GENERAL CHARACTERISTICS OF THE COMPOUNDS OF THE ALKALI METALS

Typically, compounds formed by alkali metals exhibit an ionic nature. This characteristic is common across a broad range of compounds involving alkali metals. In these compounds, the alkali metal cations, due to their low electronegativity and readiness to donate electrons, interact with anions, leading to the establishment of predominantly ionic bonds. The prevalence of ionic bonding in alkali metal compounds underscores the tendency of alkali metals to readily lose electrons and form positively charged ions, facilitating their combination with negatively charged ions to create stable and electrically neutral compounds.

Oxides and Hydrides

Alkali metals, upon combustion in air, produce various oxides. When these metals react with a limited amount of oxygen, they form normal oxides represented by the formula M_2O, where M stands for lithium (Li), sodium (Na), potassium (K), rubidium (Rb), or cesium (Cs).

This reaction is expressed as: $4M + O_2 \rightarrow 2M_2O$.

However, specific oxides are formed under different conditions.

For instance, lithium forms normal oxide (Li_2O) and some peroxide (Li_2O_2), sodium yields peroxide (Na_2O_2) and some superoxide (NaO_2), while potassium, rubidium, and cesium generate superoxide with the general formula MO_2.

$$4Li + O_2 \rightarrow \underset{\text{Lithium oxide}}{2Li_2O}$$

$$2Na + O_2 \rightarrow \underset{\text{Sodium Peroxide}}{Na_2O_2}$$

$$K + O_2 \rightarrow \underset{\text{Potassium Superoxide}}{Na_2O_2}$$

The temperature required for these reactions decreases down the group. The stability of peroxides or superoxide's increases with the size of the alkali metal due to the stabilization of large anions by large cations through lattice energy effects.

The oxides and peroxides are colorless when pure, but superoxide's exhibit yellow or orange hues. Peroxides are diamagnetic, whereas superoxide's are paramagnetic in nature.

Upon reaction with water, normal oxides readily dissolve to form hydroxides, releasing a substantial amount of heat.

This reaction is represented as:

$$M_2O(s) + H_2O(l) \rightarrow 2MOH(aq) + Heat \rightarrow 2M^+ + 2OH^-$$

Peroxides and superoxide's also undergo hydrolysis in water, leading to the formation of hydroxides and additional products.

$$M_2O_2 + 2H_2O \rightarrow 2M^+ + 2OH^+ + H_2O_2$$

$$Na_2O_2 + 2H_2O \rightarrow 2NaOH + H_2O_2$$

$$2MO_2 + 2H_2O \rightarrow 2M^+ + 2OH^- + H_2O_2 + O_2$$

$$2KO_2 + 2H_2O \rightarrow 2KOH + H_2O_2 + O_2$$

The higher oxides act as potent oxidizing agents, with sodium peroxide finding widespread use in inorganic chemistry for its oxidizing properties.

The hydroxides resulting from the reaction of oxides with water are white crystalline solids. Alkali metal hydroxides, in general, exhibit strong basic properties, and their basic character increases down the group as represented by

LiOH
NaOH
KOH
RbOH
CsOH

These hydroxides are highly soluble in water, and their dissolution is accompanied by the release of a significant amount of heat due to intense hydration.

Halides

(a) Alkali metals directly react with halogens to produce compounds of the form MX (where M represents the alkali metal and X denotes the halide ion).

(b) The ionic characteristics of MX compounds increase from LiCl to CsCl.

(c) LiCl exhibits covalent properties due to the polarization of the Cl^- ion by the small Li^+ ion, which causes it to hydrolyze with water, while the others are ionic and do not hydrolyze.

(d) Halides of potassium (K), rubidium (Rb), and cesium (Cs) react with additional halogens to form polyamides.

$$KI + I_2 \rightarrow KI_3 \xrightarrow[\text{ionisation}]{\text{On}} K^+ + I_3^-$$

$$CSBr + Br_2 \rightarrow CsBr_3 \rightarrow Cs^+ + Br_3^-$$

Salts of Oxo- Acids

Oxo-acids are characterized by having the acidic proton situated on a hydroxyl group with an attached oxo group on the same atom. Examples include carbonic acid, H_2CO_3 [$OC(OH)_2$], and sulfuric acid, H_2SO_4 [$O_2S(OH)_2$]. Alkali metals demonstrate the ability to form salts with various oxo-acids.

Generally, salts derived from oxo-acids exhibit solubility in water and possess thermal stability. The carbonates (M_2CO_3) and bicarbonates ($MHCO_3$) of alkali metals are notably stable under elevated temperatures. However, lithium carbonate (Li_2CO_3) stands out as less stable and readily undergoes decomposition when heated. This reduced stability in Li_2CO_3 is attributed to the small size of lithium ions, resulting in the polarization of large CO_3^{2-} ions and leading to the formation of stable Li_2O and CO_2 during the heating process.

$$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$

The trend in stability is influenced by the electropositive character of the alkali metals, with an observed increase in stability down the group. This pattern reflects the heightened stability of carbonates and hydrogen carbonates as the electropositive character of the alkali metal increases along the group.