Chapter 9 (AS-Level)

Chemical Periodicity

Versions of the periodic table

The most common versions of the periodic table include vertical groups I, II, VII, and horizontal periods from 1 to 7 and blocks of elements, and are named as follows:

- S-block, which contains groups I &II
- P-block, which contains groups III to VII & 0
- D-block, which contains transition metals
- F-block, which contains lanthanides & actinides

Periodic patterns of physical properties of elements (the first 36 elements only)

Electronic configuration:

- In S-block, the outermost electrons are in s-orbital, in p-block the outermost electrons are in the p-orbitals.
- Elements in same group have the same number of electrons in their outer shell
- For the elements in groups I – 0 the number of outer shell electrons is the same as the group numbers
- Group 8 (noble gases) have 8 e's in their outermost shell.

Atomic radii

Atomic radius is 2 types:

- Covalent radius, which is half the distance between nuclei in neighboring atoms in a molecule.
- Metallic radius, which is half the distance between neighbouring nuclei in metallic crystal (lattice).

Trends in atomic radii:

- Increase down a group
- Decrease across a period
- Relatively constant in T.M energies
- Opposite trends to ionization energies

These trends are due to the combined effect of:

- Nuclear charge
- Distance of outer electronic shell from nucleus (atomic size)
- Shielding effects of inner electronic shells

Ionic radii

- Ionic radii decrease across a period
- The radii of positive ions (cations) are smaller than those of corresponding atoms

- The radii of anions are bigger than those of corresponding atoms

Melting points

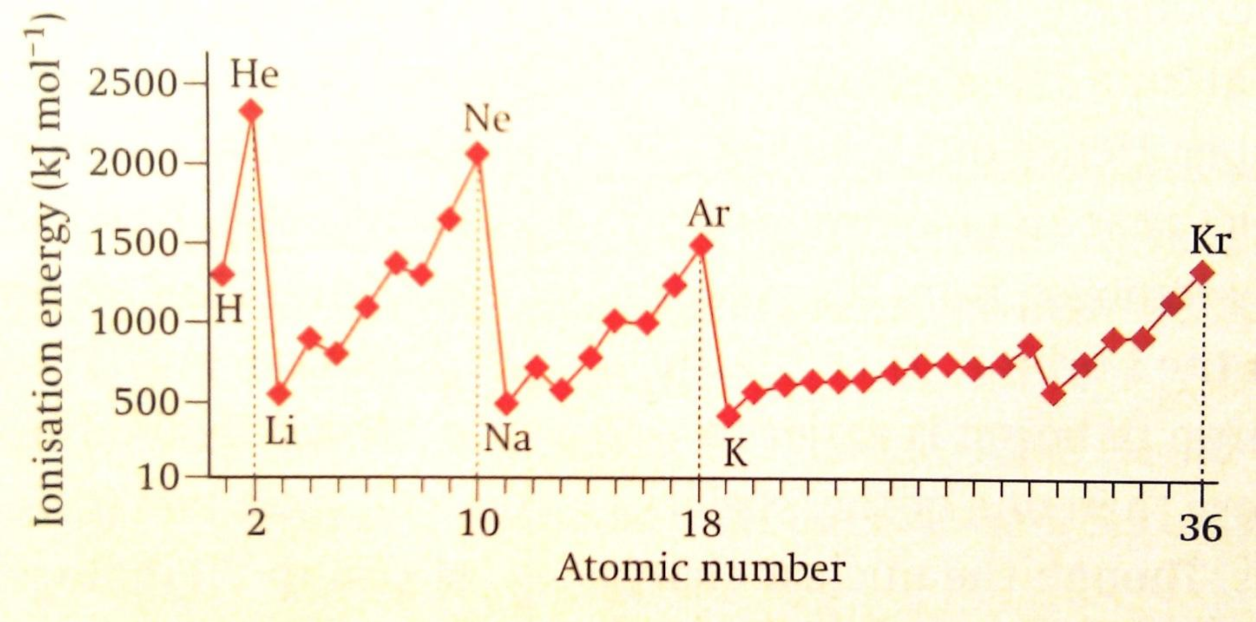
- Melting points increase across a period and reach peaks for elements in group IV. Carbon, Silicon etc. have high melting points which is due to strong covalent bonds forming a giant molecular lattice. Then a sharp decrease in melting point to form troughs for elements which form simple molecules or single atoms, H_2, N_2, O_2, F_2, He, Ne, …
- Low melting points are due to weak inter-molecular forces.
- In groups I, II, II, melting points increase due to metallic bond is much stronger.

Electrical conductivity

Unit of electrical conductivity is siemens/meter (Sm^{-1}) which is $\Omega^{-1}m^{-1}$. Electrical conductivities are much higher for metals than nonmetals and metalloids.

H:-																	He
Li: 0.108	Be: 0.25											B: 10^{-12}	C: 7 x 10^{-4}	N	O	F	Ne
Na: 0.218	Mg: 0.224											Al: 0.382	Si:2 x 10^{-10}	P: 10^{-17}	S: 10^{-23}	Cl	Ar
K: 0.143	Ca: 0.218	Sc: 0.015	Ti: 0.024	V: 0.04	Cr: 0.078	Mn: 0.054	Fe: 0.010	Co: 0.16	Ni: 0.145	Cu: 0.593	Zn: 0.167	Ga: 0.058	Ge: 2.2 x 10^{-8}	As: 0.029	Se: 0.08	Br: 10^{-18}	Kr

First Ionization energies (IE)



- Peaks are occupied by group 0 (Noble gases)
- Troughs are occupied by group I
- There is a general increase in IE across a period from group I to group 0, but the trend is uneven
- The variation in IE in transition metals is relatively small

For example, considering F, Ne and Na:

F: $1s^2$, $2s^2$, $2p^5$ → 1680 kJ/mol

Ne: $1s^2$, $2s^2$, $2p^6$ → 2080 kJ/mol

Na: $1s^2$, $2s^2$, $2p^6$, $3s^1$ → 494 kJ/mol

This is due to the combined effect of these factors:

- Nuclear charge (protons in nucleus)
- Atomic size (distance of outer electrons from nucleus)
- Shielding effect of inner shells

First ionization energies in periods

Considering Li, Be and B:

Li: 1s2, 2s1 ➔ IE = 519 kJ/mol

Be: 1s2, 2s2 ➔ IE= 900 kJ/mol (Has the same shielding effect but greater nuclear charge and smaller size).

B: 1s2, 2s2, 2p1 ➔ IE = 799 kJ/mol (The electron in the p-orbital is of higher energy level, so is easier to remove).

From the above graph, a general trend can be seen across periods, but this trend is uneven. For example look the above elements, Lithium, Beryllium and Boron. Someone might predict that Boron has the highest first ionization energy, but Beryllium does.

From experimental evidence like this, it is known that it is easier to remove electrons from a p orbital than from a s orbital in the same shell. P orbitals are higher energy levels than the s orbitals for a given quantum number. So an electron is easier to remove from the p orbital of the Boron atom than from the s orbital.

First ionization energies in Groups

Elements are placed in groups in the periodic table, as they show similar physical and chemical properties. The first ionization energies decrease down a group. This is due to:

- Nuclear charge increasing
- Atomic radii increases, so there is less attraction between electrons and protons
- Shielding effect of inner electrons

The last two factors decrease the effect of the first factor.

First ionization energies and reactivity

The lower the first ionization energy of an element in the periodic table, the higher the reactivity of that particular element with acids or bases, with metals or non-metals.

- In reactions between metals and non-metals, the metal has to form a positive ion for a reaction to occur. The metals with lower first ionization energies react faster and more vigorously.
- Group I metals have the least first ionization energies because they have the lowest first ionization energies. Reactivity increases down the group.

Reactions of period 3 elements

- MgO has a very high melting point and withstands corrosive chemicals. It is also used as an additive to cattle feed. Without it cattle become ill very fast.
- Al_2O_3 layer forms over aluminium metal, which prevents it from further reacting.
- SO_2 used to produce H_2SO_4 which is used in the manufacture of paints, dyestuff, etc.
- NaCl is used a table salt, to remove snow from roads, etc.
- $MgCl_2$ is used as a source for Mg and Cl_2
- CCl_4 is used as a grease dissolver.
- $SiCl_4$ is used as a source of pure silicon for the manufacture of Integrated circuits.

Preparation of period 3 oxides

- Na_2O:

Sodium is burned in oxygen, which makes sodium oxide. It burns with a yellow flame.

$$4\ Na + O_2 \rightarrow 2\ Na_2O$$

- MgO

Magnesium is burned in air. It burns vigorously with a white flame.

$$2\ Mg + O_2 \rightarrow 2\ MgO$$

- Al2O3

Aluminium forms Al2O3 when powdered and burned. It is also a layer over the metal.

$$4\ Al + 3\ O_2 \rightarrow 2\ Al_2O_3$$

- P_4O_{10}

Phosphorous is burned in oxygen (excess).

$$P_4 + 5\ O_2 \rightarrow P_4O_{10}$$

- SO_2 and SO_3

Sulphur is burned in air.

$$S + O_2 \rightarrow SO_2$$

SO_2 can be turned into SO_3 by using V_2O_5 as a catalyst with heat an air.

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3$$

Preparation of period 3 chlorides

- NaCl

Sodium burns in chlorine gas to make NaCl.

$$2\ Na + Cl_2 \rightarrow 2\ NaCl$$

- $MgCl_2$

Magnesium burns in chlorine gas to make $MgCl_2$.

$$Mg + Cl_2 \rightarrow MgCl_2$$

- $AlCl_3$

Aluminium is heated in chlorine gas. A white volatile solid is formed.

$$2\ Al + 2\ Cl_2 \rightarrow 2\ AlCl_3$$

- $SiCl_4$

Silicon is heated in chlorine gas. $SiCl_4$ is a volatile liquid.

$$Si + 2\ Cl_2 \rightarrow SiCl_4$$

- Phosphorous (III) and Phosphorous (V) chloride

PCl_3 is a volatile liquid (colourless).

$$P_4 + 6\ Cl_2 \rightarrow 4\ PCl_3$$

PCl_5 is made when there is an excess of chlorine gas.

$$P_4Cl_3 + Cl_2 \rightarrow PCl_5$$

The reactions of sodium and magnesium with water

- Sodium

Sodium is put in water. It floats and fizzes about. Sometimes it may catch fire.

$$2\ Na + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$$

NaOH has a pH of 12 -14 because it is very soluble and has a high concentration of OH- ions.

- Magnesium

Magnesium is put in cold water. Hydrogen bubbles are formed slowly and a solution of $Mg(OH)_2$ is formed.

$$Mg + 2\ H_2O \rightarrow Mg(OH)_2 + H_2$$

If Magnesium is put in steam, MgO is formed instead.

$$Mg + H_2O \rightarrow MgO + H_2$$

Important:

Sodium is more reactive than magnesium, so sodium hydroxide is more alkaline than $Mg(OH)_2$ because it is more soluble.

Structure and bonding of oxides and their reactions with water

- Na_2O → giant ionic lattice structure

$$Na_2O + H2O \rightarrow 2\ NaOH\ (aq)\ pH\ 12\text{-}14$$

- MgO → giant ionic lattice structure

$$MgO + H_2O \rightarrow Mg(OH)_2 \text{ (aq) pH 9-11}$$

- Al_2O_3 → giant ionic lattice structure with a significant amount of covalent bonding. Insoluble in water.
- P_4O_{10} → covalent bonding; reacts vigorously with water to make phosphoric acid pH 2-4.

$$P_4O_{10} + 6\ H_2O \rightarrow 4\ H_3PO_4$$

- SO2 → simple molecular structure with no intermolecular forces.

$$SO_2 + H_2O \rightarrow H_2SO_3$$

- SO3 → simple molecular structures with Van der Waals forces

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Structure and bonding of chlorides and their reactions with water

- NaCl and $MgCl_2$ → giant ionic lattice structures with ionic bonding

$$NaCl + H_2O \rightarrow NaCl \text{ (aq)}$$

$$MgCl_2 + H_20 \rightarrow MgCl_2 \text{ (aq)}$$

- Al_2Cl_6 is a diametric covalent molecule with 2 co-ordinate bonds. The arrangement around each aluminium atom is tetrahedral.

$$Al_2Cl_6 + 12\ H_2O \rightarrow 2\ [Al\ (H_2O)_6]^{3+} \text{ (aq)} + 6\ Cl^- \text{ (aq)}$$

- Silicon (IV) chloride and phosphorous (III) chloride have simple molecular structures with covalent bonding. PCl5 is a covalent molecule as a gas.
  Both react with water vigorously in an exothermic reaction giving off white fumes of HCl gas. This process is called hydrolysis.

Hydrolysis of silicon (IV) chloride:

$$SiCl_4 \text{ (l)} + 2\ H_2O \rightarrow SiO_2 + 4\ HCl$$

Hydrolysis of phosphorous (V) chloride:

$$PCl_5 + 4\ H_2O \rightarrow H_3PO_4 \text{ (aq)} + 5\ HCl \text{ (g)}$$

END OF LESSON