

Chapter 10

Group IA (1)

Alkali Metals

Lithium, Sodium, Potassium, Rubidium and Cesium

Similar to H^+ in that they form M^+ . (other cations that are related are NH_4^+ (like K^+) and Tl^+ (Rb^+)).

Na^+ and K^+ are very important physiologically.

Cells differentiate between them by specific complexation reactions and allows them to pass through cell membranes through ion channels.

Many ions have a concentration gradient **across the membrane**, including **potassium** (K^+), which is at a high concentration inside and a low concentration outside the **membrane**.

Sodium (Na^+) and chloride (Cl^-) ions are at high concentrations in the extracellular region, and low concentrations in the intracellular regions.

Because the inside of the **cell** is negative, **the potassium and sodium ions** outside of the **cell** will cluster around the membrane. This difference creates an electrical potential. ... When a **cell** is resting, the large **sodium ions** outside of the **cell** wall **cannot enter** because the particular channels for these **ions** are not open yet.

There are also **Potassium channels** which are designed to allow the flow of **potassium ions** across the membrane, but to block the flow of other **ions** -- in particular, **sodium ions**. It is composed of four identical protein molecules that span the width of the membrane, forming a selective pore down the center.

Li⁺ salts are used to treat manic depressive disorders.

Doctors don't know exactly how **lithium** works to stabilize a person's mood, but it is thought to help strengthen nerve cell connections in brain regions that are involved in regulating mood, thinking and behavior.

It was **first used** for mania in 1871, with Denmark leading the way, but little was published about the medication for more than half a century. Later on, in the 1940s, **lithium** was **used** as a blood pressure medication but soon proved to have too many side effects to be effective in this use

K⁺NO₃⁻ is used in fertilizers.

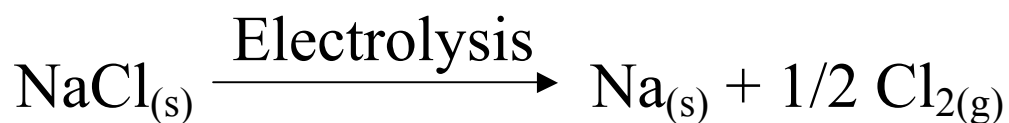
Na⁺ as NaOH, Na₂CO₃, Na₂SO₄ are among the top 50 chemicals in terms of production.

What Dictates the Chemistry of Alkali Metals?

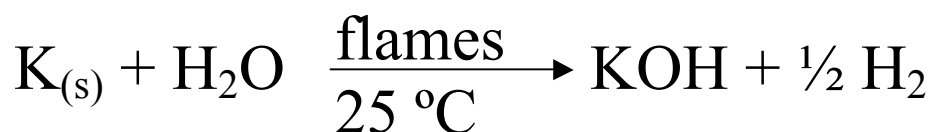
- Low ionization energies to make +1 cations
- M⁺ ions are spherical and hard (low polarizability)
- High 2nd ionization energies prevent the +2 oxidation state

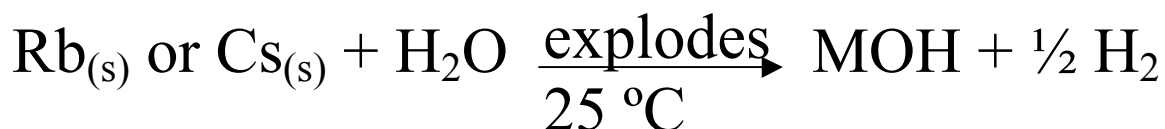
- Most bonding interactions are ionic due to low polarizability (Li^+ is strongest in terms of polarizing ability due to size/charge ratio – in other words it forms the most covalent compounds)
- Li is least reactive, Cs is most reactive

Preparation of alkali metals is mainly by electrolysis of fused salts



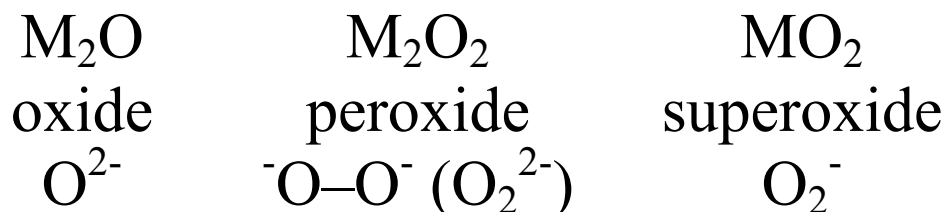
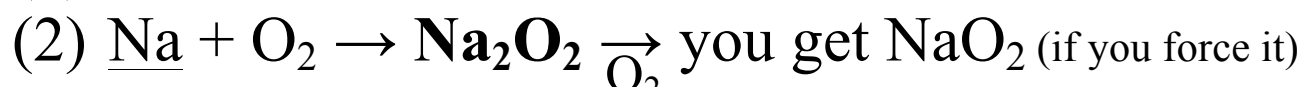
Reactivity Comparisons





A Fundamental Difference Can Be Observed in O₂ Reactions

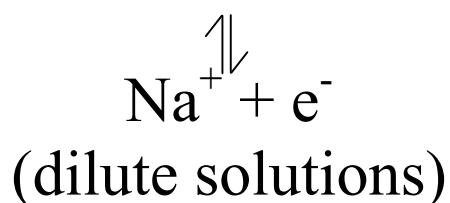
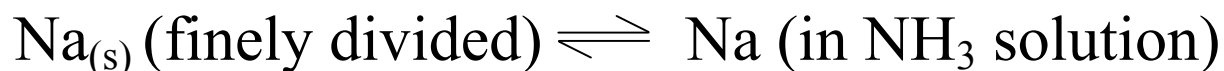
(main products in bold)



Q Why differences?

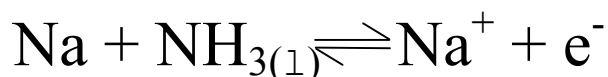
A The differences in reactivity with O₂ can be attributed to cation size.

Solutions of Alkali Metals in Ammonia NH_{3(l)}



Q What do these equilibria mean?

A That the NH₃ medium is able to “solvate” an electron. The solvated electron occupies a “cavity” in the NH_{3(l)} where it is somewhat delocalized over a large volume so that the surrounding molecules are polarized. The polarized NH₃ molecules form the cavity due to NH₃ lone pair – e⁻ repulsions.



is stable without air or water, but eventually can react further to give:



This reaction is facilitated by photochemical and catalytic routes

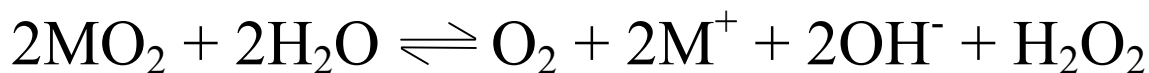
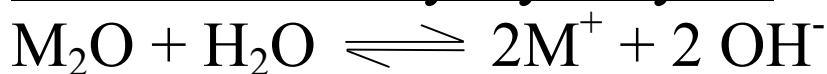
Binary Compounds (only two elements)

oxides – M_2O , M_2O_2 , MO_2

hydroxides – MOH (not really binary but these
are viewed as metal oxides as well)

salts – MX ($X =$ halide for example)

Oxides, Peroxides and Superoxides of Alkali Metals are Easily Hydrolyzed



Hydroxides

- NaOH etc., white, very hygroscopic (deliquescent) solids (means they literally dissolve in the moisture from the air)
- solids also absorb CO_2 from the atmosphere (solutions do as well)

Salts

MX X^- = many types of anions
most give colorless, crystalline ionic compounds

Anomalies arise with lithium compounds –

Why? Mainly due to its small size and its effect on lattice energies!

Li^+ is much smaller than the rest of the alkali cations and its compounds are more covalent.

This leads to different properties, in general, for Li^+ compounds. Reactivity, solubility..

compare:

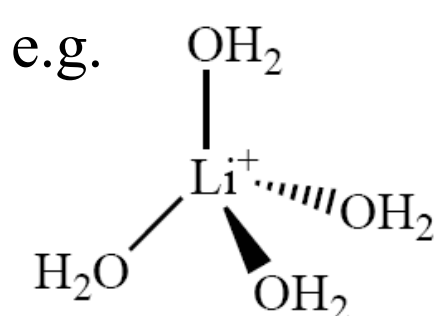
- (1) LiH stable to 900 °C
 NaH decomposes at 350 °C
- (2) Li₃N stable
 Na₃N does not exist at 25 °C
- (3) LiOH $\xrightarrow{\Delta}$ Li₂O i.e. it decomposes
 MOH_(s) $\xrightarrow{\Delta}$ MOH_(g) i.e. they sublime
- (4) LiOH is much less stable than the other
 MOH compounds
- (5) Li₂CO₃ $\xrightarrow{\Delta}$ Li₂O + CO₂, thermally unstable
 carbonate (not so much for others)
- (6) LiF is not very soluble in water (more
 covalent but still ionic as well - good match of
 ion sizes makes the lattice energy very strong)
 LiCl is soluble in pyridine and water
 (unlike NaCl which is very soluble in water but
 not organic solvents, only highly polar solvents)

LiF is insoluble in water whereas LiCl is soluble

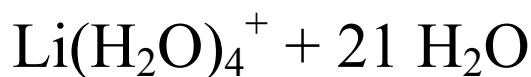
In Lithium fluoride the lattice energy is very high due to the small size of lithium and fluoride ions. In this case the hydration enthalpy is very low. Hence, LiF is insoluble in water. Whereas, in lithium chloride, the lattice enthalpy is very small due to the large size of chloride ions and hence its tendency to become hydrated (switch from solid state to ions surrounded by water) is favorable.

Solvation of M⁺ alkali metal ions issues:

- first coordination sphere
(How many waters are directly bound to M⁺?)
- total coordination sphere
(How many total water molecules?)



$\text{Li}(\text{H}_2\text{O})_4^+$ is considered the first coordination sphere (found in the solid state).



↑
additional water in the solvation shell

In other words, Li⁺ in H₂O exerts an influence on 25 H₂O molecules!

	<u>Li⁺</u>	<u>Na⁺</u>	<u>K⁺</u>	<u>Rb⁺</u>	<u>Cs⁺</u>
<u>Ionic</u> <u>Radii (Å)</u>	0.90	1.16	1.52	1.66	1.81
<u>Approximate</u> <u>Hydrated</u> <u>Radii (Å)</u>	3.40	2.76	2.32	2.28	2.28

<u>Approximate</u>					
<u>Hydration</u>	25.3	16.6	10.5	10.0	9.9
<u>Numbers</u>					
<u>(# of H₂O)</u>					

<u>Hydration</u>					
<u>Enthalpies</u>	519	406	322	293	264
<u>(kJ/mol)</u>					

Note that Li⁺, the smallest ion, exerts the most influence on water → it has the highest total hydration number.

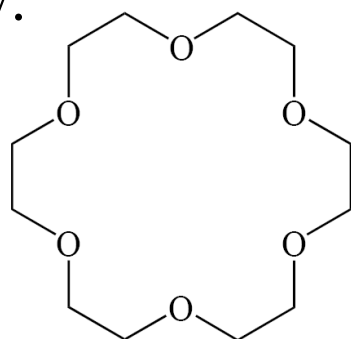
Q Why?

A greater charge density

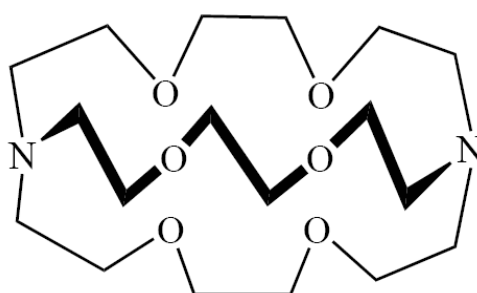
As a consequence, Li⁺, with its 25 hydration sphere H₂O molecules, will not associate with anions in ion-exchange resins very well!

Complexation of Cations by Crown Ethers and Cryptates

M^+ alkali metals are not easily dissolved in their salts into non-aqueous solvents. They need polar (usually H_2O molecules) to stabilize them in their solvated forms. To circumvent this, chemists have used the two types of molecules shown below.



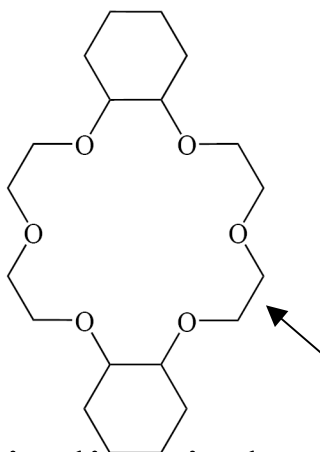
18-crown-6



2,2,2-crypt

The most common and most important cryptand is $N[CH_2CH_2OCH_2CH_2OCH_2CH_2]_3N$; the systematic IUPAC name for this compound is 1,10-diaza-4,7,13,16,21,24-hexaoxabicyclo [8.8.8]hexacosane. This compound is termed [2.2.2]cryptand or 2,2,2,-crypt where the numbers indicate the number of ether oxygen atoms (and hence binding sites) in each of the three bridges between the amine nitrogen caps. Many cryptands are commercially available under the tradename Kryptofix. All-amine cryptands exhibit particularly high affinity for alkali metal cations.

crown ethers - (cyclic ethers)



the number of O atoms and the total number of atoms in the ring are specified in the name:

“18-crown-6”

dicyclohexyl 18-crown-6

Binding is largely electrostatic in the cavity of the cyclic ether. Important to have a close size match of the cavity and the ion if you want binding to be tight.

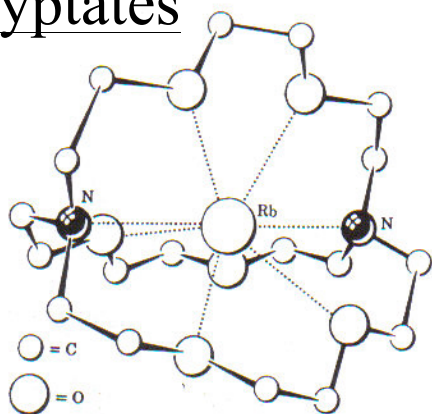
18-crown-6

$\text{Li}^+ < \text{Na}^+, \text{Cs}^+ < \text{Rb}^+ < \text{K}^+$

Binding
is less

Best size
match!

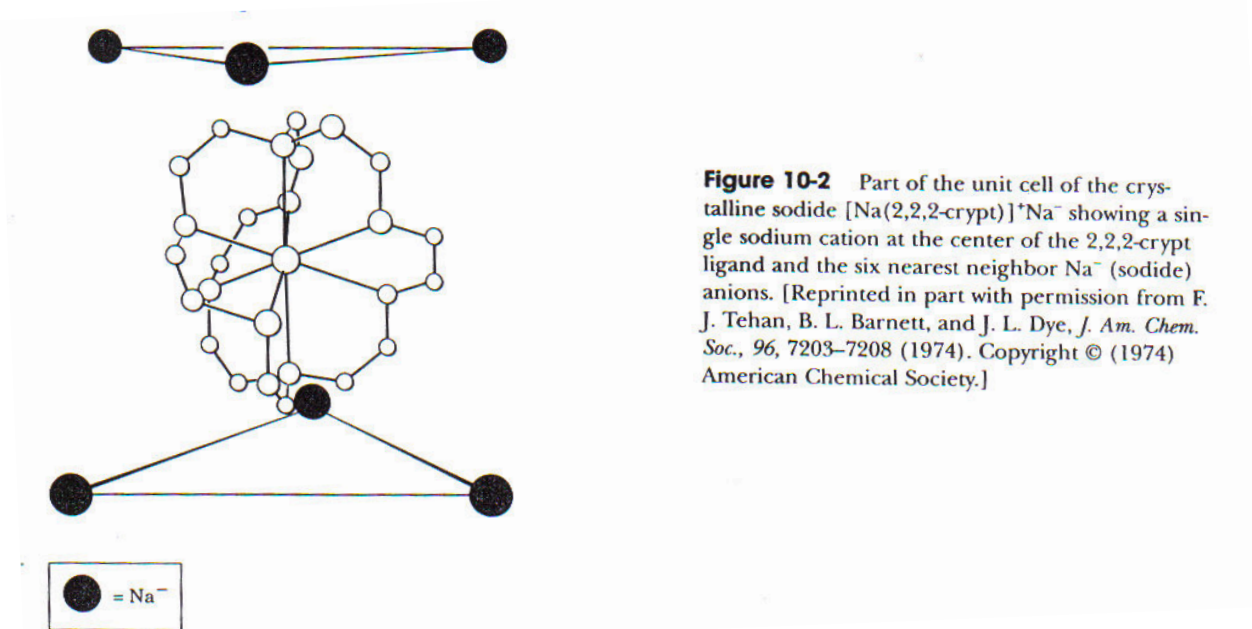
Cryptates



Rb^+ (2,2,2-crypt)

More potent and selective agents for binding alkali cations (and others). Both N and O atoms are present; they are polycyclic and can fully surround the cation.

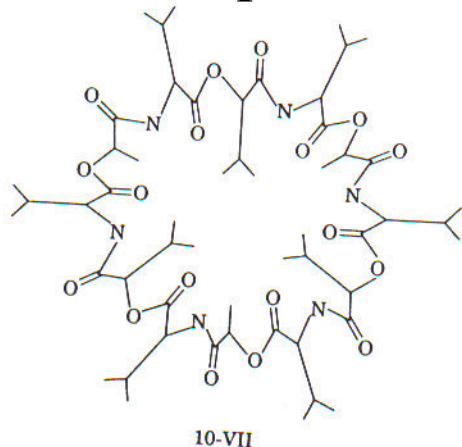
These are very important reagents in organometallic chemistry for getting salts to dissolve in non-polar or low polarity solvents.



Biological systems use a similar strategy for transporting alkali metals

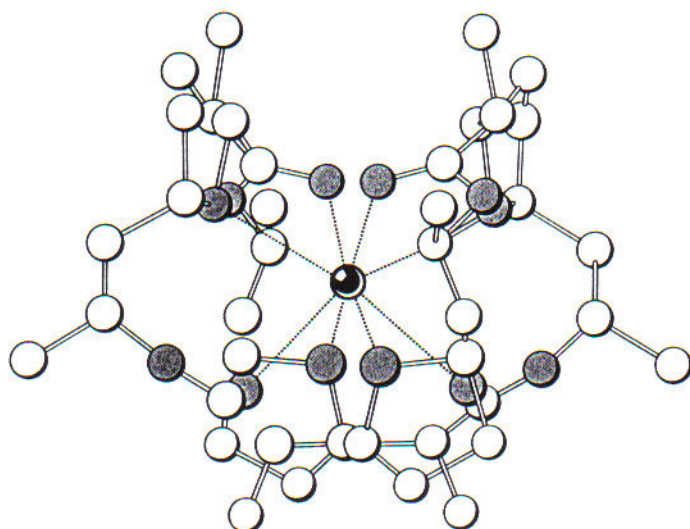
Nature uses cyclic peptides like the ones shown below to transport M^+ across membranes.

For example: for K^+



valinomycin

Valinomycin is highly selective for potassium ions over sodium ions within the cell membrane. It functions as a potassium-specific transporter and facilitates the movement of potassium ions through lipid membranes "down" the electrochemical potential gradient.



Nonactin

Nonactin is a member of a family of naturally occurring cyclic ionophores

Figure 10-3 The structure of the nonactin complex of K^+ .
[Reproduced by permission from D. A. Fenton, *Chem. Soc. Rev.*, 1977, 6, 325-343.]

Ionophore

a substance which is able to transport particular ions across a lipid membrane in a cell.

Relevant fact – especially in Texas

Ionophores are feed additives **used in cattle diets** to increase feed efficiency and body weight gain. They are compounds that alter rumen fermentation patterns. **Ionophores** can be fed to any class of cattle and can be used in any segment of the beef cattle industry.

Rumen fermentation is a process that converts ingested feed into energy sources for the host. Fiber scratches the **rumen** wall to start a series of contractions. These contractions lead to rumination, which is the process that physically breaks down the fiber source.

Rumen is the first stomach of a ruminant, which receives food or cud from the esophagus, partly digests it with the aid of bacteria.

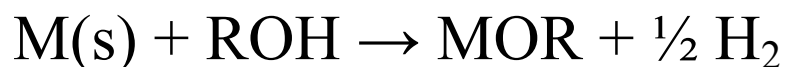
Alkali Metal Organometallics

Li^+R^- R = Me, Bu, etc., are used to deliver R^- groups in reactions. They react very swiftly with O_2 , H_2O and are pyrophoric which means that they burn in air.

Other Common Compounds Often Used In Organometallic Chemistry

Alcohols, amines, and other X-H bonds are highly reactive towards the neutral alkali metals M.

Alkoxides $M^+(OR)^-$

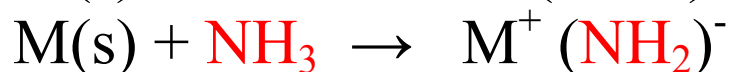


Same type of reaction as $Li + H_2O \rightarrow LiOH + \frac{1}{2} H_2$

Amides

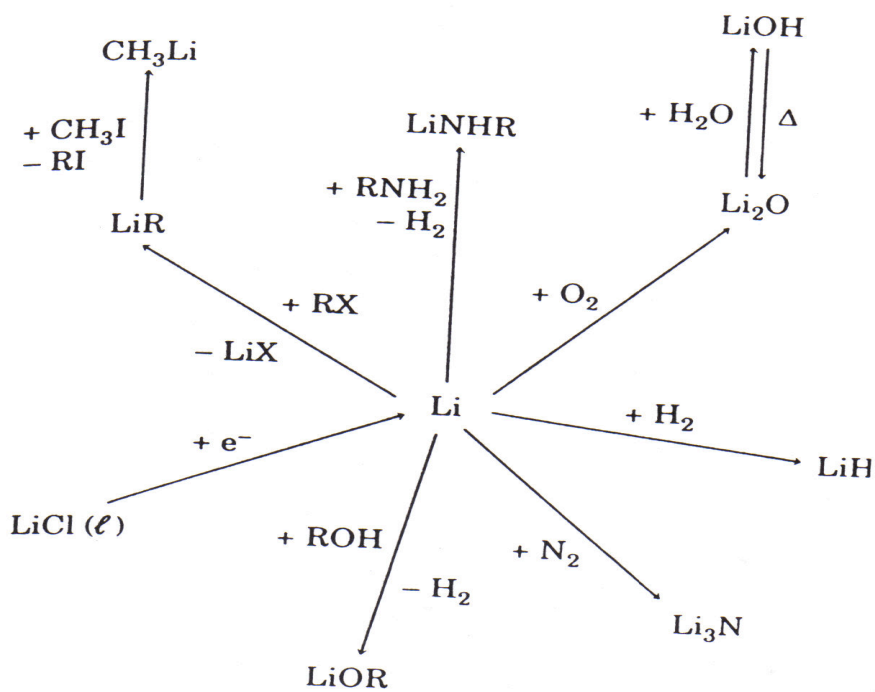
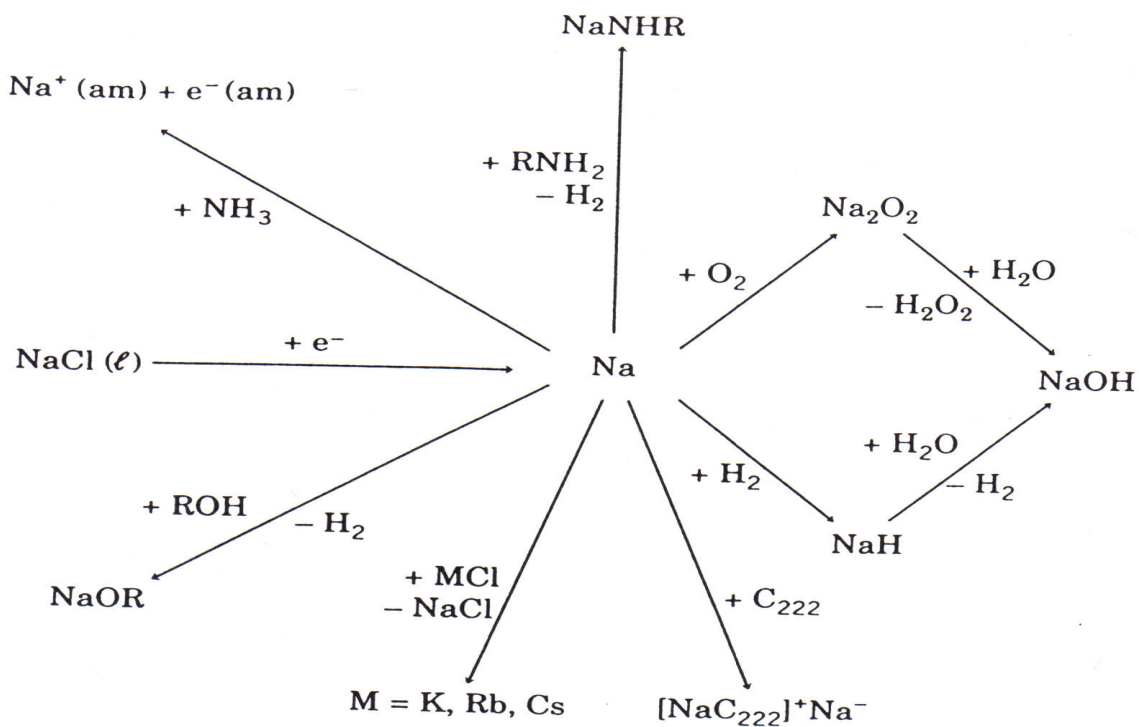


(from amines) $M(s) + NRH_2 \rightarrow M^+(NRH)^-$



What is happening here?

Redox chemistry of course. M is oxidized, H^+ is reduced



Chapter 11

Group IIA (2) Elements

Alkaline Earth Elements

Beryllium, Magnesium, Calcium, Strontium, Barium, Radium

Be important element in a negative sense – very toxic if its compounds are inhaled (destroys lungs)

The **mechanism** of **beryllium** disease is not absolutely known. Most likely, once in the body, **beryllium** combines with certain proteins, causing the release of **toxic** substances. These are responsible for the lesions seen in the lungs. Certain cells form masses of tissue called granulomas in response to **beryllium**.

minor element in terms of technical importance

Mg, Ca, Sr, Ba are in many common minerals and in the ocean

e.g. Limestone which is CaCO_3
Dolomite which is $\text{CaCO}_3 \cdot \text{MgCO}_3$
or $\text{CaMg}(\text{CO}_3)_2$

Ra - all isotopes of this element are radioactive

Group IA → Group IIA
Alkali Metals → Alkaline Earth Metals

larger atomic radii → smaller atomic radii
(increased effective nuclear charge)

lower melting and boiling point → higher melting and boiling point

lower densities → higher densities

lower ionization energies → higher ionization energies

lower hydration energies → higher hydration energies

lower lattice energies → higher lattice energies

Chemistry of Group IIA (some highlights)

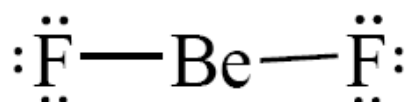
Be very small ionic radius

Be²⁺ 0.31 Å compared to:

(Li⁺ is 0.60 Å; Na⁺ is 0.96 Å; K⁺ is 1.33 Å;
Mg²⁺ is 0.65 Å; Ca²⁺ is 0.99 Å; etc.)

Due to the very small size of Be²⁺, it cannot exist as a simple cation in its compounds.

Consequently, even BeF₂ and BeO are more covalent than they are ionic unlike other M²⁺ species.



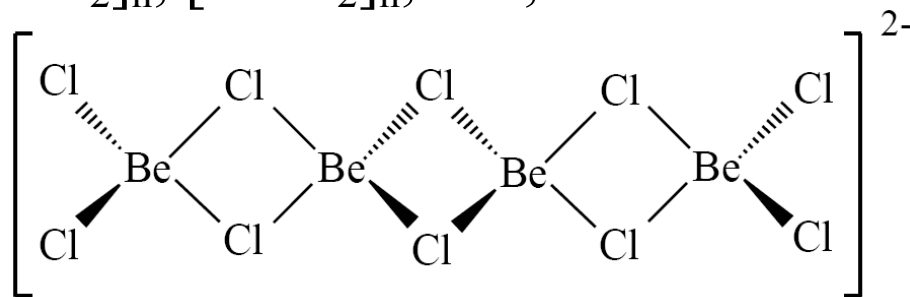
- linear

- coordinatively unsaturated

- exists only in the gas phase

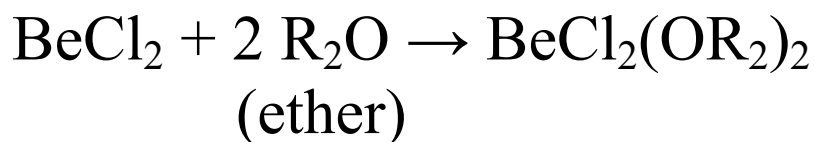
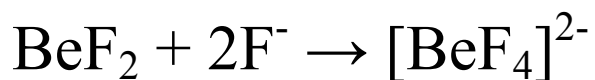
Polymerization of BeX₂ compounds is common

[BeF₂]_n, [BeCl₂]_n, etc.,



a portion of [BeCl₂]_n is above

Since BeX_2 compounds are so coordinatively unsaturated, they are useful as Lewis acids in many reactions



adopts tetrahedral coordination