

Section 3 :periodicity : review notes

I regard section 3.1 as so basic and thus am not giving you notes on it.

3.2

atomic radius: half the distance between the nuclei of 2 covalently bonded atoms.

Note that this distance is less than the radius of the component spheres.

Trend : Decreases across the period due to increased nuclear charge (extra proton) pulling electron shells further in (but no increase in number of electron shells) . Increases down a group due to the extra electron shell.

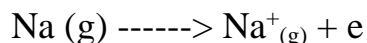
Problem : Inert gases do not form covalent bonds and their radius is simply "their radius", thus they are larger than the Group VII atom and appear to break the trend

Ionic radius : +ve ions are significantly smaller than their atoms since outer electron shell is lost. Negative ions are larger than their atoms since there is extra electron repulsion due to extra electrons in the outer shell. With each type of ion, the size decreases as the nuclear charge increases, BUT note that the largest ion of period 3 is P^{3-} (2,8,8) since it has the least +ve nucleus of those ions with an electron configuration of 2,8,8 (S^{2-} and Cl^{1-}) and thus the weakest pull on the outer electrons. (I have excluded the Si^{4+} ion here, but if you want to include it, then it is the biggest)

As one should expect, the smallest ion is Al^{3+} (2,8) as it has only 2 electron shells and the most +ve nucleus of those with an electron configuration of 2,8 and thus the greatest pull on the electrons.

The decrease in size across the period from ion to ion is greater than from atom to atom since the electron configuration (and thus electron repulsion) is the same with ions such as P^{3-} and S^{2-} , but the nucleus of S has one more proton. When one compares the atoms, then S has one extra proton and one extra e and thus electron repulsion increases and somewhat compensates for the more +ve nucleus.

Ionisation energy First ionization energy = the amount of energy required to remove 1 mole of electrons from 1 mole of isolated gaseous atoms:



ionisation energy(ie) increases across the period and decreases down a group. This is all due to the attraction of the outer electron to the nucleus...the tighter it is held, the higher the ie is. Since atomic size decreases across the period, it follows that ie must rise. Likewise, down a group...the outer electron is further from the nucleus and so is less tightly held...so ie DECREASES. (The ie of Al and S are lower than expected due to the lack of symmetry in their electronic configuration makes it easier to remove an electron)

Evidence from successive ionisation energies are used as evidence for electrons existing in shells. For example a group II element will have low first and second ionisation energies and then a much higher third ionisation energy....4th will be a bit higher still, as will 5th, 6th, through to 10th and then there will be another massive jump to 11th as an electron is removed from the next shell. This is because Group II elements have 2 electrons in their outer shell that are easy to remove. Then for the third ionisation energy, the electron is coming from the next shell which is closer to the nucleus and therefore much harder to remove.

Fine electron configurations. I DO NOT REGARD THIS AS SYLLABUS, but it has been asked several times. It can only apply to Higher level, BUT the only place on the syllabus is here...

While the general trend in ie is as stated above, there are a couple of little dips in the overall increase across the period. The ie of Al is lower than that of Mg and the reason is that the extra p electron is isolated and thus easier to remove....lack of symmetry . It is also at a higher energy level and slightly further from the nucleus thus easier to remove than the s electron and thus requires less energy The ie of S is lower than that of P because of the imbalance in the p orbitals where P is 3p³ and has symmetry of each p orbital compared to S which is 3p⁴ and has one full p orbital and two half filled orbitals. As a result of extra electron repulsion in this paired orbital (as well as the lack of symmetry), it is easier to take an electron from S than P.

When dealing with second ie's, just remember that we are talking about Na⁺ (g) -----> Na²⁺(g) + e. So you need to consider the electronic configuration of the +1 ion and determine how easy the process will be. In the above case it will be hard as we now have an inert gas structure as opposed to a group I and (of course) we are now removing a 2nd shell electron, which is much closer to the nucleus). The second ie of a group II element will be low, as we have just one electron in the outer shell and so this is easy to remove. (It will however still be higher than the 1st ie since

electron repulsion has been reduced and the electron is now closer to the nucleus)

The easiest way here is to consider the electron configuration of the species and then how easy is it to remove an electron by considering first which shell it is coming from and then charge and symmetry

Melting point(mpt) :In order to understand this you really need to have studied section 4, so do not worry unduly UNTIL you have done that!

THE HIGHER THE MPT, THE GREATER THE FORCES OF ATTRACTION BETWEEN THE PARTICLES.

In order to follow the trends here , YOU HAVE TO COMPARE LIKE WITH LIKE. There are several potential structures...metal elements have a GIANT METALLIC structure. Non-metallic elements could have EITHER a simple molecular OR a giant molecular structure...the latter is rare and confined to C and Si. Compounds can have giant ionic, giant molecular or simple molecular structures.

Mpt depends on structure...metallic melting point increases across a period and decreases down a group. This is due to a more +ve ion being more attracted to the delocalised valence electrons and thus is harder to separate.....and as you go down a group, the +ve ion is bigger and thus less charge dense.

The giant covalent structure of Si (and C) gives it a very high mpt. The simple covalent molecules of group VII and the far right of the table have low mpt's that depend upon their van der Waal forces..

The trend in mpt down a group depends upon which group is studied. Metallic mpt (ie group I) DECREASES due to the larger +1 ion. However in group VII these are simple molecular structures, so mpt INCREASES down the group due to increasing Van Der Waal forces.

Electronegativity = the attraction of an atom to the shared electrons in a covalent bond. This increases across the period, but decreases down the groups, so the most electronegative atom is F

This is all due to atomic size and attraction to the bonded electron pair. F is the smallest atom of the second period and has the most +ve nucleus and so its nucleus will be CLOSER to the shared electrons of the bond and thus there will be greater attraction. As you go down a group the nucleus does get more +ve, BUT there is also an extra electron shell to worry about. So there is more electron shielding between the bonded electrons and the nucleus AND a greater distance. As a result of this electronegativity decreases down any group.

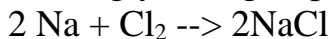
Note: no electronegativity values for the inert gases because they tend not to form covalent bonds.

3.3

Metals are electron losers...metallic strength depends on how easily they lose electrons. (a process called oxidation) Thus metallic strength decreases across the period and increases down a group. We can relate this directly to i_e 's..the lower the i_e is, the easier the element loses electrons. This works easily when we go down a group, BUT watch out across a period. Note that Mg has to lose 2 e 's and Al must lose 3 e 's. So we need to add up all the relevant i_e 's. So the fact that Al has a lower first i_e than Mg does NOT mean it is more reactive...the sum of its first 3 i_e 's far exceeds Mg's first 2... making Mg far more reactive than Al.

.Group I metals react with water to produce hydrogen gas and a hydroxide solution $2 \text{Na} + \text{H}_2\text{O} \rightarrow \text{H}_2 + 2\text{NaOH}$

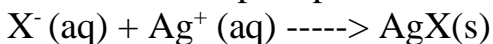
and they react strongly with group VII



Reactivity of group VII DECREASES down the group. Group VII are electron gainers and the smaller the atom is, the closer the incoming electron can get to the nucleus and so smaller halogens gain electrons easier than larger halogens.

A reactive halogen will take electrons from a less reactive halogen ion (halide) thus Cl_2 will react with Br^{1-} to produce Br_2 and Cl^{1-}but it wont react with F^{1-} .. Why does this happen? If you consider the collision of a halogen atom with a larger halide ion, then the outer electron of the halide is CLOSER to the nucleus of the halogen than it is the nucleus of the halide ion. So it is more attracted to the nucleus of the halogen and so it migrates to the halogen atom. If the halide ion is from a lower period than the halogen, then it has fewer electron shells and thus less electron shielding and thus is more attracted to the ion's nucleus. Thus the electron will not migrate to the halogen atom and no reaction occurs.

Halides form a precipitate with Ag^+ (in AgNO_3) **No longer on syllabus**



The color is white with chlorides, but quickly turns almost violet in sunlight as the AgCl decomposes into silver metal and chlorine gas.

Silver bromide is a cream color and this too decomposes in sunlight to give a faint green hue to the solid.

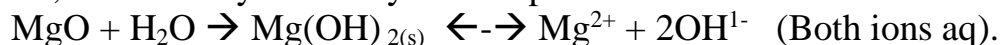
Silver iodide is a pale yellow color and does not decompose in sunlight.

3.3,2

Since metals only form IONIC COMPOUNDS with non-metals (a simplification , but still true in the vast number of cases) the oxides and chlorides of Na and Mg are ionic. The reason for this is the large difference in electronegativities...it means that the non-metal can pull electrons totally away from the metal and as a result, ions are formed. Thus these compounds consist of positive metal ions surrounded by negative non-metal ions in an infinite crystal lattice. The oxide of Al is also ionic, and again exists as ions. You can prove this by the fact that these ionics conduct electricity in their molten (melted) state. Al is a metalloid and its oxide does not behaves like those of Na and Mg.. Non-metal oxides are covalent since the difference between the electronegativities are too small for either atom to pull electrons totally away from the other.

Since ionic oxides are basic and covalent oxides are acidic, there is a trend in decreasing pH of solutions of oxides as you go across period 3

Reasoning for metallic oxides being basic: If these are ionic, they contain the oxide ion, O^{2-} and this reacts with water : $O^{2-} + H_2O \rightarrow 2OH^{-}$ Thus they are basic. However since MgO and Al_2O_3 are pretty insoluble, there is only a little hydroxide produced.



Bases will typically dissolve well in acidic solutions

Amphoteric = can act as an acid or a base....the fact that Al_2O_3 is amphoteric shows the metalloid nature of Al and that this compound is not 100% ionic. It will dissolve in both acids and bases.

Non metal oxides react in water to form acids. If you simply add H_2O to the oxide, then typically you get the acid. Example $SO_3 + H_2O \rightarrow H_2SO_4$ (you may need to divide by 2 in some cases....so Cl_2O forms the acid HClO) Acidic oxides are more soluble in basic solutions.

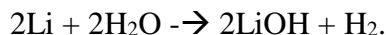
Silicon dioxide with its giant covalent structure is insoluble in water and so does not affect the pH of water when the two are mixed.

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

Required equations:

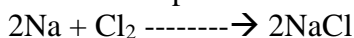
Group I metals with water:

All react the same way to produce hydroxide (and thus a highly basic solution) and hydrogen gas



Group I with Group VII

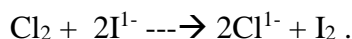
The vigor of the reaction depends on the strength of the reactants, but essentially :



The weaker group I metals (Li) react quite slowly with the weaker group VII elements (iodine)

Group VII with Group VII ions

A GpVII element will react with a Gp VII ion that is beneath it, but not one that is above it:



But iodine would not react with chloride. The halogens up the top of the group are better electron takers than those lower down . Thus the larger halide ion loses its electron to the smaller halogen atom.

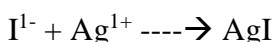
Group VII ions and Ag^+



Goes white and then purplish as it decomposes in sunlight



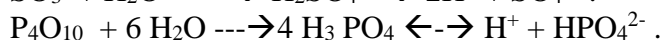
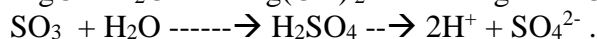
Goes cream and then a hint of greenish as it decomposes in sunlight



Pale yellow and does not decompose.

The silver nitrate is acidified with nitric acid to stop other precipitates forming...ie the silver halides are the only common insoluble silver salts in acid conditions.

Oxides of period 3 reacting with water



Sodium hydroxide dissolves fully in water to produce a highly basic solution. Magnesium hydroxide dissolves poorly and so forms a mildly basic solution with a lot of undissolved solid on the bottom of the test tube. Sulfur trioxide reacts violently with water to produce sulfuric acid , which is a strong acid and dissociates completely in water. Phosphorus V oxide reacts with water to produce weak phosphoric V acid. This splits up slightly in water to produce a medium acidic solution

Periodic trends in a HURRY

- a) Atomic Size : increases down a group (Extra electron shell); decreases across a period (No extra shell but extra pull from more +ve nucleus)
- b) Ionic size : Increases down a group (Extra shell) ; +ve ions smaller than atom(loss of valence shell) –ve ions larger(Increased electron repulsion due to e gain). . Across period size decreases rapidly to Al then massive increase at P then decrease rapidly (metals ions are 2,8, but with progressively more +ve nucleus, nonmetals ions are 2,8,8)
- c) Melting point: Steady increase to Al, massive jump to Si, even more massive fall to P, then low to Ar. (Different structures...metallic, giant covalent, simple molecular)
- d) Electronegativity: decreases down a group , increases across the period (Larger atoms have more shells and thus do not attract e as much)
- e) Ionisation energies: Decrease down a group, increase across a period (larger atoms lose electrons more easily due to large # of shells and lower attraction to valence e)
- f) Reactivity: Metals :Increases down main metal groups (larger atoms lose e easier) decreases across period(metals will need to lose more e and as they are smaller this will get MUCH harder)
- g) Reactivity- Non-metals: Decreases down a group (gets harder for larger atoms to attract an e) Increases across the period(Smaller atoms attract e better and # of e needed gets less as well.