The Creature Collage of Science and Commerce Abbottabad

Instructor: Gul Naz   **Class**: 2nd year   **Subject**: Chemistry

**Chapter**:   1   ***s & p-* Block Element**

Short questions

1. **Explain reactions of magnesium with H$_2$O?**

Reaction of magnesium with water

Magnesium does not react with water to any significant extent. This is in contrast with calcium, immediately below magnesium in the periodic table, which does react slowly with cold water. Magnesium metal does however react with steam to give magnesium oxide (MgO) (or magnesium hydroxide, Mg(OH)$_2$, with excess steam) and hydrogen gas (H$_2$).

$$Mg_{(s)} + 2H_2O_{(g)} \rightarrow Mg(OH)_{2(aq)} + H_{2(g)}$$
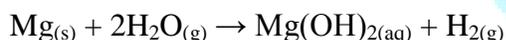
2. **Why NaCl does not conduct electricity in solid state?**

Solids do conduct electricity under some circumstances. For instance, all metals are conductors in the solid state. Graphite conducts in the solid state. There are two keys to conducting electricity there must be

Charged particles
and

The charged particles must be free to move

In the case of any form of sodium chloride there are charged particles (the positive and negative ions). However, in solid NaCl the charged particles are locked in place in the crystal lattice and not able to move, and thus solid NaCl does not conduct electricity. When the NaCl melts, or dissolves in water, the crystal lattice breaks down and the charged particles are able to move, allowing electricity to be conducted

NaCl (common salt) is solid in state and solid ions or compounds don't conduct electricity. It needs to be either melted, molten or dissolved in a solution (i.e. water) first. This is because the electrons in a solid state won't be free to move to either the Cathode (-ve) or to the Anode (+ve). In a liquid state the electrons are free enough to move.

3. **Rubidium is below potassium in group I-A predict how it will react with:**
a) **Water**
b) **Chlorine**

The reactivity of Alakli metals increase down the group therefore the bottom elements are more reactive than at the top of the group.
(a) Reactivity of water; K and Rb both react with cold water liberate H$_2$ gas and form strong alkali as KOH and RbOH.
The reactivity of K is vigorous. It cracks and pop as hydrogen exploded.
2K(s) + 2H$_2$O(l)→2 KOH + H$_2$
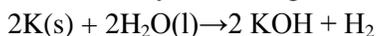
Rb explode violently when react with water. It reacts even with ice

$Rb(s) + H_2O(l) \rightarrow RbOH(aq) + H_2(g)$
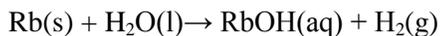
(b) With Cl; All alkali metals react with Cl form white crystalline solids.

$2K + Cl_2 \rightarrow 2KCl$

$2Rb + Cl_2 \rightarrow 2RbCl$
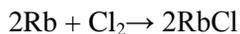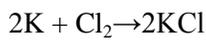
the ionic characters of chlorides increase down the group. Therefore RbCl will be more ionic than KCl (Fajan,s rule)

4. **Why halogens are so reactive?**

Atoms of elements consist of a nucleus that contains protons and neutrons. The nucleus is surrounded by electrons that move around in orbits, or levels. Atoms of an element react with other atoms based on the number of electrons found in their outer orbit. These outer electrons are called valence electrons. For an atom of an element to be nonreactive, it must have eight electrons in its outer level. All members of the halogen family have seven valence electrons.

Because these atoms are so close to having a full set of eight valence electrons, they're very reactive. They show a chemical tendency to gain one electron by forming bonds and taking the electron from other atoms to attain a full set. Because of their chemical reactivity, these elements do not exist as single elements in nature. They are only found in compounds

5. **What is flame test?**

A flame test is an analytic procedure used in chemistry to detect the presence of certain elements, primarily metal ions, based on each element's characteristic emission spectrum. The color of flames in general also depends on temperature; see flame color.

6. **Write down any four characteristics of group II-A elements?**

Alkaline earth metals make up the second group of the periodic table. This family includes the elements beryllium, magnesium, calcium, strontium, barium, and radium (Be, Mg, Ca, Sr, Ba, and Ra, respectively). Group 2 elements share common characteristics:

➢ Each metal is naturally occurring and quite reactive.
➢ These metals are silver and soft, much like the alkali metals of Group 1.
➢ These metals also react with water, though not as vigorously.
➢ Beryllium, interestingly, does not react with water.
➢ Each alkaline earth metal has two valence electrons.
➢ They will easily give these electrons up to form cations.
➢ These metals become increasingly more reactive as you go down the periodic table.
➢ This is concurrent with general periodic trends.

7. **Explain the thermal stability of nitrates and carbonates of group II-A elements?**

This page examines at the effect of heat on the carbonates and nitrates of the Group 2 elements (beryllium, magnesium, calcium, strontium and barium). It explains how the thermal stability of the compounds changes down the group.

The effect of heat on the Group 2 carbonates
All the carbonates in this group undergo thermal decomposition to the metal oxide and carbon dioxide gas. The term "thermal decomposition" describes splitting up a compound by heating it.

All the Group 2 carbonates and their resulting oxides exist as white solids. If "X" represents any one of the elements, the following describes this decomposition:

$$XCO_{3(s)} \rightarrow XO_{(s)} + CO_{2(g)}$$

Down the group, the carbonates require more heating to decompose.

The carbonates become more thermally stable down the group.

The effect of heat on the Group 2 Nitrates

The Group 2 nitrates undergo thermal decomposition to the metal oxide, nitrogen dioxide and oxygen gas. These compounds are white solids and brown nitrogen dioxide and oxygen gases are also given off when heated. Magnesium and calcium nitrates normally crystallize with water, and the solid may dissolve in its own water of crystallization to make a colorless solution before it starts to decompose.

Again, if "X" represents any one of the elements:

$$2X(NO_3)_{2(s)} \rightarrow 2XO_{(s)} + 4NO_{2(g)} + O_2$$

Down the group, the nitrates must also be heated more strongly before they will decompose.

8. **Why carbonates of group I-A elements are more thermally stable than those of group II-A?**

The size of group 1A ions is greater than the size of group 2A. Similarly charge density of group 1A is lower than 2A.higher ionic size and lower charge density decrease the polarizing power of group1A.
Cations of greater polarizing power distort the carbonate ion more easily and easily decompose it than the cation of lower polarizing power. Therefore carbonates and bicarbonates of of group 1A are more stable than that of group 2A.
$Na_2CO_3 \rightarrow$ not easily decompose
$CaCO_3 \rightarrow CaO + CO_2$
their stability increase down the group with increase in cationic size

9. **Why beryllium is differ from the members of its groups.**

Anomalous Behavior of Beryllium

Beryllium, the first member of Group 2, differs from the other members of its group. This is primarily due to its small size, relatively high electro-negativity and availability of only four orbitals (one 2s and three 2p) in the valence shell. A few points of differences are as follows.

➢ Beryllium forms bonds with appreciable covalent character.

➢ Beryllium salts hydrolyze in aqueous solution producing H_3O^+. This is due to the formation of a stronger Be-0 bond.

➢ Beryllium forms large number of complexes with coordination numbers four. The tendency for other metals to form complexes is comparatively low.

➢ $Be(OH)_2$ is amphoteric while the hydroxide of other metals are basic.

10. **Explain the structure and stability of chlorides of group IV-A elements.**

Structures

Carbon, silicon and lead tetrachlorides

Each of these compounds has the formula XCl4. They are simple covalent molecules with a typical tetrahedral shape formed by SP3 hybridization.They are liquids at room temperature (although at room temperature, lead(IV) chloride will tend to decompose to give lead(II) chloride and chlorine gas.

$PbCl4 \rightarrow \rightarrow PbCl2 + Cl2$
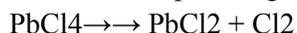
Lead(II) chloride, PbCl2

Lead(II) chloride is a white solid, melting at 501°C. It is slightly soluble in cold water, but its solubility increases with temperature. Lead(II) chloride is essentially ionic in character. Stability

At the top of Group 4, the most stable oxidation state is +4. This is the oxidation state of carbon and silicon in CCl4 and SiCl4. These compounds have no tendency to break down into dichlorides.

However, the relative stability of the +4 oxidation state decreases down the group, and the +2 oxidation state becomes the most stable for lead and below.

Lead(IV) chloride decomposes at room temperature to form the more stable lead(II) chloride and chlorine gas.

11. **Why fluorine is stronger oxidizing agent then chlorine?**

Halogens have high electronegativity and electron affinity. They have greater tendency to accept electrons or easily reduced, therefore they are strong oxidizing agent.

As the reduction potential decrease down the group, the oxidizing power decrease down the group the order of the oxidizing power will be as under

$F_2 > Cl_2 > Br_2 > I_2$
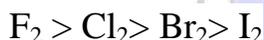
The oxidizing power depends on:

➢ Heat of dissociation of halogen molecule.
➢ Electron affinity of atom.
➢ Hydration energy of the ion.
➢ Heat of vaporization

If a halogen has low energy of dissociation, a high electron affinity, and higher hydration of its ion, it will have high oxidizing power.

F has although low electron affinity than Cl but low dissociation energy and have high hydration energy of its ion, therefore Fluorine is strongest oxidizing agent

12. **Why BeCl$_2$ is covalent bond not ionic?**

Beryllium does not form cations because its ionization energy is relatively high (900 kJ/mol). Therefore cannot form ionic bond.

Moreover Be is too small in size and fajan's rule state that small highly charged ions tend to form covalent bond

Due to small size and high charge density Be, its polarizing power is maximum, since Be+2 ion essentially pull the electrons cloud from Cl- , such that the electrons pair are effectively shared. This gives covalent character to BeCl2.

13. **Explain the amphoteric nature of Be(OH)$_2$.**

Oxides and hydroxides Oxide and hydroxide of Be are amphoteric. They act like acid as well like base.It can neutralize both acid and base.
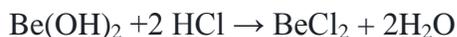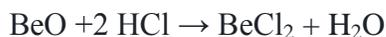
As acid

$2BeO + 4NaOH \; 2Na_2BeO_2 + 2H_2O$

$$Be(OH)_2 + 2NaOH \rightarrow Na_2[Be(OH)_4]$$
As Base;
$$BeO + 2 HCl \rightarrow BeCl_2 + H_2O$$
$$Be(OH)_2 + 2 HCl \rightarrow BeCl_2 + 2H_2O$$

14. Why the atomic radius of argon is than the entire member of third period?

➢ The number of protons in the nucleus increases so.
➢ The nuclear charge increases.
➢ There are more electrons, but the increase in shielding is negligible because each extra electron enters the same principal energy level.
➢ Therefore the force of attraction between the nucleus and the electrons increases.
➢ So the atomic radius decreases.

As the number of electrons in each atom increases going across Period 3, you might expect the atomic radius to increase. This does not happen, because the number of protons also increases and there is relatively little extra shielding from electrons in the same principal energy level.

15. Why fall in ionization energy occurs at Al and S in same period?

Ionization energy depends on the electronic configuration of the atoms.
Half-filled shells and sub shells are more stable than partially filled shell and sub shells. Or
. The electronic configuration of group 2A is ns2 while that of group 3A(Al) is 3s2,P1. Therefore it is easy to remove electron from Al (P1) than from Mg(2S2).similarly the electronic configuration of Group 5A is ns2, nP3(half-filled or more stable) and that of Sulphur is ns2 , np4, partially filled. The electron removing from N is difficult than from S. therefore I.E of Al and S is lesser than Mg and P respectively.

16. Why the compounds of Sn^{4+} are covalent in nature while those of Sn^{2+} are ionic?

The valence electronic configuration of 4A group is ns^2, np^2. It means that these elements can show the oxidation state of 4 as well as 2.the top elements like C and Si always exist in +4 oxidation state while the bottom elements like Sn and Pb show +2 as well as +4 oxidation state.
As Sn^{+4} is small in size than Sn^{+2}, and fajan's rule state that small cation of high charge density has high polarizing tendency than larger cation of lower charge density. Therefore Sn^{+4} ions pull the electrons clouds more easily from the respective anion such that the electrons are effectively shared. That is why $SnCl_4$ is covalent. Therefore $SnCl_4$ is discrete molecule or molecular compound.
$SnCl_2$ has more ionic character because of the higher size of Sn+2 ions. And exist in polymeric form.

Long Questions

1. **Explain halide ions as reducing agents and discuss their trends reducing strength.**

Halide ions as reducing agents:

the redox reactions involving halide ions and concentrated sulfuric acid, using these reactions to discuss the trend in reducing ability of the ions from fluoride to iodide. Two types of reactions might occur when concentrated sulfuric acid is added to a solid ionic halide like sodium fluoride, chloride, bromide or iodide. The concentrated sulfuric acid can act as both an acid and an oxidizing agent.

Concentrated sulfuric acid acting as an acid

The concentrated sulfuric acid transfers a proton to the halide ion to produce a gaseous hydrogen halide, which immediately escapes from the system. If the hydrogen halide is exposed to moist air, steam fumes are formed. For example, concentrated sulfuric acid reacts with solid sodium chloride at low temperatures to produce hydrogen chloride and sodium bisulfate, as in the following equation:

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$

$$NaCl + H_2SO_4 \rightarrow HCl + NaHSO_4$$
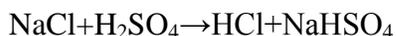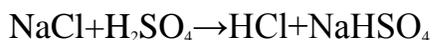
All the halide ions behave similarly.

Concentrated sulfuric acid acting as an oxidizing agent

With fluoride or chloride

Concentrated sulfuric acid is not a strong enough oxidizing agent to oxidize fluoride or chloride. In those cases, only the steamy fumes of the hydrogen halide—hydrogen fluoride or hydrogen chloride—are produced. In terms of the halide ions, fluoride and chloride are not strong enough reducing agents to reduce the sulfuric acid. This is not the case for bromides and iodides.
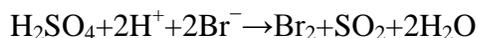
With bromide

Bromide is a strong enough reducing agent to reduce sulfuric acid. Bromide is oxidized to bromine in the process, as in the half-equation below:

$$2Br^- \rightarrow Br_2 + 2e^-$$
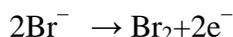
Bromide reduces sulfuric acid to sulfur dioxide gas, decreasing the oxidation state of sulfur from +6 to +4. The half-equation for this transition is as follows:

$$H_2SO_4 + 2H^+ + 2e^- \rightarrow SO_2 + 2H_2O$$
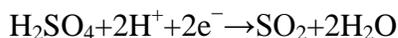
These two half-equations can be combined into the overall ionic equation for the reaction:

$$H_2SO_4 + 2H^+ + 2Br^- \rightarrow Br_2 + SO_2 + 2H_2O$$

In practice, this reaction is confirmed by the steamy fumes of hydrogen bromide contaminated with the brown color of bromine vapor. The sulfur dioxide is a colorless gas, its presence cannot be directly observed.

With Iodide

Iodide is a stronger reducing agent than bromide, and it is oxidized to iodine by the sulfuric acid:

$$2I^-\rightarrow I_2+2e^-$$
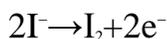
The reduction of the sulfuric acid is more complicated than with bromide. Iodide is powerful enough to reduce it in three steps:

- ➢ sulfuric acid to sulfur dioxide (sulfur oxidation state = +4)
- ➢ sulfur dioxide to elemental sulfur (oxidation state = 0)
- ➢ Sulfur to hydrogen sulfide (sulfur oxidation state = -2).

The most abundant product is hydrogen sulfide. The half-equation for its formation is as follows:

$$H_2SO_4+8H^++8e^-\rightarrow H_2S+4H_2O$$

Combining these two half-equations gives the following net ionic equation:

$$H_2SO_4+8H^++8I^-\rightarrow 4I_2+H_2S+4H_2O$$
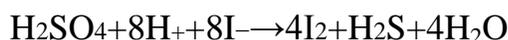
This is confirmed by a trace of steamy fumes of hydrogen iodide, and a large amount of iodine. The reaction is exothermic: purple iodine vapor is formed, with dark gray solid iodine condensing around the top of the reaction vessel. There is also a red color where the iodine comes into contact with solid iodide salts. The red color is due to the I_3^- ion formed by reaction between I_2 molecules and I^- ions. Hydrogen sulfide gas can be detected by its "rotten egg" smell, but this gas is intensely poisonous.

Explaining the trend

An over-simplified explanation

The following explanation is only (partially) accurate if fluoride is neglected works. When a halide ion acts as a reducing agent, it transfers electrons to something else. That means that the halide ion itself loses electrons. The larger the halide ion, the farther the outer electrons are from the nucleus, and the more they are shielded by inner electrons. It therefore gets easier for the halide ions to lose electrons down the group because there is less attraction between the outer electrons and the nucleus. This argument seems valid, but it is flawed. The energetics of the change must be examined.

A more detailed explanation

Enthalpy change variation between halogens

The amount of heat evolved or absorbed when a solid halide (like sodium chloride) is converted into an elemental halogen must be considered. Taking sodium chloride as an example, the following energetic quantities are important:

- ➢ The energy required to break the attractions between the ions in the sodium chloride (the lattice enthalpy).
- ➢ The energy required to remove the electron from the chloride ion. This is the reverse of the electron affinity of the chlorine (the electron affinity can be acquired from a data table and negated).
- ➢ The energy recovered when the chlorine atoms convert to diatomic chlorine. Energy is released when these bonds are formed. Chlorine is simple because it is a gas. In bromine and iodine, heat is also released during condensation to a liquid or a solid, respectively. To account for this, it is simpler to

think in terms of atomization energy rather than bond energy. The value of interest is the reverse of atomization energy.

Atomization energy is the energy needed to produce 1 mole of isolated gaseous atoms starting from an element in its standard state (gas for chlorine, and liquid for bromine, for example - both of them as X_2). The figure below shows how this information fits together:
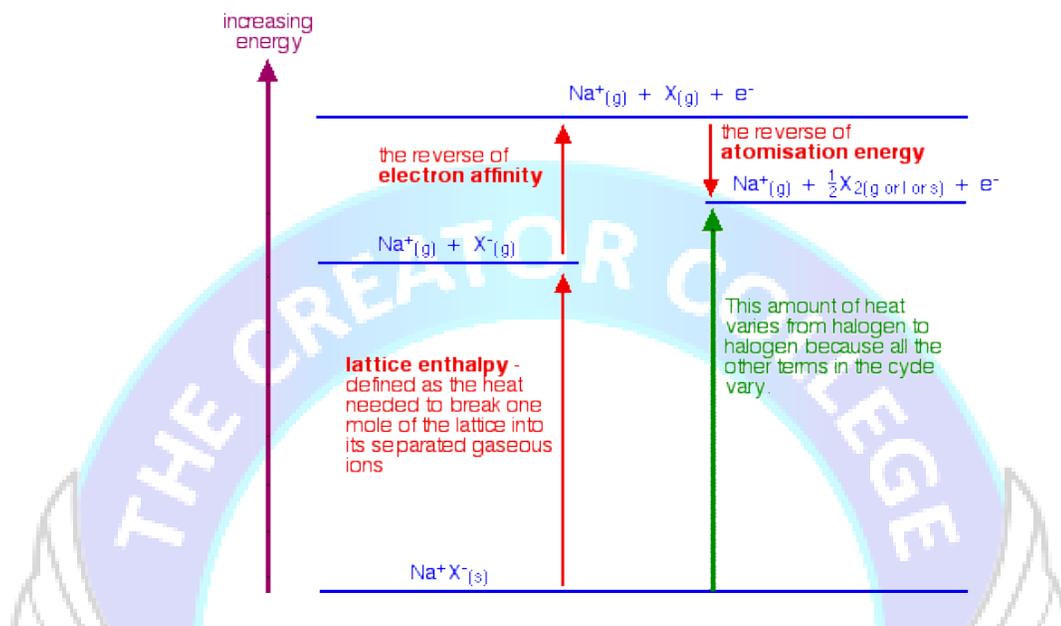
The enthalpy change shown by the green arrow in the diagram for each of the halogens must be compared. The diagram shows that the overall change involving the halide ions is endothermic (the green arrow is pointing up toward a higher energy).

This is not the total enthalpy change for the whole reaction. Heat is emitted when the changes involving the sulfuric acid occur. That is the same irrespective of the halogen in question. The total enthalpy change is the sum of the enthalpy changes for the halide ion half-reaction and the sulfuric acid half-reaction.

The table below shows the energy changes that vary from halogen to halogen. The process is assumed to start from the solid sodium halide. The values for the lattice enthalpies for other solid halides would be different, but the pattern would be the same.

	heat needed to break up NaX lattice (kJ mol^{-1})	heat needed to remove electron from halide ion (kJ mol^{-1})	heat released in forming halogen molecules (kJ mol^{-1})	sum of these (kJ mol^{-1})
F	+902	+328	-79	+1151
Cl	+771	+349	-121	+999
Br	+733	+324	-112	+945
I	+684	+295	-107	+872

The overall enthalpy change for the halide half-reaction:

The sum of the enthalpy changes, in the final column, is decreasingly endothermic down the group. The total change in enthalpy (including the sulfuric acid) is also less positive.

The amount of heat produced in the half-reaction involving the sulfuric acid must be great enough to make the reactions with the bromide or iodide feasible, but not enough to compensate for the more positive values produced by the fluoride and chloride half-reactions.

Exploring the changes in the various energy terms

In this section, the individual energy terms in the table that are most important in making the halogen half-reaction less endothermic down the group are determined.

Chlorine to iodine

From chlorine to iodine, the lattice enthalpy changes most, decreasing by 87 kJ mol^{-1}. By contrast, the energy required to remove the electron decreases by only 54 kJ mol^{-1}. Both of these terms matter, but the decrease in lattice enthalpy is the more significant. This quantity decreases because the ions are getting larger. That means that they are farther away from each other, and so the attractions between positive and negative ions in the solid lattice are lessened.

The simplified explanation mentioned earlier is misleading because it concentrates on the less-important decrease in the amount of energy needed to remove the electron from the ion.

Fluorine

Fluoride ions are very difficult to oxidize to fluorine. The table above shows that this has nothing to do with the amount of energy required to remove an electron from a fluoride ion. It actually takes less energy to remove an electron from a fluoride ion than from a chloride ion. The generalization that an electron becomes easier to remove as the ion becomes larger does not apply here.

Fluoride ions are so small that the electrons experience strong repulsion from each other. This outweighs the effect of their closeness to the nucleus and makes them easier to remove than the simplified argument predicts.

There are two important reasons why fluoride ions are so difficult to oxidize. The first is the comparatively high lattice enthalpy of the solid fluoride. This is due to the small size of the fluoride ion, which means that the positive and negative ions are very close together and therefore strongly attracted to each other. The other factor is the small amount of heat that is released when the fluorine atoms combine to make fluorine molecules (see the table above). This is due to the low bond enthalpy of the F-F bond. The reason for this low bond enthalpy is discussed on a separate page.

2.   **Discuss the atomic and physical properties of halogens.**

The trends in the atomic and physical properties of the Group 7 elements (the halogens): fluorine, chlorine, bromine and iodine. Sections below cover the trends in atomic radius, electronegativity, electron affinity, melting and boiling points, and solubility, including a discussion of the bond enthalpies of halogen-halogen and hydrogen-halogen bonds.

Trends in Atomic Radius

Atomic radii of the Group 7 elements
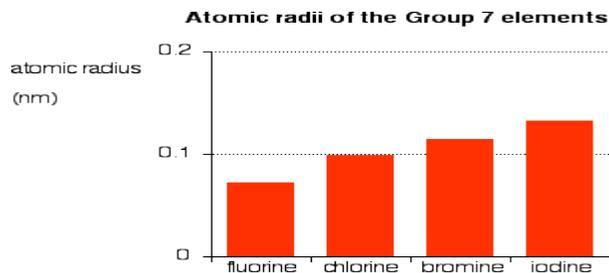
The figure above shows the increase in atomic radius down the group.

Explaining the increase in atomic radius

The radius of an atom is determined by:

➢ The number of layers of electrons around the nucleus
➢ The pull the outer electrons feel from the nucleus.

Compare the numbers of electrons in each layer of fluorine and chlorine:

F		2,7
Cl		2,8,7

In each case, the outer electrons feel a net +7 charge from the nucleus. The positive charge on the nucleus is neutralized by the negative inner electrons.
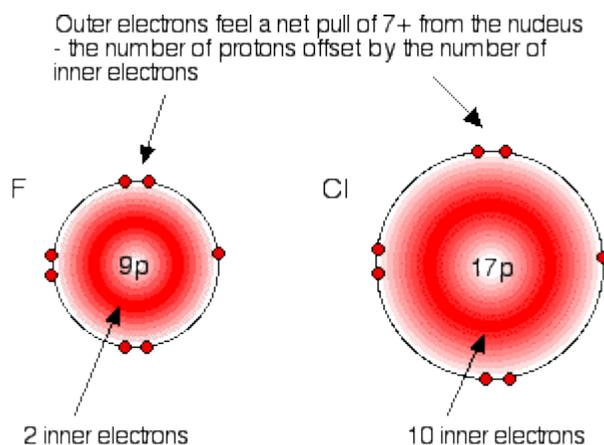
This is true for all the atoms in Group 7: the outer electrons experience a net charge of +7..

The only factor affecting the size of the atom is therefore the number of layers of inner electrons surrounding the atom. More layers take up more space due to electron repulsion, so atoms increase in size down the group.

Trends in Electronegativity

Electronegativity is a measure of the tendency of an atom to attract a bonding pair of electrons. It is usually measured on the Pauling scale, on which the most electronegative element (fluorine) is assigned an electronegativity of 4.0. The figure below shows electronegativities for each halogen:

Electronegativity of the Group 7 elements
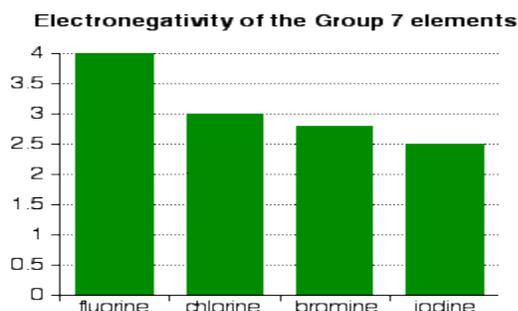
Notice that electronegativity decreases down the group. The atoms become less effective at attracting bonding pairs of electrons. This effect is illustrated below using simple dots-and-crosses diagrams for hydrogen fluoride and hydrogen chloride:

HF   HCl
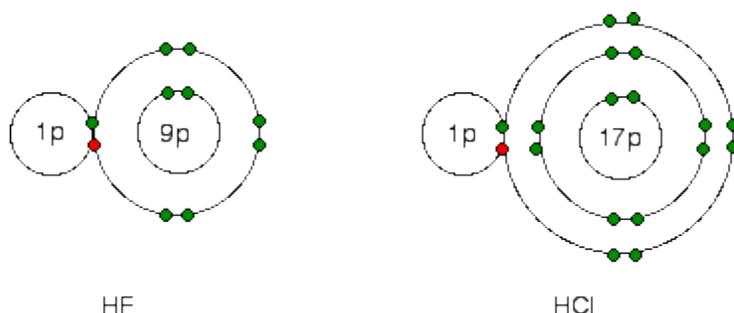
The bonding pair of electrons between the hydrogen and the halogen experiences the same net pull of +7 from both the fluorine and the chlorine. However, in the chlorine case, the nucleus is farther away from the bonding electrons, which are therefore not as strongly attracted as in the fluorine case.

The stronger attraction from the closer fluorine nucleus makes fluorine more electronegative than chlorine.

Summarizing the trend down the Group

As the halogen atoms increase in size, any bonding pair gets farther away from the halogen nucleus, and so is less strongly attracted toward it. Hence, down the group, the elements become less electronegative.

Trends in First Electron Affinity

The first electron affinity is the energy released when 1 mole of gaseous atoms each acquire an electron to form 1 mole of gaseous 1- ions. In other words, it is the energy released in the following process:

$X_{(g)} + e^- \rightarrow X^-_{(g)}$
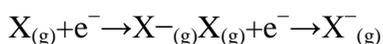
First electron affinities have negative values by convention. For example, the first electron affinity of chlorine is -349 kJ mol^{-1}. The negative sign indicates a release of energy.

The first electron affinities of the Group 7 elements

The electron affinity is a measure of the attraction between the incoming electron and the nucleus. There is a positive correlation between attraction and electron affinity. The trend down the group is illustrated below:
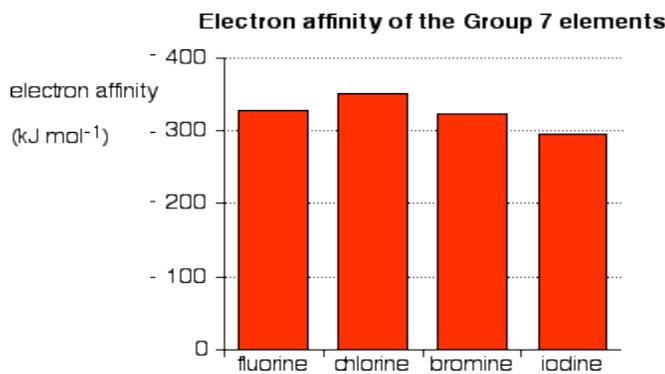
Notice that the trend down the group is inconsistent. The electron affinities generally decrease (meaning less heat is emitted), but the fluorine value deviates from this trend.
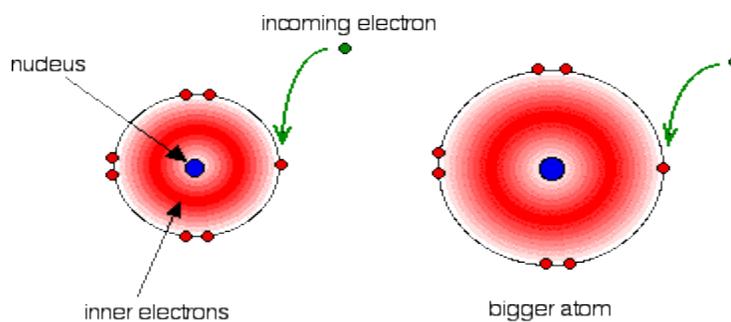

In the larger atom, the attraction from the more positive nucleus is offset by the additional screening electrons, so each incoming electron feels the effect of a net +7 charge from the center.

As the atom increases in size, the incoming electron is farther from the nucleus and so feels less attraction. The electron affinity therefore decreases down the group. However fluorine is a very small atom, with the incoming electron relatively close to the nucleus, and yet the electron affinity is smaller than expected.

Another effect must be considered in the case of fluorine. As the new electron comes approaches the atom, it enters a region of space already very negatively charged because of the existing electrons. The resulting repulsion from these electrons offsets some of the attraction from the nucleus.

Because the fluorine atom is very small, its existing electron density is very high. Therefore, the extra repulsion is particularly great and diminishes the attraction from the nucleus enough to lower the electron affinity below that of chlorine.

Trends in Melting Point and Boiling Point

Melting and boiling points of the Group 7 elements
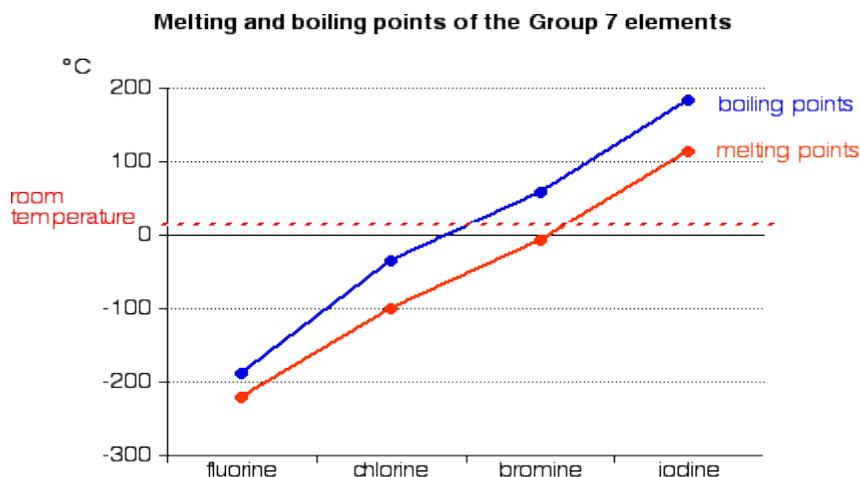
Melting and boiling points increase down the group. As indicated by the graph above, fluorine and chlorine are gases at room temperature; bromine is a liquid and iodine a solid.

Explaining the trends in melting point and boiling point

All the halogens exist as diatomic molecules—F_2, Cl_2, and so on. Van der Waals dispersion forces are the primary intermolecular attractions between one molecule and its neighbors. Larger molecules farther down the group have more electrons which can move around and form the temporary dipoles that create these forces.

The stronger intermolecular attractions down the group require more heat energy for melting or vaporizing, increasing their melting or boiling points.
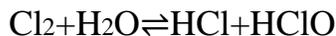
Solubilities:

Solubility in water

Fluorine reacts violently with water to produce aqueous or gaseous hydrogen fluoride and a mixture of oxygen and ozone; its solubility is meaningless. Chlorine, bromine and iodine all dissolve in water to some extent, but there is again no discernible pattern. The following table shows the solubility of the three elements in water at 25°C:

	solubility (mol dm^{-3})
chlorine	0.091
bromine	0.21
iodine	0.0013

Chlorine dissolved in water produces a pale green solution. Bromine solution adopts a range of colors from yellow to dark orange-red depending on the concentration. Iodine solution in water is very pale brown. Chlorine reacts with water to some extent, producing a mixture of hydrochloric acid and chloric(I) acid (also known as hypochlorous acid). The reaction is reversible, and at any time only about a third of the chlorine molecules have reacted.

$$Cl_2 + H_2O \rightleftharpoons HCl + HClO$$

Chloric(I) acid is sometimes symbolized as HOCl, indicating the actual pattern bonding pattern. Bromine and iodine form similar compounds, but to a lesser extent. In both cases, about 99.5% of the halogen remains unreacted.

The solubility of iodine in potassium iodide solution

Although iodine is only slightly soluble in water, it dissolves freely in potassium iodide solution, forming a dark red-brown solution. A reversible reaction between iodine molecules and iodide ions gives I_3^- ions. These are responsible for the color. In the laboratory, iodine is often produced through oxidation of iodide ions. As long as there are any excess iodide ions present, the iodine reacts to form I_3^-. Once the iodide ions have all reacted, the iodine is precipitated as a dark gray solid.

Solubility in hexane

The halogens are much more soluble in organic solvents such as hexane than they are in water. Both hexane and the halogens are non-polar molecules, so the only intermolecular forces between them are van der Waals dispersion forces. Because of this, the attractions broken (between hexane molecules and between halogen molecules) are similar to the new attractions made when the two substances mix. Organic solutions of iodine are pink-purple in color.

Bond enthalpies (bond energies or bond strengths)

Bond enthalpy is the heat required to break one mole of covalent bonds to produce individual atoms, starting from the original substance in the gas state, and ending with gaseous atoms. For chlorine, $Cl_{2(g)}$, it is the heat energy required for the following reaction, per mole:

$$Cl-Cl_{(g)} \rightarrow 2Cl_{(g)}$$
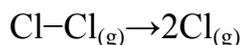
Although bromine is a liquid, the bond enthalpy is defined in terms of gaseous bromine molecules and atoms, as shown below:


Br — Br$_{(g)}$ ⟶ 2Br$_{(g)}$

Note: GAS not liquid!

Bond enthalpy in the halogens, $X_{2(g)}$

Covalent bonding is effective because the bonding pair is attracted to both the nuclei at either side of it. It is that attraction which holds the molecule together. The extent of the attraction depends in part on the distances between the bonding pair and the two nuclei. The figure below illustrates such a covalent bond:
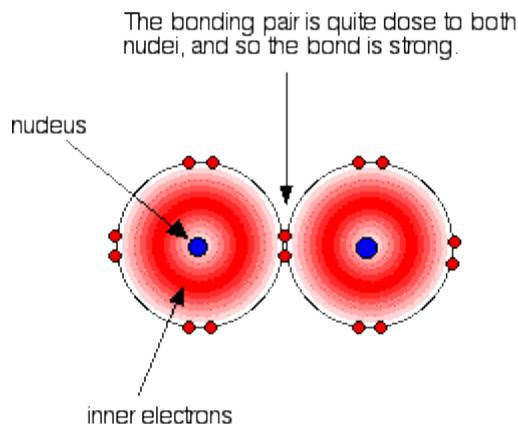

In all halogens, the bonding pair experiences a net +7 charge from either end of the bond, because the charge on the nucleus is offset by the inner electrons. As the atoms get larger down the group, the bonding pair is further from the nuclei and the strength of the bond should, in theory, decrease, as indicated in the figure below. The question is whether experimental data matches this prediction.
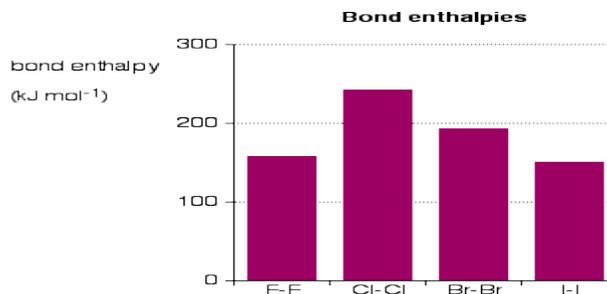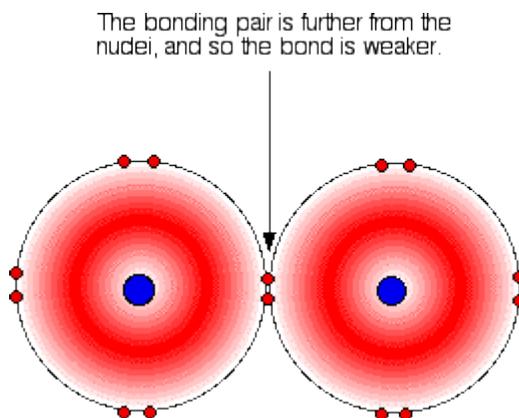
As is clear from the figure above, the bond enthalpies of the Cl-Cl, Br-Br and I-I bonds decreases as predicted, but the F-F bond enthalpy deviates.

Because fluorine atoms are so small, a strong bond is expected—in fact, it is remarkably weak. There must be another factor for consideration.

In addition to the bonding pair of electrons between the two atoms, each atom has 3 lone pairs of electrons in the outer shell. If the bond is very short, as in F-F, the lone pairs on the two atoms are close enough to cause significant repulsion, illustrated below:

As the atoms get smaller, lone pairs on the two atoms get close enough together to experience serious repulsion.

lone pairs
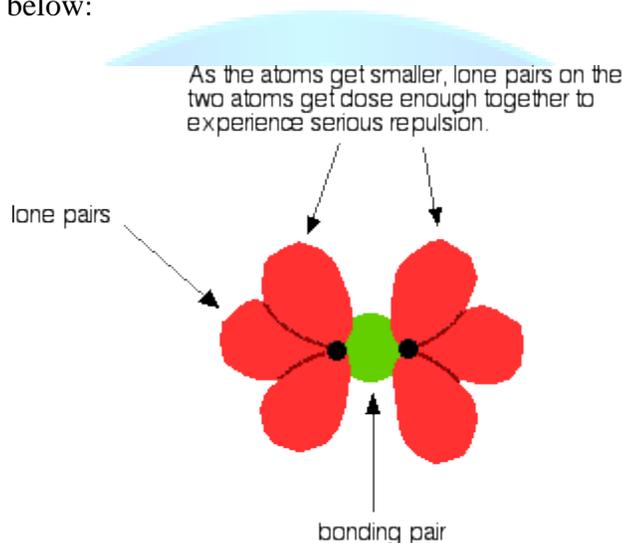
bonding pair

In the case of fluorine, this repulsion is great enough to counteract much of the attraction between the bonding pair and the two nuclei. This weakens the bond.

Bond enthalpies in the hydrogen halides, $H_{X(g)}$

If the halogen atom is attached to a hydrogen atom, this does not occur; there are no lone pairs on a hydrogen atom. Bond enthalpies for halogen-hydrogen bonds are given below:

Bond enthalpies

bond enthalpy
$(kJ\ mol^{-1})$

H-F	H-Cl	H-Br	H-I
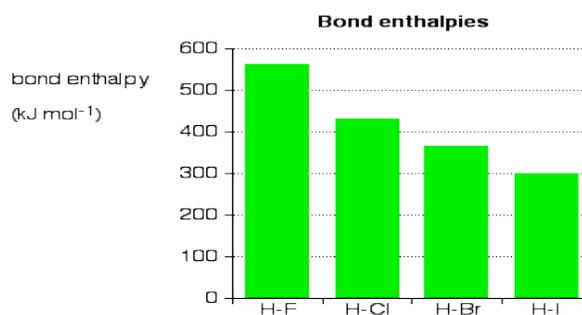
As larger halogens are involved, the bonding pair is more distant from the nucleus. The attraction is lessened, and the bond should be weaker; this is supported by the data, without exception. This fact has significant implications for the thermal stability of the hydrogen halides— they are easily broken into hydrogen and the halogen on heating.

Hydrogen fluoride and hydrogen chloride are thermally very stable under typical laboratory conditions. Hydrogen bromide breaks down to some extent into hydrogen and bromine on heating, and hydrogen iodide is even less stable when heated. Weaker bonds are more easily broken.

What is meant by bond enthalpy? Explain the bond enthalpies in halogens and hydrogen halides.

The amount of energy released during the formation of one mole of bonds from the gaseous atoms is called bond energy or bond enthalpy.
OR
The amount of energy required to break one mole of bonds into their gaseous atoms is called bond enthalpy or bond energy.
Bond Enthalpy of Halogens; Bond enthalpy depends on atomic size. Greater the atomic size lower the bond enthalpy. Bond enthalpy of F2 is unexpectedly lower than Cl2 due to the extra ordinary low atomic size of fluorine which create a little repulsion between two fluorine atoms.

F — F	158kj/mol
Cl — Cl	242 kj/mol
Br — Br	193 kj/mol
I —I	151 kj/mol

Bond Enthalpy of Hydrogen Halides
Bond enthalpy also depends on the difference in electronegativity. Greater the difference in electronegativity of two atoms, high is the polarity or ionic character and higher the bond enthalpy.
As the electronegativity difference in halogen acids decrease down the group therefore bond enthalpy decrease down the group. Therefore H — F is the strongest and H — I is the weakest among them.
The trends in bond enthalpy of Halogen acids are given as follow
Bond --

H — F

H — Cl

H — Br

H — I
Bond enthalpy in kj/mol 568 --------432-- 366 --------298

3.   **Discuss physical properties of IV-A elements.**

- The atomic radii increases down the group as the elements gain extra energy levels. The increased shielding effect of the full inner shells more than outweighs the increased nuclear charge and so the outer electrons are attracted less strongly.
- Ionic radii increase down the group. Ions are much smaller than atoms because they have lost the outer energy level and the nuclear charge is attracting four fewer electrons.
- Ionization energies decrease down the group as the outer electrons become further from the nucleus and more highly shielded from the inner shells.

The Inert-pair effect

Each element has four outer electrons $ns^2 np^2$. The shielding of the outer shell for C and Si is quite efficient.

However, as we descend the group due to the presence of d and f electrons, which offer poor shielding, the outer s electrons are withdrawn into the atomic core and begin to behave as inner electrons.

Hence, Pb and Sn often behave as if they only have two outer electrons and show valencies of +2 and +4.

Structure of the elements

C, Si, Ge are all giant covalent, Sn and Pb are metallic.

This trend reflects the decreased ionization energies and the increasing importance of the inert-pair effect.

Properties related to structure

Melting and boiling points all decrease as we descend the group. There is a dramatic decrease after Ge which reflects this change in structure.

Density and conductivity increase down the group reflecting the increasing metallic character.

Electronegativity drops dramatically between C and Si due to the increased shielding effect and weaker attraction for the outer bonding electrons. There is little decrease after this due to the ineffectiveness of d and f electrons in shielding.

Oxidation states

There are two stable oxidation states in Group IV, +2 and +4.

The relative stabilities of the oxidation states vary within the group as shown in the following graph.

ox. state stability
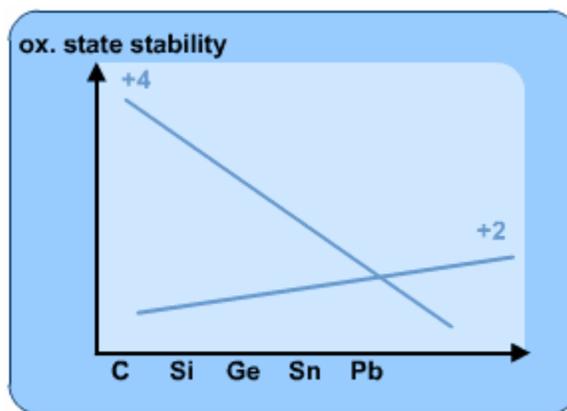
+4 Oxidation State

a) All elements have four outer electrons and so the main oxidation state for most elements is +4. The bonding in most compounds is covalent as too much energy would be needed to form M^{4+} ion.

Only PbF_4 and SnF_4 are truly ionic. Most compounds have a tetrahedral arrangement around the metal.

b) +4 is the most stable state for C, Si, Ge and Sn but is the least stable for Pb. Compounds of Pb(IV) are easily reduced to Pb(II) and are strong oxidising agents.

For example:

$$PbO_{2(s)} + 4HCl_{(aq)} \rightarrow PbCl_{2(s)} + 2H_2O_{(l)} + Cl_{2(g)}$$

+2 Oxidation State

In this oxidation state only the p electrons are used in bonding and the s electrons exhibit the inert-pair effect. It is most unstable for C and Si but is most stable for Pb.

Compounds of both Pb(II) and Sn(II) are common and the bonding in them ionic. Compounds of C(II), Si(II), Ge(II) and Sn(II) are easily oxidised and are therefore strong reducing agents.

For example:

$$2CO_{(g)} + O_{2(g)} \rightarrow 2CO_{2(g)}$$
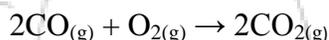
4. **Discuss oxides of carbon family and explain the inert pair effect in the formation of ionic and covenant bond.**

These elements form two types of oxides, *i.e.* monoxides and dioxides. In which these oxides show oxidation state +2 and +4. Monoxides are CO, SnO, PbO , while dioxides are CO_2, SnO_2, PbO_2. The oxides of C and Si are non-metals oxides and are covalent in nature while oxides of tin and lead are metallic and ionic inert pair effect in formation of ionic and covalent bond.

Electronic configuration of group 4A is ns^2, np^2. The oxidation state of +4 is found where all these 4 electrons of valence shell are involved in bonding. The involvement of 4 electrons in bonding must be due to hybridization. Hybridized orbitals form sigma bonds. It means that the compounds showing +4 oxidation states in their compounds will be covalent like $PbCl_4$ and SnCl4 these are discrete molecules. If the elements of group 4 form +2 oxidation state they will involve 2 electrons of p sub shell and keep s electron inert (called inert pair effect). This is

its stable oxidation state .and the compounds like $PbCl_2$ and $SnCl_2$ will formed they will show more ionic character.

As the size of Pb^{+2} is larger than Pb^{+4}. According to fajan's rule larger size cation has low polarizability than ion of smaller size. Therefore the cation of larger size has greater tendency to form ionic bond.

5.   What are the trend in thermal stability of nitrate and carbonates of group II-A elements.

Both carbonates and nitrates of Group 2 elements become more thermally stable down the group. The larger compounds further down require more heat than the lighter compounds in order to decompose.

All the carbonates in this group undergo thermal decomposition to the metal oxide and carbon dioxide gas. The term "thermal decomposition" describes splitting up a compound by heating it.

All the Group 2 carbonates and their resulting oxides exist as white solids. If "X" represents any one of the elements, the following describes this decomposition:

$$XCO_{3(s)} \rightarrow XO_{(s)} + CO_{2(g)}$$

Down the group, the carbonates require more heating to decompose. The carbonates become more thermally stable down the group.

The Group 2 nitrates undergo thermal decomposition to the metal oxide, nitrogen dioxide and oxygen gas. These compounds are white solids and brown nitrogen dioxide and oxygen gases are also given off when heated. Magnesium and calcium nitrates normally crystallize with water, and the solid may dissolve in its own water of crystallization to make a colorless solution before it starts to decompose.
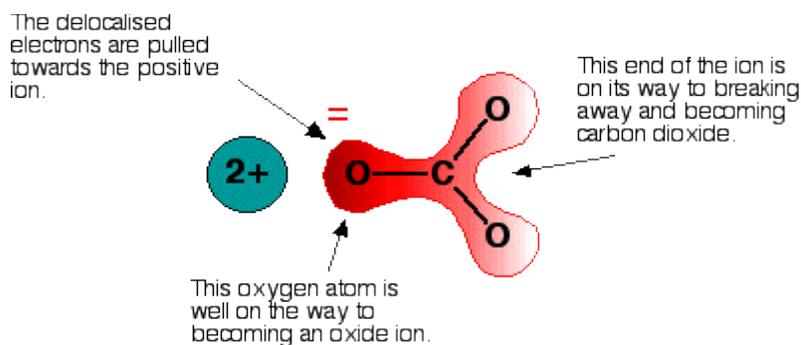
Again, if "X" represents any one of the elements:

$$2X(NO_3)_{2(s)} \rightarrow 2XO_{(s)} + 4NO_{2(g)} + O_{2(g)}$$

Down the group, the nitrates must also be heated more strongly before they will decompose. Group 2 nitrates also become more thermally stable down the group.

Why?

➢ A small 2+ ion has a lot of charge packed into a small volume of space. In other words, it has a high charge density and has a marked distorting effect on any negative ions which happen to be near it. A bigger 2+ ion has the same charge spread over a larger volume of space, so its charge density is lower; it causes less distortion to nearby negative ions.

➢ If carbonate ion is placed next to a cation, such as a Group 2 ion, the cation attracts the delocalized electrons in the carbonate ion, drawing electron density toward itself. The carbonate ion becomes polarized.

The delocalised electrons are pulled towards the positive ion.

This end of the ion is on its way to breaking away and becoming carbon dioxide.

This oxygen atom is well on the way to becoming an oxide ion.

If the carbonate is heated the carbon dioxide breaks free, leaving the metal oxide.

The amount of heating required depends on the degree to which the ion is polarized. More polarization requires less heat. The smaller the positive ion is the higher the charge density, and the greater effect it will have on the carbonate ion. As the positive ions get larger down the group, they effect on the carbonate ions near them less. More heat must be supplied for the carbon dioxide to leave the metal oxide.

In other words, the carbonates become more thermally stable down the group.

- **Enthalpy changes**

The enthalpy changes for the decomposition of the various carbonates indicate that the reactions are strongly endothermic, implying that the reactions likely require constant heating to proceed. Remember that the reaction in question is the following:

$$XCO_{3(s)} \rightarrow XO_{(s)} + CO_{2(g)}$$

The calculated enthalpy changes (in kJ mol-1) are given in the table below (there is no available data for beryllium carbonate).

Carbonat	$\Delta H \Delta H$
$MgCO_3$	+117
$CaCO_3$	+178
$SrCO_3$	+235
$BaCO_3$	+267

The reactions are more endothermic down the group, as expected, because the carbonates become more thermally stable, as discussed above.

6.   Write down atomic and physical properties of group I-A and group II-A elements.

Groups, by the way, are the vertical columns on a periodic table, and **group 1A** is on the far left. Sometimes you'll see group 1A written with a Roman numeral, or **group IA**. It's a good idea to get used to seeing it both ways.

All of the alkali metals are in the same group because they share similar properties, so it might not appear that batteries, bananas, and table salt have a whole lot in common, but the elements that make them up (lithium, potassium, and sodium) sure do!

Properties

Let's take a look at some of these similarities. **Valence electrons** are the outermost electrons and give elements a lot of their properties. All of the elements in group 1A have one valence electron, so that should be easy to remember! Having one valence electron makes alkali metals extremely reactive, meaning they desperately want to bond (or attach) to other elements.

As you go down the group, the alkali metals become more reactive, meaning potassium is much more reactive than sodium. When exposed to water, the alkali metals actually cause an explosion! In addition to causing an explosion, these elements form an alkaline substance when they react with water, hence the name alkali metal. Alkaline substances are also called bases and are substances that have a pH greater than seven.

You might not know it, but you are familiar with some alkali metals that have combined with water. For example, hair relaxers, shaving creams, hair-removing creams, and drain cleaners all contain at least a small amount of a base that was formed from the reaction of an alkali metal with water.

Let's talk a little bit more on how alkali metals bond, or attach to other elements. Do you remember when I said alkali metals have one valence electron? The valence electrons are gained, lost, or shared when elements bond together.

Having just one valence electron makes alkali metals unstable, so when they come into contact with an element that needs some electrons, it gives up its one electron and becomes a **cation**, or a positively charged atom. Electrons are negatively charged, so if an element gives up an electron, it becomes positively charged. So, since alkali metals lose one electron, they have a +1 charge. Since they give up an electron, they tend to form **ionic bonds**, or bonds that are formed when one atom gives its electrons to another atom.

7.   Explain the reaction of Group II-A elements with oxygen.

Reactions with Group 2 Elements

The elements of Group 2 are beryllium, magnesium, calcium, strontium, barium, and radioactive radium. Alkaline earth metals also react with oxygen, though not as rapidly as Group 1 metals; these reactions also require heating. Similarly to Group 1 oxides, most group 2 oxides and hydroxides are only slightly soluble in water and form basic or alkaline solutions.

All Group 2 metals all react similarly, burning to form oxides (compounds containing the O^{2-} ion) as shown:

$$2M_{(s)} + O2_{(g)} \rightarrow 2MO_{(s)}$$
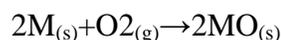
Once initiated, the reactions with oxygen are vigorous. The only peroxides (compounds containing the O_2^{2-} ion) that can be formed from alkaline metals are strontium peroxide and barium peroxide. Both reactions require heat and *excess* oxygen. The general reaction is given below:

$$M_{(s)} + O_{2(g)} \rightarrow MO_{2(s)}$$
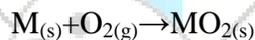
Where M represents Sr or Ba.

Beryllium

Beryllium is unreactive with air and water. The chemical behavior of beryllium is best attributed to its small size and high ionization energy of its atoms.
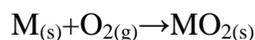
All other group 2 metals

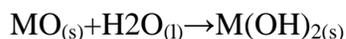Except beryllium, the other alkaline earth metals form oxides in air at *room temperature*.

$$2M_{(s)} + O_{2(g)} \rightarrow 2MO_{(s)}$$
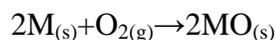
where M represents Be, Mg, Ca, Sr, Ba, or Ra.

Peroxides, of the form MO_2, are formed for all these elements except beryllium as shown:

$$M_{(s)} + O_{2(g)} \rightarrow MO_{2(s)}$$

Magnesium, calcium, strontium and barium oxides react with water to form hydroxides:

$$MO_{(s)} + H2O_{(l)} \rightarrow M(OH)_{2(s)}$$

All the oxides and hydroxides of the group 2 metals, except of those of beryllium, are bases:

$$M(OH)_{2(s)} \rightarrow M_2^+{}_{(aq)} + 2OH^-{}_{(aq)}$$

8. Explain the properties of Hydroxide of third period elements.

Sodium and magnesium hydroxides

These contain hydroxide ions, and are simple basic hydroxides.

Aluminum hydroxide

Aluminum hydroxide, like aluminum oxide, is amphoteric (it has both basic and acidic properties).

The other "hydroxides"

All the other hydroxides have -OH groups covalently bound to the atom from period 3. These compounds are all acidic, ranging from the very weak silicic acids (one of which is shown below) to the very strong sulfuric or chloric(VII) acids.
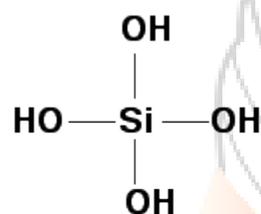
orthosilicic acid
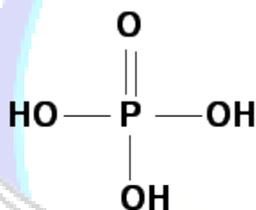
phosphoric(V) acid
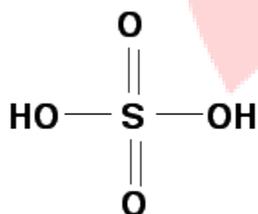
sulphuric acid
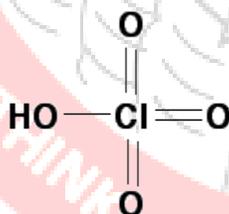
chloric(VII) acid

There are other acids (also containing -OH groups) formed by these elements, but these are the ones where the Period 3 element is in its highest oxidation state.

Additional details

Sodium and Magnesium Hydroxides

Sodium hydroxide and magnesium hydroxide are both basic because they contain hydroxide ions, which are strongly basic when solvated. Both species react with acids to form salts. For example, in dilute hydrochloric acid, sodium hydroxide and magnesium hydroxide form solutions of sodium chloride and magnesium chloride, respectively:

$$NaOH+HCl \rightarrow NaCl+H_2O$$

$$Mg(OH)_2+2HCl \rightarrow MgCl_2+2H_2O$$
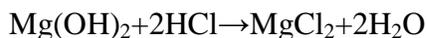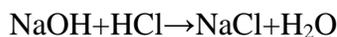
Aluminum Hydroxide

Aluminum hydroxide is amphoteric. Like sodium or magnesium hydroxides, it reacts with acids, showing basic character. When reacted with dilute hydrochloric acid, it forms a colorless solution of aluminum chloride:

$$Al(OH)_3+3HCl \rightarrow AlC_3+3H_2O$$
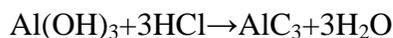
Aluminum hydroxide can also act as an acid, reacting (for example) with sodium hydroxide to give a colorless solution of sodium tetrahydroxoaluminate:

$$Al(OH)_3+NaOH \rightarrow NaAl(OH)$$

The other "hydroxides"

None of these compounds contain hydroxide ions. In each case the -OH group is covalently bound to the Period 3 element, and in each case it is possible for the hydrogen atoms on these -OH groups to be removed by a base. In other words, these compounds are acidic. However, their acidities vary considerably in strength:

Orthosilicic acid is very weak .

Phosphoric(V) acid is weak, but somewhat stronger than simple organic acids like ethanoic acid.

Sulfuric acid and chloric(VII) acid are both very strong.

The main consideration in determining the strength of the acid is the stability of the anion once the proton has been removed. This in turn depends on how much the negative charge can be delocalized (spread out) over the rest of the ion.

If the negative charge is entirely on the oxygen atom left behind from the -OH group, the anion is very unstable and thus attractive to protons. The lost proton is easily recaptured; therefore, the acid is weak.

Alternatively, if the charge can be distributed over the whole of the ion, the charge becomes so "dilute" that it cannot attract the hydrogen back very easily; therefore, the acid is strong.

In these compounds, the negative charge of the anion is delocalized through interaction with doubly-bonded oxygen atoms. For example, in chloric(VII) acid, the ion produced is the chlorate(VII) ion (also known as the perchlorate ion), ClO_4^-. The commonly-drawn structure of chloric acid, shown below, incorrectly shows the negative charge isolated to one oxygen atom:
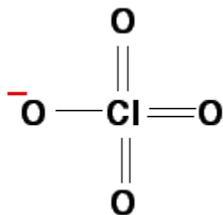
Instead, the charge is delocalized over the whole ion. Because of this, all four chlorine-oxygen bonds are identical, as shown:
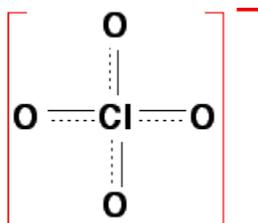
When sulfuric acid loses a hydrogen ion to form the hydrogen sulfate ion, HSO_4^-, the resulting negative charge is spread over three oxygen atoms (the original, deprotonated atom, and the two atoms doubly-bonded to sulfur). The charge is not as widely distributed as in perchlorate, but the delocalization is still quite effective; sulfuric acid is almost as strong as chloric(VII) acid.

Phosphoric(V) acid is much weaker than sulfuric acid because there is only one phosphorus-oxygen double bond which can be involved in charge delocalization; the charge is therefore delocalized less effectively.

In orthosilicic acid, there are no silicon-oxygen double bonds to delocalize the charge. The anion formed by deprotonation is not stabilized, and easily recovers its proton

9. Explain the acid base behavior of oxides of third period elements.

The oxides: The oxides of interest are given below:

Na_2O	MgO	Al_2O_3	SiO_2	P_4O_{10}	SO_3	Cl_2O_7
				P_4O_6	SO_2	Cl_2O

This trend applies only to the highest oxides of the individual elements (see the top row of the table), in the highest oxidation states for those elements. The pattern is less clear for other oxides. Non-metal oxide acidity is defined in terms of the acidic solutions formed in reactions with water—for example, sulfur trioxide reacts with water to forms sulfuric acid. They will all, however, react with bases such as sodium hydroxide to form salts such as sodium sulfate as explored in detail below.
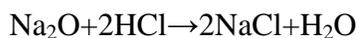
Sodium Oxide

Sodium oxide is a simple strongly basic oxide. It is basic because it contains the oxide ion, O^{2-}, which is a very strong base with a high tendency to combine with hydrogen ions.

Reaction with water: Sodium oxide reacts exothermically with cold water to produce sodium hydroxide solution. A concentrated solution of sodium oxide in water will have pH 14.

$$Na_2O+H_2O \rightarrow 2NaOH$$
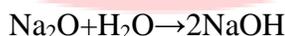
Reaction with acids: As a strong base, sodium oxide also reacts with acids. For example, it reacts with dilute hydrochloric acid to produce sodium chloride solution.

$$Na_2O+2HCl \rightarrow 2NaCl+H_2O$$

Magnesium oxide

Magnesium oxide is another simple basic oxide, which also contains oxide ions. However, it is not as strongly basic as sodium oxide because the oxide ions are not as weakly-bound. In the sodium oxide, the solid is held

together by attractions between 1+ and 2- ions. In magnesium oxide, the attractions are between 2+ and 2- ions. Because of the higher charge on the metal, more energy is required to break this association. Even considering other factors (such as the energy released from ion-dipole interactions between the cations and water), the net effect is that reactions involving magnesium oxide will always be less exothermic than those of sodium oxide.

Reaction with water: At first glance, magnesium oxide powder does not appear to react with water. However, the pH of the resulting solution is about 9, indicating that hydroxide ions have been produced. In fact, some magnesium hydroxide is formed in the reaction, but as the species is almost insoluble, few hydroxide ions actually dissolve. The reaction is shown below:

$$MgO + H_2O \rightarrow Mg(OH)_2$$
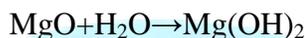
Reaction with acids: Magnesium oxide reacts with acids as predicted for a simple metal oxide. For example, it reacts with warm dilute hydrochloric acid to give magnesium chloride solution.

$$MgO + 2HCl \rightarrow MgCl_2 + H_2O$$
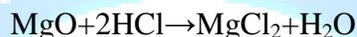
Aluminum Oxide

Describing the properties of aluminum oxide can be confusing because it exists in a number of different forms. One of those forms is very unreactive (known chemically as alpha-Al_2O_3) and is produced at high temperatures. The following reactions concern the more reactive forms of the molecule. Aluminium oxide is amphoteric. It has reactions as both a base and an acid.

Reaction with water: Aluminum oxide is insoluble in water and does not react like sodium oxide and magnesium oxide. The oxide ions are held too strongly in the solid lattice to react with the water.

Reaction with acids: Aluminum oxide contains oxide ions, and thus reacts with acids in the same way sodium or magnesium oxides do. Aluminum oxide reacts with hot dilute hydrochloric acid to give aluminum chloride solution.

$$Al_2O_3 + 6HCl \rightarrow 2AlCl_3 + 3H_2O$$
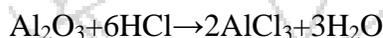
This reaction and others display the amphoteric nature of aluminum oxide.

Reaction with bases: Aluminum oxide also displays acidic properties, as shown in its reactions with bases such as sodium hydroxide. Various aluminates (compounds in which the aluminum is a component in a negative ion) exist, which is possible because aluminum can form covalent bonds with oxygen. This is possible because the electronegativity difference between aluminum and oxygen is small, unlike the difference between sodium and oxygen, for example (electronegativity increases across a period)

Aluminum oxide reacts with hot, concentrated sodium hydroxide solution to produce a colorless solution of sodium tetrahydroxoaluminate:

$$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2NaAl(OH)_4$$

**Silicon dioxide (silicon(IV) oxide)**

Silicon is too similar in electronegativity to oxygen to form ionic bonds. Therefore, because silicon dioxide does not contain oxide ions, it has no basic properties. In fact, it is very weakly acidic, reacting with strong bases.

Reaction with water: Silicon dioxide does not react with water, due to the thermodynamic difficulty of breaking up its network covalent structure.

Reaction with bases: Silicon dioxide reacts with hot, concentrated sodium hydroxide solution, forming a colorless solution of sodium silicate:

$$SiO_2 + 2NaOH \rightarrow Na_2SiO_3 + H_2O$$
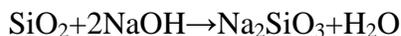
In another example of acidic silicon dioxide reacting with a base, the Blast Furnace extraction of iron, calcium oxide from limestone reacts with silicon dioxide to produce a liquid slag, calcium silicate:

$$SiO_2 + CaO \rightarrow CaSiO_3$$
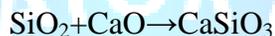
Phosphorus Oxides

Two phosphorus oxides, phosphorus(III) oxide, P_4O_6, and phosphorus(V) oxide, P_4O_{10}, are considered here.

Phosphorus(III) oxide: Phosphorus(III) oxide reacts with cold water to produce a solution of the weak acid, H_3PO_3—known as phosphorous acid, orthophosphorous acid or phosphonic acid:

$$P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$$

The fully-protonated acid structure is shown below:
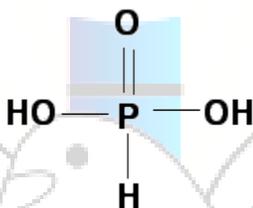
The protons remain associated until water is added; even then, because phosphorous acid is a weak acid, few acid molecules are deprotonated. Phosphorous acid has a pK_a of 2.00, which is more acidic than common organic acids like ethanoic acid ($pK_a = 4.76$).

Phosphorus(III) oxide is unlikely to be reacted directly with a base. In phosphorous acid, the two hydrogen atoms in the -OH groups are acidic, but the third hydrogen atom is not. Therefore, there are two possible reactions with a base like sodium hydroxide, depending on the amount of base added:

$$NaOH + H_3PO_3 \rightarrow NaH_2PO_3 + H_2O$$

$$2NaOH + H_3PO_3 \rightarrow Na_2HPO_3 + 2H_2O$$
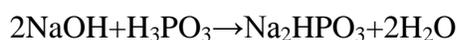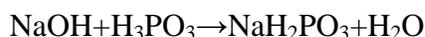
In the first reaction, only one of the protons reacts with the hydroxide ions from the base. In the second case (using twice as much sodium hydroxide), both protons react.

If instead phosphorus(III) oxide is reacted directly with sodium hydroxide solution, the same salts are possible:

$$4NaOH+P_4O_6+2H_2O\rightarrow 4NaH_2PO_3$$

$$9NaOH+P_4O_6\rightarrow 4Na_2HPO_3+2H_2O$$
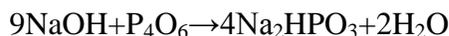
Phosphorus(V) oxide: Phosphorus(V) oxide reacts violently with water to give a solution containing a mixture of acids, the nature of which depends on the reaction conditions. Only one acid is commonly considered, phosphoric(V) acid, H_3PO_4 (also known as phosphoric acid or as orthophosphoric acid).
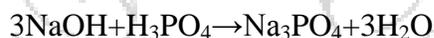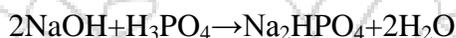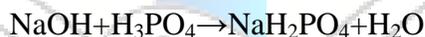
$$P_4O_{10}+6H_2O\rightarrow 4H_3PO_4$$

This time the fully protonated acid has the following structure:
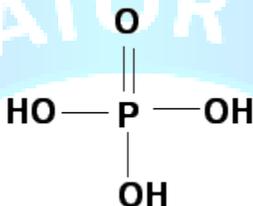
Phosphoric(V) acid is another weak acid with a pK_a of 2.15, marginally weaker than phosphorous acid. Solutions of each of these acids with concentrations around 1 mol dm^{-3} have a pH of about 1.

Phosphoric (V) oxide is also unlikely to be reacted directly with a base, but the hypothetical reactions are considered. In its acid form, molecule has three acidic -OH groups, which can cause a three-stage reaction with sodium hydroxide:

$$NaOH+H_3PO_4\rightarrow NaH_2PO_4+H_2O$$

$$2NaOH+H_3PO_4\rightarrow Na_2HPO_4+2H_2O$$

$$3NaOH+H_3PO_4\rightarrow Na_3PO_4+3H_2O$$

Similar to phosphorus (III) oxide, if phosphorus(V) oxide reacts directly with sodium hydroxide solution, the same possible salt as in the third step (and only this salt) is formed:

$$12NaOH+P_4O_{10}\rightarrow 4Na_3PO_4+6H_2O$$

Sulfur Oxides

Two oxides are considered: sulfur dioxide, SO_2, and sulfur trioxide, SO_3.

Sulfur dioxide: Sulfur dioxide is fairly soluble in water, reacting to give a solution of sulfurous acid (also known as sulfuric(IV) acid), H_2SO_3, as shown in the reaction below. This species only exists in solution, and any attempt to isolate it gives off sulfur dioxide.

$$SO_2+H_2O\rightarrow H_2SO_3$$

The protonated acid has the following structure:

$$\begin{array}{c} O \\ \parallel \\ HO\!-\!S\!-\!OH \end{array}$$
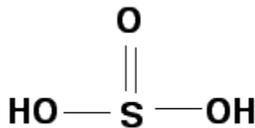
Sulfurous acid is also a relatively weak acid, with a pK_a of around 1.8, but slightly stronger than the two phosphorus-containing acids above. A reasonably concentrated solution of sulfurous acid has a pH of about 1.

Sulfur dioxide also reacts directly with bases such as sodium hydroxide solution. Bubbling sulfur dioxide through sodium hydroxide solution first forms sodium sulfite solution, followed by sodium hydrogen sulfite solution if the sulfur dioxide is in excess.

$$SO_2+2NaOH\rightarrow Na_2SO_3+H_2O$$

$$Na_2SO_3+H_2O\rightarrow 2NaHSO_3$$
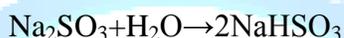
Another important reaction of sulfur dioxide is with the base calcium oxide to form calcium sulfite (also known as calcium sulfate(IV)). This is of the important methods of removing sulfur dioxide from flue gases in power stations.

$$CaO+SO_2\rightarrow CaSO_3$$
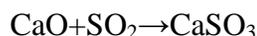
Sulfur trioxide: Sulfur trioxide reacts violently with water to produce a fog of concentrated sulfuric acid droplets.

$$SO_3+H_2O\rightarrow H_2SO_4$$
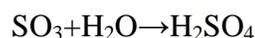
Pure, fully-protonated sulfuric acid has the structure:

$$\begin{array}{c} O \\ \parallel \\ HO\!-\!S\!-\!OH \\ \parallel \\ O \end{array}$$
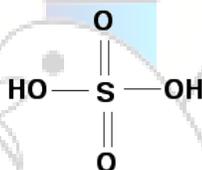
Sulfuric acid is a strong acid, and solutions will typically have a pH around 0. The acid reacts with water to give a hydronium ion (a hydrogen ion in solution) and a hydrogen sulfate ion. This reaction runs essentially to completion:

$$H_2SO_{4(aq)}+H_2O\rightarrow H_3P^++HSO^{-4}_{(aq)}$$

The second proton is more difficult to remove. In fact, the hydrogen sulfate ion is a relatively weak acid, similar in strength to the acids discussed above. This reaction is more appropriately described as an equilibrium:

$$HSO^-_{4(aq)}+H_2O\rightleftharpoons H_3O_{+(aq)}+SO2^{-4}_{(aq)}$$
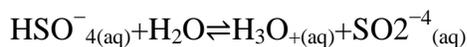
It is useful if you understand the reason that sulfuric acid is a stronger acid than sulfurous acid. You can apply the same reasoning to other acids that you find on this page as well.

Sulfuric acid is stronger than sulfurous acid because when a hydrogen ion is lost from one of the -OH groups on sulfuric acid, the negative charge left on the oxygen is spread out (delocalized) over the ion by interacting with the

doubly-bonded oxygen atoms. It follows that more double bonded oxygen atoms in the ion make more delocalization possible; more delocalization leads to greater stability, making the ion less likely to recombine with a hydrogen ion and revert to the non-ionized acid.

Sulfurous acid only has one double bonded oxygen, whereas sulfuric acid has two; the extra double bond provides much more effective delocalization, a much more stable ion, and a stronger acid. Sulfuric acid displays all the reactions characteristic of a strong acid. For example, a reaction with sodium hydroxide forms sodium sulfate; in this reaction, both of the acidic protons react with hydroxide ions as shown:

$$2NaOH + H_2SO_4 \rightarrow Na_2SO_4 + 2H_2O$$
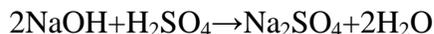
In principle, sodium hydrogen sulfate can be formed by using half as much sodium hydroxide; in this case, only one of the acidic hydrogen atoms is removed.

Sulfur trioxide itself also reacts directly with bases such as calcium oxide, forming calcium sulfate:

$$CaO + SO_3 \rightarrow CaSO_4$$
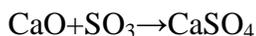
This reaction is similar to the reaction with sulfur dioxide discussed above.

**Chlorine Oxides**

Chlorine forms several oxides, but only two (chlorine(VII) oxide, Cl_2O_7, and chlorine(I)oxide, Cl_2O) are considered here. Chlorine(VII) oxide is also known as dichlorine heptoxide, and chlorine(I) oxide as dichlorine monoxide.

Chlorine(VII) oxide: Chlorine(VII) oxide is the highest oxide of chlorine—the chlorine atom is in its maximum oxidation state of +7. It continues the trend of the highest oxides of the Period 3 elements towards being stronger acids. Chlorine(VII) oxide reacts with water to give the very strong acid, chloric(VII) acid, also known as perchloric acid.

$$Cl_2O_7 + H_2O \rightarrow 2HClO_4$$
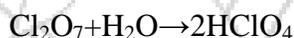
As in sulfuric acid, the pH of typical solutions of perchloric acid are around 0. Neutral chloric(VII) acid has the following structure:

$$\begin{array}{c} O \\ \| \\ HO-Cl=O \\ \| \\ O \end{array}$$
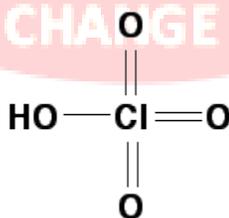
When the chlorate(VII) ion (perchlorate ion) forms by loss of a proton (in a reaction with water, for example), the charge is delocalized over every oxygen atom in the ion. That makes the ion very stable, making chloric(VII) acid very strong.

Chloric(VII) acid reacts with sodium hydroxide solution to form a solution of sodium chlorate(VII):

$$NaOH+HClO_4 \rightarrow NaClO_4+H_2O$$
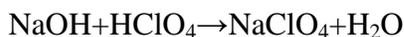
Chlorine(VII) oxide itself also reacts directly with sodium hydroxide solution to give the same product:

$$2NaOH+Cl_2O_7 \rightarrow 2NaClO_4+H_2O$$
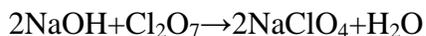
Chlorine(I) oxide: Chlorine(I) oxide is far less acidic than chlorine(VII) oxide. It reacts with water to some extent to give chloric(I) acid, HOCl−HOCl− also known as hypochlorous acid.

$$Cl_2O+H_2O \rightleftharpoons 2HOCl$$
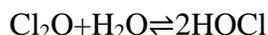
The structure of chloric(I) acid is exactly as shown by its formula, HOCl. It has no doubly-bonded oxygens, and no way of delocalizing the charge over the negative ion formed by loss of the hydrogen. Therefore, the negative ion formed not very stable, and readily reclaims its proton to revert to the acid. Chloric(I) acid is very weak (pK_a = 7.43) and reacts with sodium hydroxide solution to give a solution of sodium chlorate(I) (sodium hypochlorite):

$$NaOH+HOCl \rightarrow NaOCl+H_2O$$
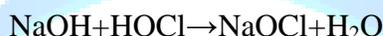
Chlorine(I) oxide also reacts directly with sodium hydroxide to give the same product:

$$2NaOH+Cl_2O \rightarrow 2NaOCl+H_2O$$
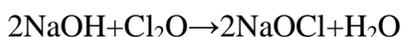
10.   What is meant by inert pair effect? Explain inert pair effect in formation of ionic and covalent bond.

 Inert pair effect: the tendency of an atom to keep their s –electrons inert is called inert pair effect. Explanation: the electronic configuration of carbon family is nS^2, nP^2. Carbon and Silicon involve all the four electrons for covalent bond formation by SP3 hybridization. And its oxidation state is always +4, but the bottom elements like Sn and Pb has the tendency to keep their S electrons inert (non-reactive) in chemical bond formation. Therefore they show +2 oxidation shows along with +4. This phenomenon shown by Sn and Pb is called inert pair effect. This tendency increase from top to bottom:

Effect of inert pair effect on the nature of bonds:
In periodic table the inert pair affects tendency increase down the group. Therefore the probability of involvement of S electrons decreases from top to bottom. Therefore the bottom elements show +2 oxidation states. If the elements in Group 4 form 2+ ions, they lose their p electrons, leaving the s^2 pair unused. For example, to form a lead(II) ion, lead loses its two 6p electrons, but the 6s electrons are left unchanged, an "inert pair". This is more stable and more ionic. It means that the ionic characters increase with increase in inert pair effect tendency. Since $PbCl_2$ and $SnCl_2$ are ionic while $PbCl_4$ and $SnCl_4$ are covalent. $PbCl_2$ will be more ionic than $SnCl_2$ because Pb show greater inert pair effect than Sn.