

## 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 also 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<sup>+</sup> 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<sup>+</sup>NO<sub>3</sub><sup>-</sup>** is used in fertilizers.

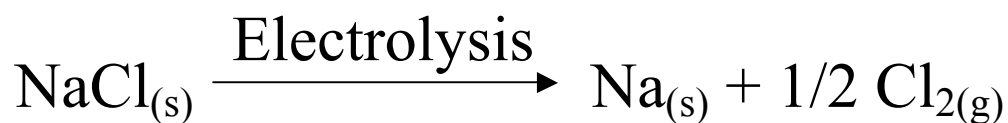
**Na<sup>+</sup>** as NaOH, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub> are among the top 50 chemicals in terms of production.

What Dictates the Chemistry of Alkali Metals?

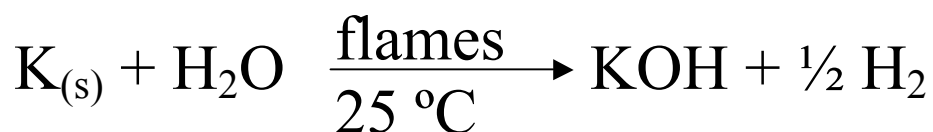
- Low ionization energies to make +1 cations
- M<sup>+</sup> ions are spherical and hard (low polarizability)
- High 2<sup>nd</sup> ionization energies prevent the +2 oxidation state

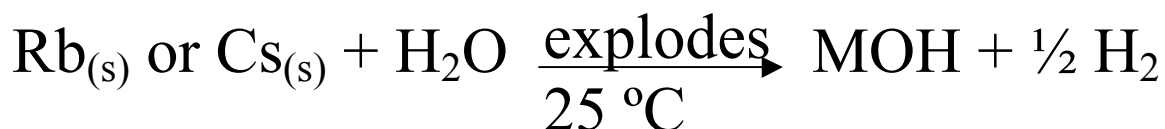
- Most bonding interactions are ionic due to low polarizability ( $\text{Li}^+$  is strongest in terms of polarizing ability due to size/charge ratio – in other words it forms the most covalent compounds)
- Li is least reactive, Cs is most reactive

**Preparation of alkali metals is mainly by electrolysis of fused salts**



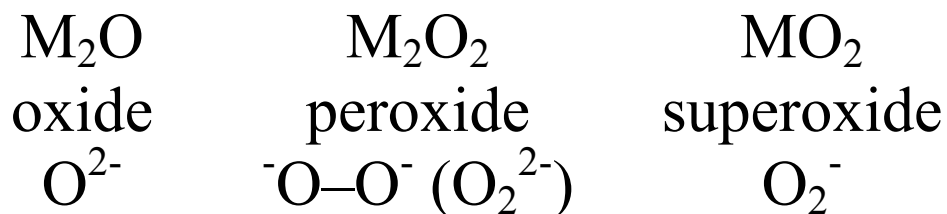
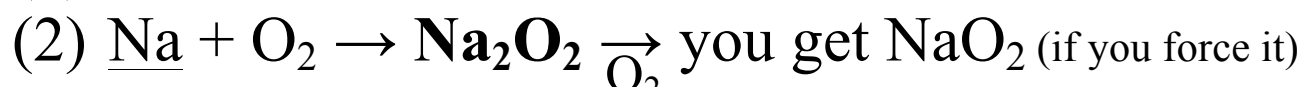
### Reactivity Comparisons





## A Fundamental Difference Can Be Observed in O<sub>2</sub> Reactions

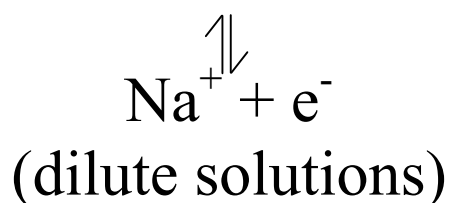
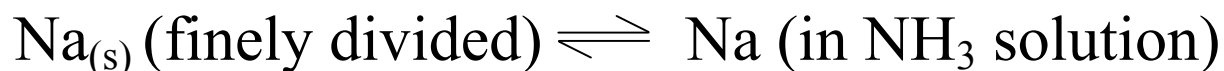
(main products in bold)



**Q** Why differences?

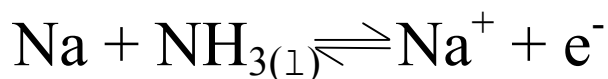
**A** The differences in reactivity with O<sub>2</sub> can be attributed to cation size.

## Solutions of Alkali Metals in Ammonia NH<sub>3(l)</sub>



**Q** What do these equilibria mean?

**A** That the NH<sub>3</sub> medium is able to “solvate” an electron. The solvated electron occupies a “cavity” in the NH<sub>3(l)</sub> where it is somewhat delocalized over a large volume so that the surrounding molecules are polarized. The polarized NH<sub>3</sub> molecules form the cavity due to NH<sub>3</sub> lone pair – e<sup>-</sup> repulsions.



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



This reaction is facilitated by photochemical and catalytic routes

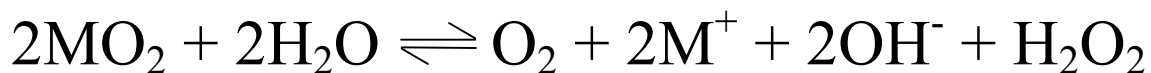
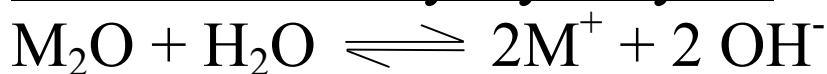
### **Binary Compounds (only two elements)**

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  $\text{CO}_2$  from the atmosphere (solutions do as well)

## Salts

$\text{MX}$   $\text{X}^-$  = 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!

compare:

(1)  $\text{LiH}$  stable to  $900\text{ }^\circ\text{C}$

$\text{NaH}$  decomposes at  $350\text{ }^\circ\text{C}$

(2)  $\text{Li}_3\text{N}$  stable

$\text{Na}_3\text{N}$  does not exist at  $25\text{ }^\circ\text{C}$

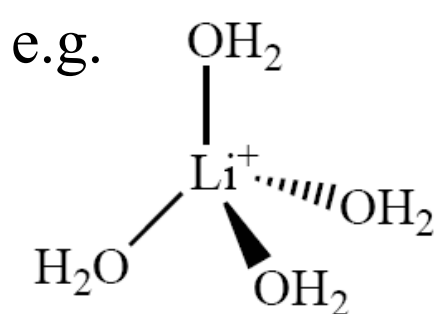
(3)  $\text{LiOH} \xrightarrow{\Delta} \text{Li}_2\text{O}$  i.e. it decomposes

$\text{MOH}_{(s)} \xrightarrow{\Delta} \text{MOH}_{(g)}$  i.e. they sublime

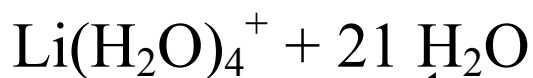
- (4) LiOH is much less stable than the other MOH compounds
- (5)  $\text{Li}_2\text{CO}_3 \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{CO}_2$ , thermally unstable carbonate (not so much for others)
- (6) LiF is not very soluble (more covalent)  
LiCl is soluble in pyridine  
(unlike NaCl which is very soluble in water)

### Solvation of $\text{M}^+$ alkali metal ions issues:

- first coordination sphere  
(How many waters are directly bound to  $\text{M}^+$ ?)
- 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  $\text{Li}^+$  in  $\text{H}_2\text{O}$  exerts an influence on 25  $\text{H}_2\text{O}$  molecules!**

	<u><math>\text{Li}^+</math></u>	<u><math>\text{Na}^+</math></u>	<u><math>\text{K}^+</math></u>	<u><math>\text{Rb}^+</math></u>	<u><math>\text{Cs}^+</math></u>
<u>Ionic Radii (<math>\text{\AA}</math>)</u>	0.90	1.16	1.52	1.66	1.81
<u>Approximate Hydrated Radii (<math>\text{\AA}</math>)</u>	3.40	2.76	2.32	2.28	2.28
<u>Approximate Hydration Numbers (# of <math>\text{H}_2\text{O}</math>)</u>	25.3	16.6	10.5	10.0	9.9
<u>Hydration Enthalpies (kJ/mol)</u>	519	406	322	293	264

Note that  $\text{Li}^+$ , the smallest ion, exerts the most influence on water  $\rightarrow$  it has the highest total hydration number.

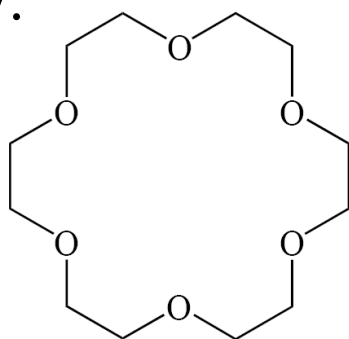
**Q** Why?

**A** greater charge density

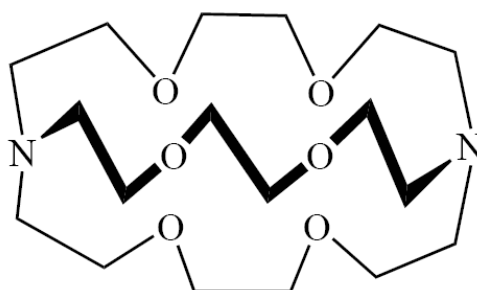
As a consequence,  $\text{Li}^+$ , with its 25 hydration sphere  $\text{H}_2\text{O}$  molecules, will not associate with anions in ion-exchange resins very well!

## Complexation of Cations by Crown Ethers and Cryptates

$\text{M}^+$  alkali metals are not easily dissolved in their salts into non-aqueous solvents. They need polar (usually  $\text{H}_2\text{O}$  molecules) to stabilize them in their solvated forms. To circumvent this, chemists have used the two types of molecules shown below.



18-crown-6

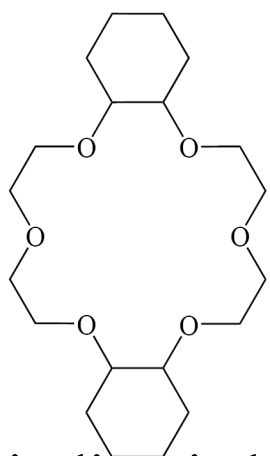


2,2,2-crypt

The most common and most important cryptand is  $\text{N}[\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2]_3\text{N}$ ; 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”

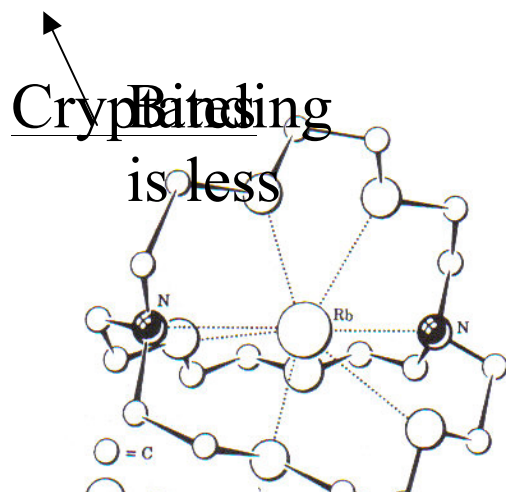
dicyclohexyl 18-crown-6

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**

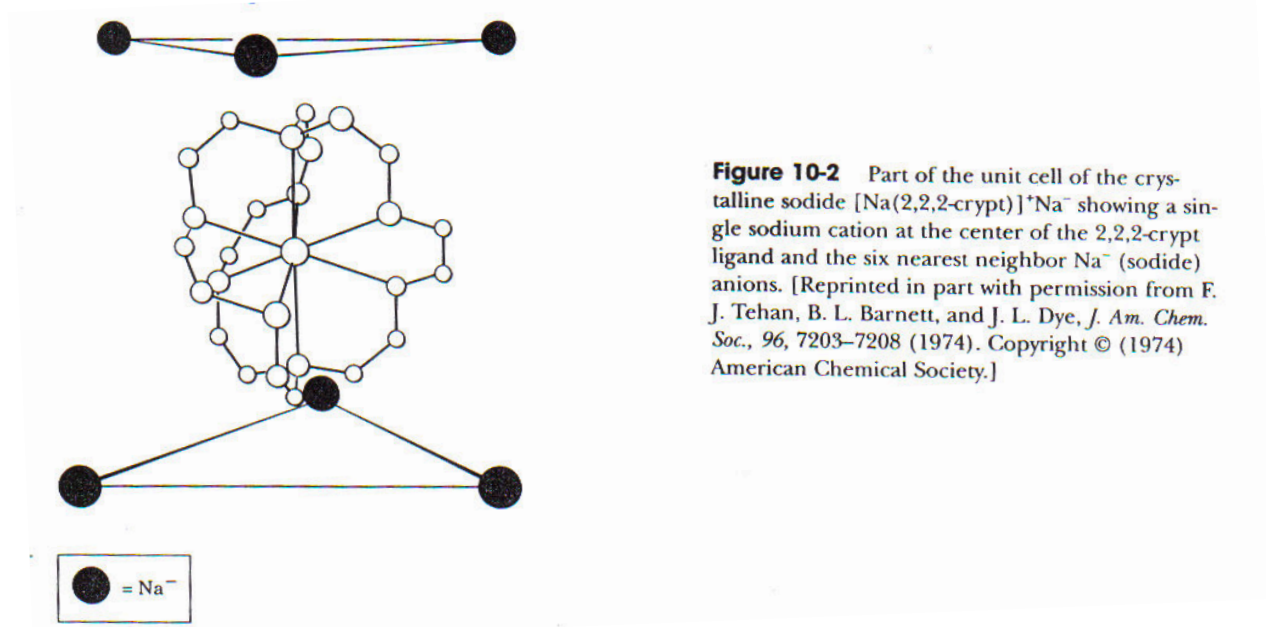
$\text{Li}^+ < \text{Na}^+, \text{Cs}^+ < \text{Rb}^+ < \text{K}^+$



Best size  
More potent and selective  
match!  
agents for binding alkali

cations (and others). Both N and O atoms are present; they are polycyclic which means they can fully surround a cation.

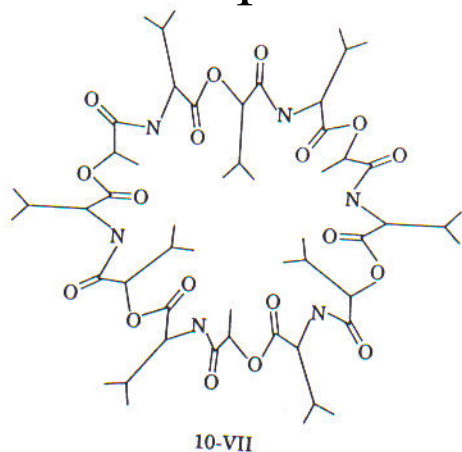
These are very important reagents in organometallic chemistry for getting salts to dissolve in non-polar or low polarity solvents.



Biological systems use a similar strategy for transporting alkali metals

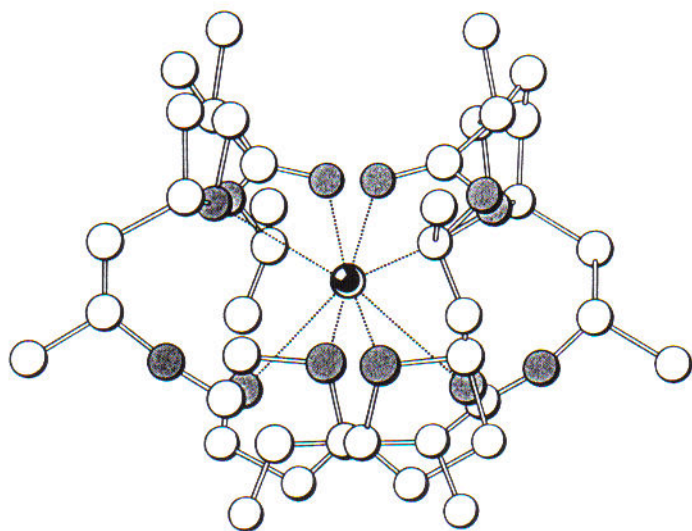
Nature uses cyclic peptides like the ones shown below to transport  $M^+$  across membranes.

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

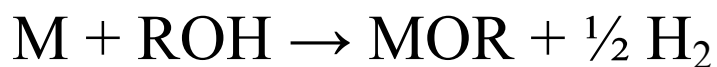


$\text{Li}^+\text{R}^-$  R = Me, Bu, etc., are used to deliver  $\text{R}^-$  groups in reactions. They react very swiftly with  $\text{O}_2$ ,  $\text{H}_2\text{O}$  and are pyrophoric which means that they burn in air.

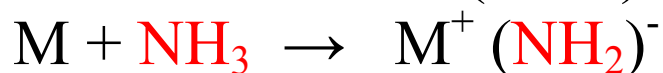
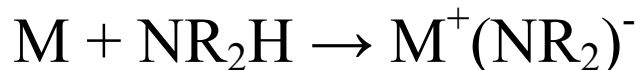
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## Other Common Compounds Often Used In Organometallic Chemistry

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

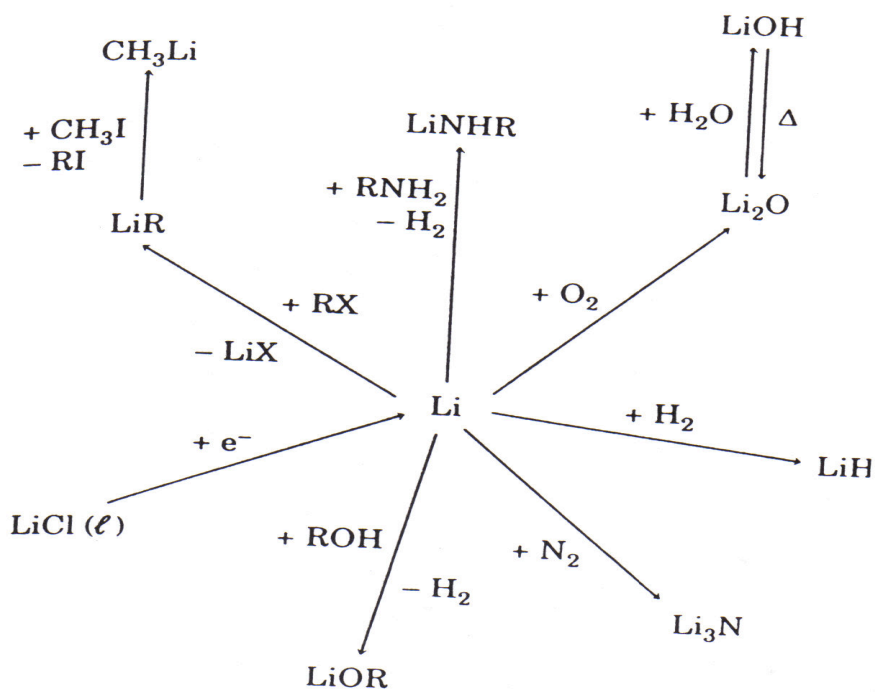
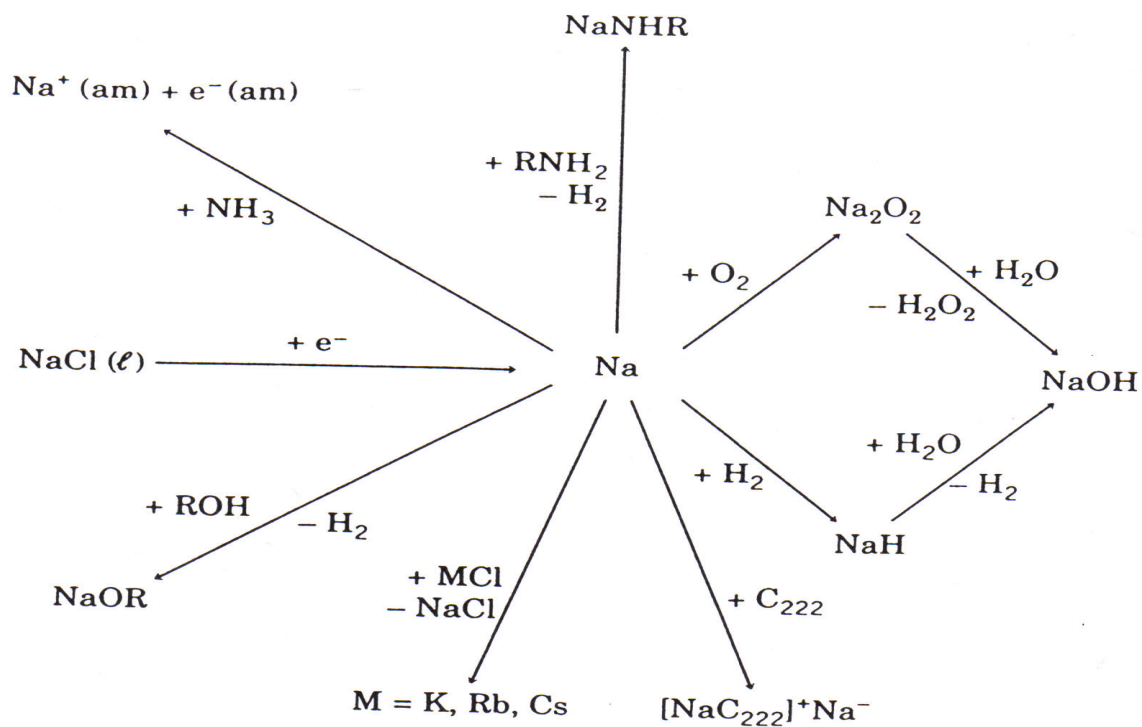
Alkoxides

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

Amides

What is happening here?

Redox chemistry of course. M is oxidized, H<sup>+</sup> 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  $\text{CaCO}_3$   
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  $\rightarrow$  higher lattice energies

## Chemistry of Group IIA (some highlights)

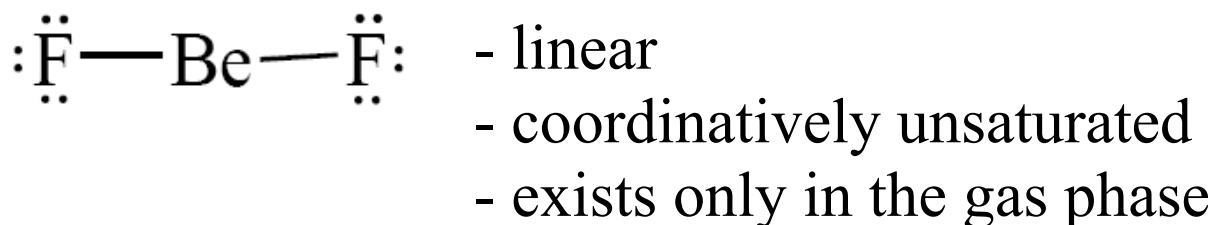
Be very small ionic radius

Be<sup>2+</sup> 0.31 Å compared to:

(Li<sup>+</sup> is 0.60 Å; Na<sup>+</sup> is 0.96 Å; K<sup>+</sup> is 1.33 Å;  
Mg<sup>2+</sup> is 0.65 Å; Ca<sup>2+</sup> is 0.99 Å; etc.)

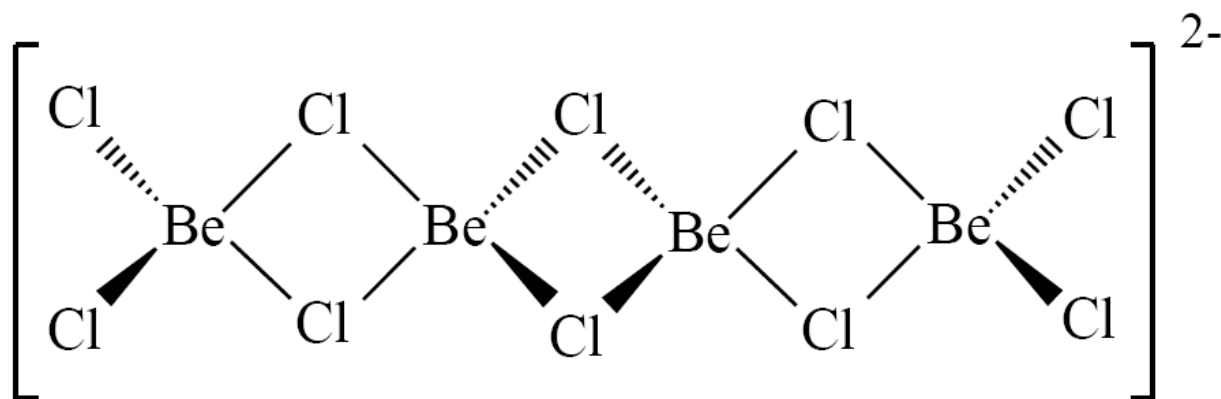
Due to the very small size of Be<sup>2+</sup>, it cannot exist as a simple cation in its compounds.

Consequently, even BeF<sub>2</sub> and BeO are more covalent than they are ionic unlike other M<sup>2+</sup> species.



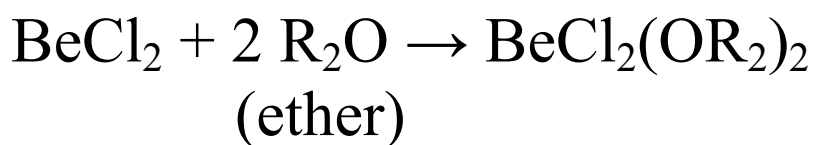
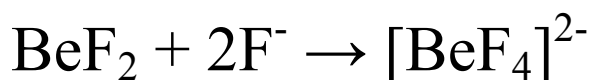
Polymerization of  $\text{BeX}_2$  compounds is common

$[\text{BeF}_2]_n$ ,  $[\text{BeCl}_2]_n$ , etc.,



a portion of  $[\text{BeCl}_2]_n$  is above

Since  $\text{BeX}_2$  compounds are so coordinatively unsaturated, they are useful as Lewis acids in many reactions



**adopts tetrahedral coordination**