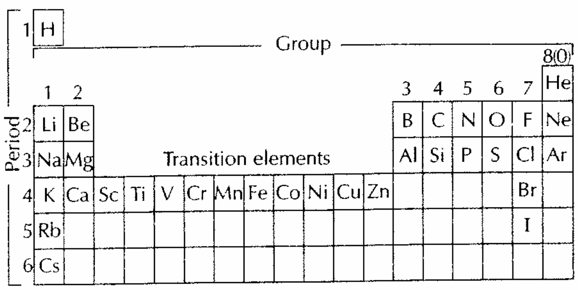
The Periodic Table and physical properties (1)

THE PERIODIC TABLE

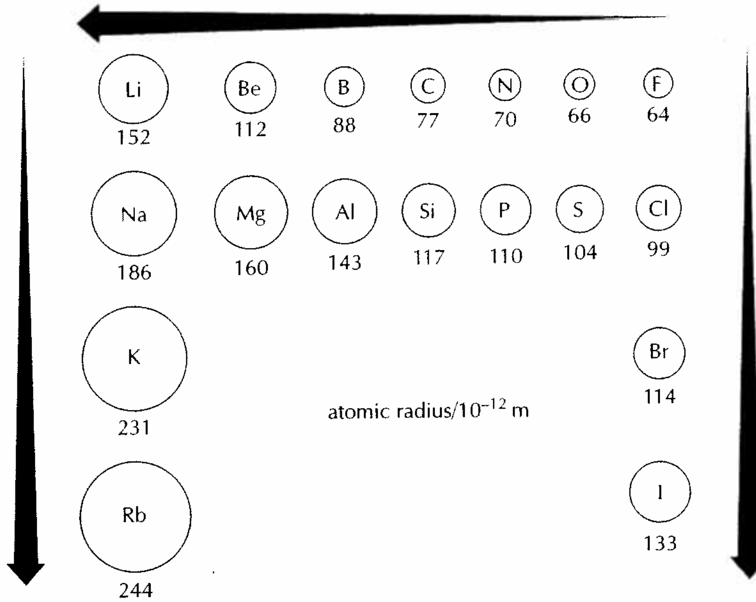


In the Periodic Table elements are placed in order of increasing atomic number. Elements with the same number of valence electrons are placed vertically in the same **group**. The groups are numbered from 1 to 8 (or 0). Some groups have their own name:

- Group 1 – alkali metals
- Group 7 – halogens
- Group 8 or 0 – noble gases (sometimes also called rare gases or inert gases).

Elements with the same outer shell of valence electrons are placed horizontally in the same **period**. The transition elements are located between groups 2 and 3.

ATOMIC RADIUS



The atomic radius is the distance from the nucleus to the outermost electron. Since the position of the outermost electron can never be known precisely, the atomic radius is usually defined as half the distance between the nuclei of two bonded atoms of the same element.

As a group is descended the outermost electron is in a higher energy level, which is further from the nucleus, so the radius increases.

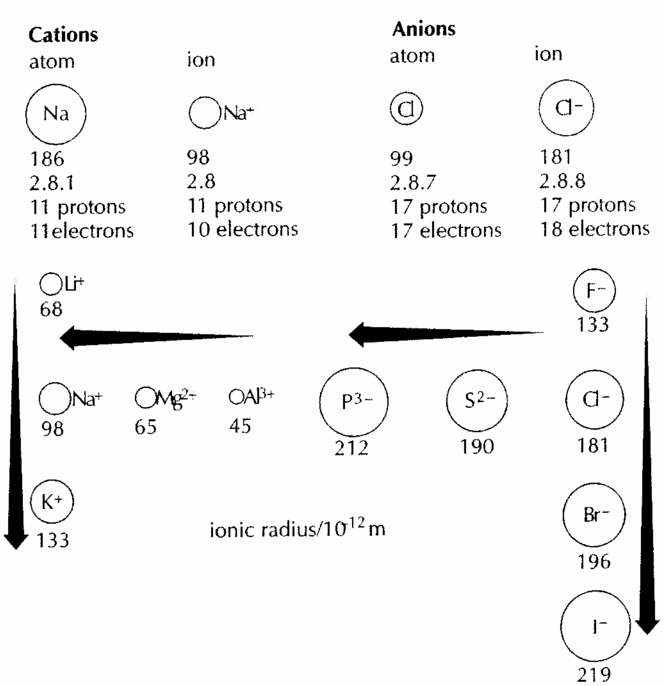
Across a period electrons are being added to the same energy level, but the number of protons in the nucleus increases. This attracts the energy level closer to the nucleus and the atomic radius decreases across a period.

IONIC RADIUS

It is important to distinguish between positive ions (**cations**) and negative ions (**anions**). Both cations and anions increase in size down a group as the outer level gets further from the nucleus.

Cations contain fewer electrons than protons so the electrostatic attraction between the nucleus and the outermost electron is greater and the ion is smaller than the parent atom. It is also smaller because the number of electron shells has decreased by one. Across the period the ions contain the same number of electrons (**isoelectronic**), but an increasing number of protons, so the ionic radius decreases.

Anions contain more electrons than protons so are larger than the parent atom. Across a period the size decreases because the number of electrons remains the same but the number of protons increases.



The Periodic Table and physical properties (2)

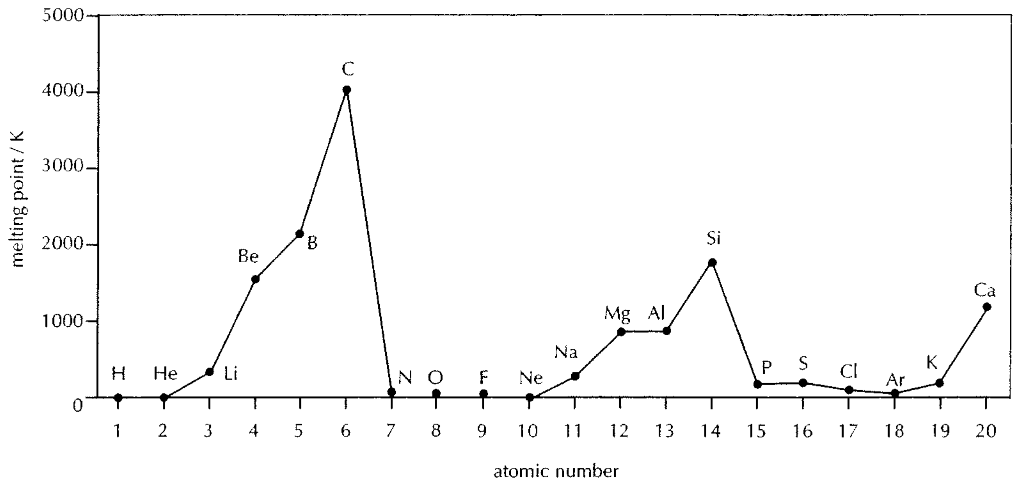
PERIODICITY

Elements in the same group tend to have similar chemical and physical properties. There is a change in chemical and physical properties across a period. The repeating pattern of physical and chemical properties shown by the different periods is known as **periodicity**.

These periodic trends can clearly be seen in atomic radii, ionic radii, ionization energies, electronegativities and melting points.

MELTING POINTS

Melting points depend both on the structure of the element and on the type of attractive forces holding the atoms together. Using period 3 as an example:



- At the left of the period elements exhibit metallic bonding (Na, Mg, Al), which increases in strength as the number of valence electrons increases.
- Silicon in the middle of the period has a macromolecular covalent structure with very strong bonds resulting in a very high melting point.
- Elements in groups 5, 6, and 7 (P_4, S_8, and Cl_2) show simple molecular structures with weak van der Waals' forces of attraction between the molecules.
- The noble gases (Ar) exist as **monatomic molecules** (single atoms) with extremely weak forces of attraction between the atoms.

Within groups there are also clear trends:

- In group 1 the melting point decreases down the group as the atoms become larger and the strength of the metallic bond decreases.

	Li	Na	K	Rb	Cs
M. pt / K	454	371	336	312	302

- In group 7 the van der Waals' attractive forces between the diatomic molecules increase down the group so the melting points increase.

	F_2	Cl_2	Br_2	I_2
M. pt / K	53	172	266	387

ELECTRONEGATIVITY

Electronegativity is a relative measure of the attraction that an atom has for a shared pair of electrons when it is covalently bonded to another atom. As the size of the atom decreases the electronegativity increases, so the value increases across a period and decreases down a Group. The three most electronegative elements are F, N, and O.

H 2.1						
Li 1.0	Be 1.5	B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
Na 0.9						Cl 3.0
K 0.8						Br 2.8
						I 2.5

FIRST IONIZATION ENERGY

The definition of first ionization energy has been given on page 9. The values decrease down each group as the outer electron is further from the nucleus and therefore less energy is required to remove it, e.g. for the group 1 elements, Li, Na and K.

Element:	Li	Na	K
Electron arrangement	2.1	2.8.1	2.8.8.1
First ionization energy (kJ mol^{-1})	519	494	418

Generally the values increase across a period. This is because the extra electrons are filling the same energy level and the extra protons in the nucleus attract this energy level closer making it harder to remove an electron, e.g. for the third period.

Element	Na	Mg	Al	Si	P	S	Cl	Ar
Number of protons	11	12	13	14	15	16	17	18
Electron arrangement	2.8.1	2.8.2	2.8.3	2.8.4	2.8.5	2.8.6	2.8.7	2.8.8
First ionization energy (kJ mol^{-1})	494	736	577	786	1060	1000	1260	1520

The Periodic Table and chemical properties

CHEMICAL PROPERTIES OF ELEMENTS IN THE SAME GROUP

Group 1 – the alkali metals

Li
Na
K
Rb
Cs

increasing reactivity

Lithium, sodium, and potassium all contain one electron in their outer shell. They are all reactive metals and are stored under liquid paraffin to prevent them reacting with air. They react by losing their outer electron to form the metal ion. Because they can readily lose an electron they are good reducing agents. The reactivity increases down the group as the outer electron is in successively higher energy levels and less energy is required to remove it.

They are called alkali metals because they all react with water to form an alkali solution of the metal hydroxide and hydrogen gas. Lithium floats and reacts quietly, sodium melts into a ball which darts around on the surface, and the heat generated from the reaction with potassium ignites the hydrogen.

$$2Li(s) + 2H_2O(l) \rightarrow 2Li^+(aq) + 2OH^-(aq) + H_2(g)$$

$$2Na(s) + 2H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq) + H_2(g)$$

$$2K(s) + 2H_2O(l) \rightarrow 2K^+(aq) + 2OH^-(aq) + H_2(g)$$

They all also react readily with chlorine, bromine and iodine to form ionic salts, e.g.

$$2Na(s) + Cl_2(g) \rightarrow 2Na^+Cl^-(s)$$

$$2K(s) + Br_2(l) \rightarrow 2K^+Br^-(s)$$

$$2Li(s) + I_2(g) \rightarrow 2Li^+I^-(s)$$

Group 7 – the halogens

F_2
Cl_2
Br_2
I_2

increasing reactivity

The halogens react by gaining one more electron to form halide ions. They are good oxidizing agents. The reactivity decreases down the group as the outer shell is increasingly at higher energy levels and further from the nucleus. This, together with the fact that there are more electrons between the nucleus and the outer shell, decreases the attraction for an extra electron.

Chlorine is a stronger oxidizing agent than bromine, so can remove the electron from bromide ions in solution to form chloride ions and bromine. Similarly both chlorine and bromine can oxidize iodide ions to form iodine.

$$Cl_2(aq) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(aq)$$

$$Cl_2(aq) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(aq)$$

$$Br_2(aq) + 2I^-(aq) \rightarrow 2Br^-(aq) + I_2(aq)$$

Test for halide ions

The presence of halide ions in solution can be detected by adding silver nitrate solution. The silver ions react with the halide ions to form a precipitate of the silver halide. The silver halides can be distinguished by their colour. These silver halides react with light to form silver metal. This is the basis of photography.

$$Ag^+(aq) + X^-(aq) \rightarrow AgX(s) \quad \text{where } X = Cl, Br, \text{ or } I$$

$$AgX(s) \xrightarrow{\text{light}} Ag(s) + \tfrac{1}{2}X_2$$

AgCl white
AgBr cream
AgI yellow

CHANGE FROM METALLIC TO NON-METALLIC NATURE OF THE ELEMENTS ACROSS PERIOD 3

Metals tend to be shiny and are good conductors of heat and electricity. Sodium, magnesium, and aluminium all conduct electricity well. Silicon is a semi-conductor and is called a **metalloid** as it possesses some of the properties of a metal and some of a non-metal. Phosphorus, sulfur, chlorine, and argon are non-metals and do not conduct electricity. Metals can also be distinguished from non-metals by their chemical properties. Metal oxides tend to be basic, whereas non-metal oxides tend to be acidic.

Sodium oxide and magnesium oxide are both basic and react with water to form hydroxides,

e.g. $Na_2O(s) + H_2O(l) \rightarrow 2NaOH(aq)$ $\qquad$ $MgO(s) + H_2O(l) \rightarrow Mg(OH)_2$

Aluminium is a metal but its oxide is amphoteric, that is, it can be either basic or acidic depending on whether it is reacting with an acid or a base.

The remaining elements in period 3 have acidic oxides. For example, sulfur trioxide reacts with water to form sulfuric acid, and phosphorus pentoxide reacts with water to form phosphoric(V) acid.

$$SO_3(g) + H_2O(l) \rightarrow H_2SO_4(aq) \qquad P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$$

Oxides of the third period (sodium → argon)

OXIDES OF PERIOD 3 ELEMENTS

The oxides of sodium, magnesium, and aluminium are all ionic. This accounts for their high melting points and electrical conductivity when molten. Silicon dioxide has a diamond-like macromolecular structure with a high boiling point. At the other end of the period the difference in electronegativities between the element and oxygen is small, resulting in simple covalent molecular structures with low melting and boiling points.

The acid–base properties of the oxides are also linked to their structure. The oxides of the electropositive elements are very basic and form solutions that are alkaline.

$Na_2O(s) + H_2O(l) \rightarrow 2Na^+(aq) + 2OH^-(aq)$

$MgO(s) + H_2O(l) \rightarrow Mg(OH)_2$

The amphoteric nature of aluminium oxide can be seen from its reactions with hydrochloric acid and sodium hydroxide.

Acting as a base: $Al_2O_3(s) + 6HCl(aq) \rightarrow 2AlCl_3(aq) + 3H_2O(l)$

Acting as an acid: $Al_2O_3(s) + 2NaOH(aq) + 3H_2O(l) \rightarrow \underset{\text{sodium aluminate}}{2NaAl(OH)_4(aq)}$

Silicon dioxide behaves as a weak acid. It does not react with water but will form sodium silicate with sodium hydroxide.

$SiO_2(s) + 2NaOH(aq) \rightarrow Na_2SiO_3(aq) + H_2O(aq)$

The oxides of phosphorus, sulfur, and chlorine are all strongly acidic.

$SO_2(g) + H_2O(l) \rightarrow H_2SO_3$ sulfurous acid

$P_4O_{10}(s) + 6H_2O(l) \rightarrow 4H_3PO_4(aq)$ phosphoric acid

$Cl_2O_7(l) + H_2O(l) \rightarrow 2HClO_4(aq)$ perchloric acid

Oxides of period 3 elements

Formula	Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10} (P_4O_6)	SO_3 (SO_2)	Cl_2O_7 (Cl_2O)
State at 25 °C	Solid	Solid	Solid	Solid	Solid (Solid)	Liquid (Gas)	Liquid (Gas)
Melting point / °C	1275	2852	2027	1610	24	17	–92
Boiling point / °C	–	3600	2980	2230	175	45	80
Electrical conductivity in molten state	Good	Good	Good	Very poor	None	None	None
Structure		Ionic		Covalent macromolecular		Simple covalent molecular	
Reaction with water	Forms NaOH(aq), an alkaline solution	Forms $Mg(OH)_2$, weakly alkaline	Does not react	Does not react	P_4O_{10} forms H_3PO_4, an acidic solution	SO_3 forms H_2SO_4, a strong acid	Cl_2O_7 forms $HClO_4$, an acidic solution
Nature of oxide	Basic		Amphoteric		Acidic		

Chlorides of the third period (sodium → argon)

CHLORIDES OF PERIOD 3 ELEMENTS

The physical properties of the chlorides are related to the structure in the same way as the oxides. Sodium chloride and magnesium chloride are ionic – they conduct electricity when molten and have high melting points. Aluminium chloride is covalent and is a poor conductor. Unlike silicon dioxide, silicon tetrachloride has a simple molecular structure as do the remaining chlorides in the period. These molecules are held together by weak van der Waals' forces, which results in low melting and boiling points.

Sodium chloride dissolves in water to give a neutral solution, magnesium chloride gives a slightly acidic solution with water. All the other chlorides including aluminium chloride react vigorously with water to produce acidic solutions of hydrochloric acid together with fumes of hydrogen chloride.

$$2AlCl_3(s) + 3H_2O(l) \rightarrow Al_2O_3(s) + 6HCl(aq)$$

$$SiCl_4(l) + 4H_2O(l) \rightarrow Si(OH)_4(aq) + 4HCl(aq)$$

$$PCl_3(l) + 3H_2O(l) \rightarrow H_3PO_3(aq) + 3HCl(aq)$$

Chlorine itself reacts with water to some extent to form an acidic solution.

$$Cl_2(aq) + H_2O(l) \rightleftharpoons HCl(aq) + HClO(aq)$$

Chlorides of period 3 elements

Formula	$NaCl$	$MgCl_2$	Al_2Cl_6	$SiCl_4$	PCl_3 (PCl_5)	(S_2Cl_2)	Cl_2
State at 25 °C	Solid	Solid	Solid	Liquid	Liquid (Solid)	Liquid	Gas
Melting point / °C	801	714	178 (sublimes)	–70	–112	–80	–101
Boiling point / °C	1413	1412	–	58	76	136	–35
Electrical conductivity in molten state	Good	Good	Poor	None	None	None	None
Structure	Ionic		Simple covalent molecular				
Reaction with water	Dissolve easily		Fumes of HCl produced				Some reaction with water
Nature of solution	Neutral	Weakly acidic	Acidic				

d-block elements (first row)

THE FIRST ROW TRANSITION ELEMENTS

Element	(Sc)	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	(Zn)
Electron configuration [Ar]	$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$

A transition element is defined as an element that possesses an incomplete d sub-level in one or more of its oxidation states. Scandium is not a typical transition metal as its common ion Sc^{3+} has no d electrons. Zinc is not a transition metal as it contains a full d sub-level in all its oxidation states. (Note: for Cr and Cu it is more energetically favourable to half-fill and completely fill the d sub-level respectively so they contain only one 4s electron).

Variable oxidation states

The 3d and 4s sub-levels are very similar in energy. When transition metals lose electrons they lose the 4s electrons first. All transition metals can show an oxidation state of +2. Some of the transition metals can form the +3 or +4 ion (e.g. Fe^{3+}, Mn^{4+}) as the ionization energies are such that up to two d electrons can also be lost. The M^{4+} ion is rare and in the higher oxidation states the element is usually found not as the free metal ion but either covalently bonded or as the oxyanion, such as MnO_4^-. Some common examples of variable oxidation states in addition to +2 are:

Cr(+3)	$CrCl_3$	chromium(III) chloride
Cr(+6)	$Cr_2O_7^{2-}$	dichromate(VI) ion
Mn(+4)	MnO_2	manganese(IV) oxide
Mn(+7)	MnO_4^-	manganate(VII) ion
Fe(+3)	Fe_2O_3	iron(III) oxide
Cu(+1)	Cu_2O	copper(I) oxide

Formation of complex ions

Because of their small size d-block ions attract species that are rich in electrons. Such species are known as **ligands**. Ligands are neutral molecules or anions which contain a non-bonding pair of electrons. These electron pairs can form co-ordinate covalent bonds with the metal ion to form **complex ions**.

A common ligand is water and most (but not all) transition metal ions exist as hexahydrated complex ions in aqueous solution, e.g. $[Fe(H_2O)_6]^{3+}$. Ligands can be replaced by other ligands. A typical example is the addition of ammonia to an aqueous solution of copper(II) sulfate to give the deep blue colour of the tetraaminecopper(II) ion. Similarly if concentrated hydrochloric acid is added to a solution of $Cu^{2+}(aq)$ the yellow tetrachlorocopper(II) anion is formed. Note: in this ion the overall charge on the ion is −2 as the four ligands each have a charge of −1.

$$[CuCl_4]^{2-} \underset{H_2O}{\overset{Cl^-}{\rightleftharpoons}} [Cu(H_2O)_4]^{2+} \underset{H_2O}{\overset{NH_3}{\rightleftharpoons}} [Cu(NH_3)_4]^{2+}$$

The number of lone pairs bonded to the metal ion is known as the **co-ordination number**. Compounds with a co-ordination number of six are octahedral in shape, those with a co-ordination number of four are tetrahedral or square planar, whereas those with a co-ordination number of two are usually linear.

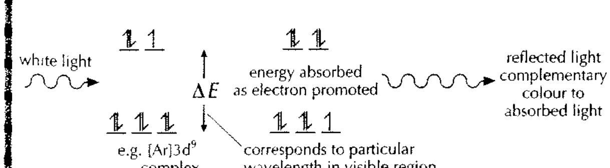
Co-ordination number	6	4	2
Examples	$[Fe(CN)_6]^{3-}$	$[CuCl_4]^{2-}$	$[Ag(NH_3)_2]^+$
	$[Fe(OH)_3(H_2O)_3]$	$[Cu(NH_3)_4]^{2+}$	

CHARACTERISTIC PROPERTIES OF TRANSITION ELEMENTS

Coloured complexes

In the free ion the five d orbitals are degenerate (of equal energy). However, in complexes the d orbitals are split into two distinct levels. The energy difference between the levels corresponds to a particular wavelength or frequency in the visible region of the spectrum. When light falls on the complex, energy of a particular wavelength is absorbed and electrons are excited from the lower level to the higher level.

$Cu^{2+}(aq)$ appears blue because it is the complementary colour to the wavelengths that have been absorbed. The amount the orbitals are split depends on the nature of the transition metal, the oxidation state, the shape of the complex, and the nature of the ligand, which explains why different complexes have different colours. If the d orbital is completely empty, as in Sc^{3+}, or completely full, as in Cu^+ or Zn^{2+}, no transitions within the d level can take place and the complexes are colourless.



Catalytic behaviour

Many transition elements and their compounds are very efficient catalysts, that is, they increase the rate of chemical reactions. This helps to make industrial processes, such as the production of ammonia and sulfuric acid, more efficient and economic. Platinum and palladium are used in catalytic converters fitted to cars. In the body, iron is found in haem and cobalt is found in vitamin B_{12}. Other common examples include:

Iron in the Haber process	$3H_2(g) + N_2 \overset{Fe(s)}{\rightleftharpoons} 2NH_3(g)$
Vanadium(V) oxide in the Contact process	$2SO_2(g) + O_2(g) \overset{V_2O_5(s)}{\rightleftharpoons} 2SO_3(g)$
Nickel in hydrogenation reactions	$C_2H_4(g) + H_2(g) \xrightarrow{Ni(s)} C_2H_6(g)$
Manganese(IV) oxide with hydrogen peroxide	$2H_2O_2(aq) \xrightarrow{MnO_2(s)} 2H_2O(l) + O_2(g)$

IB QUESTIONS – PERIODICITY

1. In the periodic table, elements are arranged in order of increasing

   A. atomic number. **C.** number of valence electrons.

   B. atomic mass. **D.** electronegativity.

2. Which one of the following series is arranged in order of increasing value?

   A. The first ionisation energies of: oxygen, fluorine, neon.

   B. The radii of: H^- ion, H atom, H^+ ion.

   C. The electronegativities of: chlorine, bromine, iodine.

   D. The boiling points of: iodine, bromine, chlorine.

3. Which property increases with increasing atomic number for both the alkali metals and the halogens?

   A. Ionisation energies **C.** Electronegativities

   B. Melting points **D.** Atomic radii

4. Which set of reactants below is expected to produce the most vigorous reaction?

   A. $Na(s) + Cl_2(g)$ **C.** $K(s) + Cl_2(g)$

   B. $Na(s) + Br_2(g)$ **D.** $K(s) + Br_2(g)$

5. Which one of the following statements about the halogen group is correct?

   A. First ionisation energies increase from F to I.

   B. Fluorine has the smallest tendency to be reduced.

   C. Cl_2 will oxidise $I^-(aq)$.

   D. I_2 is a stronger oxidising agent than F_2.

6. Strontium is an element in Group 2 of the Periodic Table with atomic number 38. Which of the following statements about strontium is NOT correct?

   A. Its first ionisation energy is lower than that of calcium.

   B. It has two electrons in its outermost energy level.

   C. Its atomic radius is smaller than magnesium.

   D. It forms a chloride with the formula $SrCl_2$.

7. Which one of the following elements has the lowest first ionisation energy?

   A. Li **C.** Mg

   B. Na **D.** Al

8. Which element is most similar chemically to the element with 14 electrons?

   A. Al **C.** Ge

   B. As **D.** P

9. 0.01 mole samples of the following oxides were added to separate 1 dm^3 portions of water. Which will produce the most acidic solution?

   A. $Al_2O_3(s)$ **C.** $Na_2O(s)$

   B. $SiO_2(s)$ **D.** $SO_3(g)$

10. Which reaction occurs readily?

    I. $Br_2(aq) + 2I^-(aq) \rightarrow I_2(aq) + 2Br^-(aq)$

    II. $Br_2(aq) + 2Cl^-(aq) \rightarrow Cl_2(aq) + 2Br^-(aq)$

    A. I only **C.** Both I and II

    B. II only **D.** Neither I nor II

HL

11. In which region of the Periodic Table would the element with the electronic structure below be located?

    $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^65s^2$

    A. group 6 **C.** s block

    B. noble gases **D.** d block

12. A certain element has the electronic configuration $1s^22s^22p^63s^23p^64s^23d^3$. Which oxidation state(s) would this element most likely show?

    A. +2 only **C.** +2 and +5 only

    B. +3 only **D.** +2, +3, +4, +5

13. Which ion is colourless?

    A. $[Cr(H_2O)_6]^{3+}$ **C.** $[Cu(NH_3)_4]^{2+}$

    B. $[Fe(CN)_6]^{4-}$ **D.** $[Zn(H_2O)_4]^{2+}$

14. Which of the following chlorides give neutral solutions when added to water?

    I. NaCl

    II. Al_2Cl_6

    III. PCl_3

    A. I only **C.** II and III only

    B. I and II only **D.** I, II and III

15. Based on melting points, the dividing line between ionic and covalent chlorides of the elements Mg to S lies between

    A. Mg and Al. **C.** Si and P.

    B. Al and Si. **D.** P and S.

16. The colours of the compounds of d-block elements are due to electron transitions

    A. between different d orbitals.

    B. between d orbitals and s orbitals.

    C. among the attached ligands.

    D. from the metal to the attached ligands.