ANOMALOUS PROPERTIES OF LITHIUM

The unique behavior of lithium can be attributed to two primary factors:

1. Its atom and ion are extraordinarily small in size.
2. It possesses a high polarizing power, indicated by the charge-to-radius ratio. Consequently, lithium compounds exhibit an elevated covalent character, leading to their solubility in organic solvents. Additionally, lithium shares a diagonal relationship with magnesium.

S.No.	Property	Li
1.	Hardness	Li is much harder.
2.	M.P and B. P	Higher M.P and B. P
3.	Reactivity	Less reactive
4.	Reducing agent	Strong
5.	Combustion in air	Li form monoxide (Li_2O) and nitride (Li_3N); not for other.
6.	Hydration of ion	Favored for $Li^{\oplus}$; not for other. $Li^{\oplus}$ has maximum degree of hydration for this reason. Lithium salts are mostly hydrated. E.g., $LiCl.2H_2O$.
7.	Hydrogen Carbonate	Li is not obtained in the solid form while all other elements form solid hydrogen carbonates.
8.	Ethnize	Favored for $Li^{\oplus}$; not for other.
9.	Lithium nitrate	$4LiNO_3 \xrightarrow{\triangle} 2Li_2O + 4Na_2 + O_2$ Lithium Oxide Whereas other alkali metal nitrates decompose to give the corresponding nitrite. $2NaNo_3 \xrightarrow{\triangle} 2NaNO_2 + O_2$ Sodium nitrite
10.	LiF and Li2O	These are much less soluble in water. Solubility in water is less than the corresponding compounds of other alkali metal.
11.	Carbide	Li reacts directly with carbon to form anionic carbide.
12.	Hydroxide	Lithium hydroxide is less basic Li_2CO_3, $LiNO_3$ and LiOH all form the oxides on gentle heating.
13.	Carbonate	Less stable.
14.	Nitrite	Less stable.
15.	Bicarbonate	Lithium forms a bicarbonate in solution it does not form a solid bicarbonate. Whereas the other all forms stable solid bicarbonates.
16.	Complex ion formation	Lithium has a great tendency to form. Complexes not for other. Due to small size of Lithium.
17.	Reaction with NH_3	Li when heated in NH_3 imide (Li_2NH) while other alkali metals form amides (MNH_2)

Points of Difference between Lithium and Other Alkali Metals

(i) In comparison to the other alkali metals, lithium exhibits greater hardness and has higher melting and boiling points.

(ii) Within the alkali metal group, lithium stands out as the least reactive yet possesses strong reducing properties. Upon combustion in air, lithium predominantly forms monoxide (Li_2O) and nitride (LiN), a behavior distinct from other alkali metals.

(iii) Lithium chloride (LiCl) demonstrates deliquescence and crystallizes as a hydrate, $LiCl \cdot 2H_2O$, a feature not observed in the chlorides of other alkali metals.

(iv) With the exception of lithium, the hydrogen carbonates of the remaining alkali metals are obtained in solid form.

(v) Unlike the other alkali metals, lithium does not form an ethynide when reacting with ethyne.

(vi) Upon heating, lithium nitrate ($LiNO_3$) undergoes a unique transformation, yielding lithium oxide (Li_2O), whereas other alkali metal nitrates decompose to form the corresponding nitrites.

Equation: $4LiNO_3 \rightarrow 2Li_2O + 4NO_2 + O_2$

Comparison: $2NaNO_3 \rightarrow 2NaNO_2 + O_2$

(vii) Both lithium fluoride (LiF) and lithium oxide (Li_2O) exhibit significantly lower solubility in water compared to the corresponding compounds of other alkali metals.

Points of Similarities between Lithium and Magnesium

- Lithium deviates from the typical characteristics of other alkali metals due to its compact size, but it shares similarities with magnesium. This resemblance is attributed to their comparable sizes, leading to a diagonal relationship formed by ions with identical sizes.
- Lithium and magnesium both exhibit substantial hardness.
- The hydroxides of both lithium and magnesium are categorized as weak bases and undergo decomposition when subjected to heat.
- In their reactions with nitrogen, both lithium and magnesium form nitrides.
- Both of these elements display covalent characteristics.
- The chlorides of both lithium and magnesium exhibit solubility in ethanol.
- The reaction of both lithium and magnesium in water proceeds at a sluggish pace.

Ore of alkali metals

Alkali Metal Ores Due to their high reactivity, alkali metals are not found in their elemental form in nature. However, sodium and potassium are relatively abundant in the Earth's crust, ranking 7th and 8th in terms of elemental abundance. These metals are typically encountered in the form of their respective ores.

(A) Ores of Lithium

(i) Spodumene, $LiAlSi_2O_6$ (ii) Lepidolite, $(Li)_2\ Al_2\ (SiO_3)_3\ .\ (FOH)_2$

(B) Ores of Sodium

(i) Common salt or rock salt, NaCl (ii) Chile salt patre, $NaNO_3$

(iii) Albite (Soda Feldspar), $NaAlSi_3O_8$ (iv) Glauber's salt, $Na_2SO_4 .\ 10H_2O$

(C) Ores of Potassium

(i) Camallite, $KCl .\ MgCl_2 .\ 6H_2O$ (ii) Feldspar, $KAlSi_3O_8$

(iii) Sylvine, KCl

Extraction of Alkali Metals

(i) Lithium

The extraction process for lithium comprises two key steps:

1. The preparation of LiCl from the ore.
2. Electrolysis of LiCl. For the electrolysis, an electrolyte containing 55% LiCl and 45% KCl is utilized. The electrolyte is maintained in a molten state by heating it to approximately 723 K.

(ii) Sodium –

Down's Process

In the Down's Process, sodium is produced through the electrolysis of a fused mixture consisting of 40% sodium chloride and 60% calcium chloride. The role of calcium chloride is to lower the operating temperature from 1080 K (the melting point of NaCl) to approximately 850 K.

The following reactions occur:

$$NaCl \rightarrow Na^{+} + Cl^{-} \text{ (Ionization)}$$

At cathode: $Na^{+} + e^{-} \rightarrow Na$

At anode: $Cl^{-} \rightarrow Cl + e^{-}$

$$Cl + Cl \rightarrow Cl_2 \uparrow$$

The sodium metal obtained through this method is approximately 99% pure. Chlorine is the by-product of this process.

(iii) Potassium:

The production of potassium involves the electrolysis of molten potassium hydroxide (KOH). The reactions are as follows:

$$KOH \rightarrow K^{+} + OH^{-}$$

At cathode: $K^{+} + e^{-} \rightarrow K$

At anode: $4OH^{-} \rightarrow O_2 + 2H_2O + 4e^{-}$