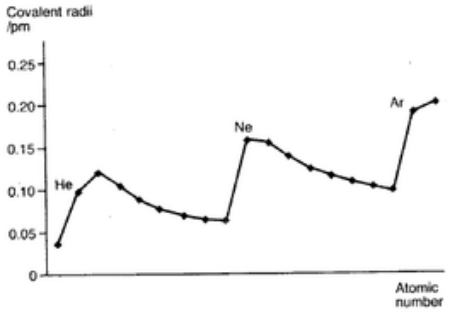
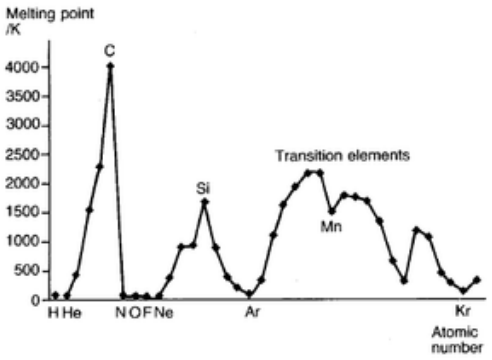
STUDY PACK 9

UNIVERSITY OF CAMBRIDGE

CHEMICAL PERIODICITY





Since 2005
Chembase
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1. Explain the meaning of the term 'chemical periodicity'

Periodicity is the repeating pattern of the chemical & physical properties of the elements across the periods of the periodic table.

2. Describe & state why it is important to measure the atomic radius in terms of metallic & covalent radii

Atomic radii is the distance between the nucleus & the outermost electron. The point is that it is impossible to say precisely where the atom begins & ends. The idea that an atom has a fixed size is not correct according to the electron density diagrams.

Therefore, the size of an atom can be estimated by measuring the distance between the nuclei of atoms when they are bonded together in a metal or in a covalent molecule. By dividing the distance by 2 the size of the atom can be estimated. Therefore, measurements on metals provide us with metallic radii & on covalent molecules covalent radii.

3. Explain van der waals radii of molecules

The van der waal's radii is the half distance between the two molecules which is attracted by van der waal's forces. The van der waal's radius of an atom is larger than covalent radius. Elements of group 18 does not form bonds with each other thus their atomic radii is determined in terms of van der Waals' radius.

4. Describe qualitatively the variations in atomic radius across the 3rd period from sodium to argon

Across the period from left to right the atomic radius of elements decreases due to the increase nuclear charge resulting electrons being more attracted towards the nucleus. The shielding is constant at the outer electrons due to the constant number of shells. Therefore, as a result effective nuclear attraction increases across the period resulting electrons being more attracted towards the nucleus.

5. Plot a graph to show the variations in covalent radii against the atomic number of period 3 elements



6. Explain the variations in ionic radius across the 3rd period from sodium to argon

The size of the atoms changes when it is positively or negatively charged. This can be explained in terms of shielding effect. The ionic radii of positive ions are smaller than the radii of the neutral atoms & the ionic radii of the negative ions are greater than the radii of the neutral atoms.

When an atom loses electrons, the amount of shielding is reduced as a result the effective nuclear attraction increases. These electrons will be pulled towards the nucleus resulting decrease in radius. When an atom loses electrons, the amount of shielding is reduced as a result the effective nuclear attraction increases. As more electrons are removed the radii will be reduced more.

E.g.: $Na^{+} > Mg^{+2} > Si^{+4}$

Similarly, when an atom gains electrons the shielding effect increases as a result the electron will feel less effective nuclear attraction. Thus, the electron will be far away from the nucleus resulting increase in radius. As more 'e' ns are attached the size will increase more

$P^{3-} > S^{2-} > Cl^{-}$

7. Plot a graph to show the variations in ionic radii against the atomic number of period 3 elements



8. Describe the periodicity of melting points of elements across the period 3

For simple Covalent molecules the boiling and melting point depends on the strength of the van der waal's forces between the molecules, not the strength of the covalent bond within the molecule, except in giant atomic solids (often referred to as giant molecular) or ionic compounds. When a giant atomic (giant molecular) solid such as diamond or graphite is heated, the covalent bonds between the atoms are broken. But the covalent bonds are not broken when a simple molecular substance is melted. Therefore, the strength of the covalent bonds within the molecules does not influence the boiling and melting points of a molecular substance.

The melting & boiling points tell us how strongly the ions in an ionic compound held together. If it a metal how strong the metallic bond is. If the compound is a simple covalent then the strength of the van der waal's attraction determines the melting & boiling points if it is ionic then the strength of the ionic bond determines the melting and boiling point. For metals the strength of the metallic bond determines the boiling & melting points.

From 'Na' to 'Al' the strength of the metallic bond increases due to increased number of delocalized electrons & decrease ionic radii. As a result, the melting point increases from Na-Al.

'Si' forms giant atomic structures (giant molecular) similar to diamond where the melting point is extremely higher. Melting 'Si' involves breaking of all four covalent bonds.

Elements from 'P' to 'Ar' form simple covalent molecules such as P_4, S_8 the melting point decreases due to decrease in the strength of dispersion forces which depends on number of electrons.

9. Plot a graph to show the variations of melting points against the atomic number of period 3 elements



10. Describe the periodicity of electrical conductivity of elements across the period 3

Electrical conductivity increases from Na-Al due to the increased number of electrons in the metallic structure.
Silicon is a semi-conductor. Elements from 'P' to 'Ar' are non-metals hence do not possess free electrons to carry electricity thus are non-conductors.

11. Explain the variation in first ionization energy from sodium to argon

The size of the atom decreases across a period due to increased nuclear attraction, which is result of increased atomic number. Therefore, the effective nuclear attraction generally increases across a period resulting an increase in the first ionization energy.

Electronic configuration for 'Be' & 'B' shows that 'B'e has a stable S^2 configuration than that of 'B'.

$^4Be = 1s^2, 2s^2$ $^5B = 1s^2, 2s^2\ 2p^1$

To remove an electron from 'Be' requires more energy due to its stability. Fully filled or half-filled orbital (e.g.: S^2,P^3,P^6,d^5,d^{10}) are more stable. Therefore, they show unexpected high first ionization energy.

Also, the electronic configurations for N & O will explain why N has high ionization energy.

$^7N = 1s^2, 2s^2 2p^3$ $^8O = 1s^2, 2s^2\ 2p^4$

The outer electrons in 'N' are in p3 stable form. Therefore, needs lot of energy to remove an electron from 'N'. unlike in 'O' where the paired electron in the p-orbital results in repulsion between them. This makes it easier, for the electron to be removed. But the second ionization energy of oxygen will be greater due to the stable p3 configuration.

The variation of the first ionization energy of Mg to Al and P to S can be explained in a similar manner.

Mg Al

P S

12. Plot the first ionization energy of elements from sodium to argon against their atomic numbers



12. Explain the strength, high melting point and electrical insulating properties of ceramics such as magnesium oxide, aluminum oxide and silicon dioxide in terms of their structure and bonding.

- Magnesium oxide :

Ceramics made from magnesium oxide are used in furnace linings (refractory bricks), because the ceramic has a high melting point due to strong forces in the giant structure also in heating elements (for example for electric cookers), because the ceramic is good electrical insulator as no free electrons, and the ions aren't free to move in the solid.

- Aluminum oxide :

Aluminum oxide ceramics are used in high temperature and high voltage electrical insulators as it possess high melting point and acts as a good electrical insulator. This is due to strong attractions in the giant structure, no free electrons, and the ions aren't free to move.

- Silicon(IV) oxide (silicon dioxide) :

Silicon dioxide ceramics are used as furnace linings (refractory bricks) in furnaces and in the manufacture of glass, because the giant covalent structure has a very high melting point due to the strength of the Si-O covalent bonds in three dimensions;

01. Describe the reaction of below elements with Oxygen.

a) Sodium:

Sodium burns vigorously with a bright yellow flame when heated and placed in a jar of oxygen. Also, it reacts at room temperature when exposed to air, resulting white ionic solid sodium oxide.

b) Magnesium:

Magnesium also reacts vigorously when burnt in air, producing bright sparkles, resulting white ionic solid magnesium oxide. At room temperature reacts very slowly resulting a grey solid

c) Aluminum:

Due to the presence of the protective oxide coating aluminum does not react well with oxygen. Pure aluminum metal burns with bright white flame resulting aluminum oxide.

d) Silicon:

Silicon reacts slowly with Oxygen to produce white solid of giant covalent substance, silicon dioxide (silica/sand)

e) Phosphorous:

Burns in air with a bright yellow or white flame, resulting white clouds of solid phosphorus (V) oxide.

f) Sulphur:

When ignited sulfur burns gently with a blue flame producing the toxic SO_2 gas.

SO_2 further reacts with oxygen in the presence of V_2O_5 catalyst and temperature of 450 ^0C, to produce Sulfur (VI) oxide, SO_3

g) Chlorine & Argon:

Chlorine and Argon does not react with oxygen.

02. <u>Reactions with Chlorine.</u>

All elements in the 3rd period react with chlorine to form chlorides. Reactivity depends on the bonding structure & stability of the chlorides. Chlorides formed falls under 3 categories.
Ionic, Covalent, Covalent with ionic character

a) Reaction of Sodium:

When heated sodium metal is put in to a jar of chlorine gas, a vigorous reaction occurs resulting white ionic solid NaCl.

b) Reaction of Magnesium:

When Mg reacts with dry Cl_2 gas in the absence of air produces the white ionic solid $MgCl_2$

c) Reaction of Aluminium:

Aluminum reacts with chlorine gas resulting the dimer Al_2Cl_6 rather than the monomer $AlCl_3$. A lone pair from chlorine atom of an $AlCl_3$ molecule forms a dative bond with an empty orbital of Al of another $AlCl_3$ molecule resulting the dimer Al_2Cl_6 as shown below:

d) Reaction of Silicon:

Si reacts slowly with chlorine forming a series of chlorides with the general formula Si_nCl_{2n+2}. First such member is $SiCl_4$ which is a colorless liquid.

e) Reaction of Phosphorus:

When chlorine gas is passed over heated Phosphorous forms two chlorides, Colourless PCl_3 liquid and with excess Cl_2, PCl_3 is further oxidized to white solid PCl_5

03. State and explain the variation in oxidation number of the oxides from sodium to sulfur.

The oxygen in the compound is always the more electronegative element, and so always has a negative oxidation number which is -2. Thus, the oxidation number can be calculated;

Na in Na_2O	+1	P in P_4O_{10}	+5
Mg in MgO	+2	S in SO_3	+6
Al in Al_2O_3	+3	S in SO_2	+4
Si in SiO_2	+4		

The maximum oxidation state shown by the elements in this period is the same as the number of outer electrons. (Valency shell electrons) except for 'S' in SO_2 which is +4

04. Likewise, State and explain the variation in oxidation number of the chlorides from sodium to phosphorus.

The chlorine in the compound is always the more electronegative element, and so always has a negative oxidation number which is -1. Thus, the oxidation number can be calculated as;

$NaCl$	+1	$SiCl_4$	+4
$MgCl_2$	+2	PCl_3	+3
$AlCl_3$	+3	PCl_5	+5

Notice that the last two chlorides possess two oxidation states +3 and +5

05. <u>Reactions with water.</u>

a) Reaction of Sodium:

Reacts vigorously with cold water to produce NaOH & hydrogen gas.

Observations: floats and fizzes around water, melts into a ball of molten metal, giving off a gas.

b) Reaction of Magnesium:

- 'Mg' almost shows no reaction with cold water. But if left for several days it reacts very slowly. The reaction is speeded if warm water is used. It produce an alkaline suspension of $Mg(OH)_2$ & H_2 gas.

If 'Mg' is reacted with steam, a much more vigorous reaction occurs resulting MgO & H_2 gas.

06. Reactions of the oxides with water

a) Sodium oxide (Na_2O) :

Sodium oxide is a basic oxide which dissolves instantly in water to form an alkaline solution of NaOH which is colourless. No effervescence is observed & the resulting solution turns red litmus blue.

b) Magnesium oxide (MgO) :

MgO is a basic oxide which is insoluble in water. This is due to its strong lattice energy.

c) Aluminium oxide (Al_2O_3) :

Alumina has a greater lattice enthalpy than MgO thus insoluble in water.

d) Silicon dioxide (SiO_2) :

SiO_2 is a giant covalent structure which is highly stable, thus insoluble in water. But reacts with hot, concentrated alkali as shown below. It does not react with acids, therefore classed as an acidic oxide.

$$SiO_2 + 2NaOH \longrightarrow \underset{\text{(sodium silicate)}}{Na_2SiO_{3(aq)}} + H_2O$$

e) Oxides of phosphorus (P_4O_{10}/P_4O_6) :

Both P_4O_{10} (dimer of P_2O_5) & P_4O_6 (dimer of P_2O_3) react with water resulting weak phosphoric (III) acid & weak phosphoric (V) acid

f) Oxides of Sulphur (SO_2/SO_3) :

Both acidic oxides of sulfur react with water to form the corresponding acids. The reaction of SO_3 with water is very vigorous & dangerous due to the reaction being exothermic. Hence in the contact process SO_3 is first absorbed in conc.H_2SO_4 to form oleum which is then reacted with water to form sulfuric acid.

07. <u>Classification of Oxides.</u>

a) Classify oxides as Acidic, Basic & Amphoteric

- Metal oxides are basic oxides (Some dissolves in water to form alkalis)
  Eg: Na_2O, MgO

- Non-metal oxides are acidic (dissolves in water to form acids)
  Eg: P_4O_6, SO_2, Cl_2O_7

- Oxides of semi-metals (metalloids) are amphoteric they react with both acids & alkalis to give salt & water.
  Eg: Al_2O_3

The trend in acid-base behaviour is shown in various reactions which in short can be summarized as:

The trend is from strongly basic oxides on the left-hand side to strongly acidic ones on the right, via an amphoteric oxide (aluminum oxide) in the middle. An amphoteric oxide is one which shows both acidic and basic properties.

b) Write the formula of oxides & hydroxides of metals, oxides of non-metals, hence indicate their structure, acid-base nature & the solubilities

Elements	**Na**	**Mg**	**Al**	**Si**	**P**	**S**	**Cl**
Formula of Oxide							Cl_2O_7 Cl_2O
Formula of hydroxide				----	---	----	---
Structure	Giant ionic			Giant Covalent	Simple molecular		
Solubility	Very soluble	Slightly soluble	Insoluble		Soluble		
Acid-Base nature	Basic		Amphoteric	Acidic			

08. Explain the Amphoteric behaviour of Aluminium oxide in the reaction with acids & alkalis

Al_2O_3 reacts both with acids and alkali resulting salt & water as shown below. Therefore, Al_2O_3 is amphoteric.

With Acids: $Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$

With Alkali: $Al_2O_3 + 2NaOH \longrightarrow 2NaAlO_2 + H_2O$

Hot. Conc. alkali: $Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2NaAl(OH)_{4\,(aq)}$

09. **<u>Reaction of Chlorides with water.</u>**

a) Sodium Chloride & Magnesium Chloride:

NaCl & $MgCl_2$ are both ionic & possess ionic lattices. They do not react with water rather dissolve in water resulting aqueous ions. This is due to their hydration energy being greater than the lattice energy.

b) Anhydrous Aluminium Chloride:

Al_2Cl_6 reacts with water as shown below:

The covalent chloride is violently hydrolyzed by water resulting steamy acidic fumes of HCl. However a white precipitate $Al(OH)_3$ is not observed as it dissolves in acidic medium.

c) Silicon tetra Chloride:

$SiCl_4$ violently hydrolyzed by water resulting SiO_2 as a white solid & steamy fumes of HCl will be evolved.

d) Chlorides of Phosphorous: (PCl_3 & PCl_5)

Phosphorus (III) chloride is readily hydrolysed by water to form phosphoric (III) acid which is a weak acid.

Phosphorus (V) chloride fume even in moist air reacts vigorously with water resulting phosphoric (V) acid which is a weak acid.

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