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\(^+\) 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\(^+\)NO\(_3\)\(^-\)** is used in fertilizers.

**Na\(^+\)** as NaOH, Na\(_2\)CO\(_3\), Na\(_2\)SO\(_4\) 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 2\(^{nd}\) 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**

\[
\text{NaCl(s)} \xrightarrow{\text{Electrolysis}} \text{Na(s)} + \frac{1}{2} \text{Cl}_2(g)
\]

**Reactivity Comparisons**

\[
\text{Li(s)} + \text{H}_2\text{O} \xrightarrow{\text{slow \ 25 \ ^\circ\ C}} \text{LiOH} + \frac{1}{2} \text{H}_2
\]

\[
\text{Na(s)} + \text{H}_2\text{O} \xrightarrow{\text{vigorous \ 25 \ ^\circ\ C}} \text{NaOH} + \frac{1}{2} \text{H}_2
\]

\[
\text{K(s)} + \text{H}_2\text{O} \xrightarrow{\text{flames \ 25 \ ^\circ\ C}} \text{KOH} + \frac{1}{2} \text{H}_2
\]
Rb\(_{(s)}\) or Cs\(_{(s)}\) + H\(_2\)O \(\xrightarrow{explodes\ 25\ ^\circ\text{C}}\) MOH + \(\frac{1}{2}\) H\(_2\)

6Li + N\(_2\) \(\xrightarrow{\text{slow}\ 25\ ^\circ\text{C}}\) 2Li\(_3\)N ruby-red crystals unique among the alkali metals

A Fundamental Difference Can Be Observed in O\(_2\) Reactions

(main products in bold)

1. Li + O\(_2\) → Li\(_2\)O + trace Li\(_2\)O\(_2\)
2. Na + O\(_2\) → Na\(_2\)O\(_2\) → you get NaO\(_2\) (if you force it)
3. K, Rb or Cs + O\(_2\) → MO\(_2\)

\[\text{M}_2\text{O} \text{ oxide} \quad \text{M}_2\text{O}_2 \text{ peroxide} \quad \text{MO}_2 \text{ superoxide} \]
\[\text{O}^2- \quad \text{O}^1-\text{O}^- (\text{O}_2^{2-}) \quad \text{O}_2^-\]

Q Why differences?
A The differences in reactivity with O\(_2\) can be attributed to cation size.
**Solutions of Alkali Metals in Ammonia NH$_3^{1(1)}$**

Na$_{(s)}$ (finely divided) $\rightleftharpoons$ Na (in NH$_3$ solution) 
\[
\uparrow\downarrow
\]
Na$^+$ + e$^-$
(dilute solutions)

Q: What do these equilibria mean?

A: That the NH$_3$ medium is able to “solvate” an electron. The solvated electron occupies a “cavity” in the NH$_3^{1(1)}$ where it is somewhat delocalized over a large volume so that the surrounding molecules are polarized. The polarized NH$_3$ molecules form the cavity due to NH$_3$ lone pair – e$^-$ repulsions.

\[
\text{Na} + \text{NH}_3^{1(1)} \rightleftharpoons \text{Na}^+ + \text{e}^-
\]
is stable without air or water, but eventually can react further to give:

\[
\text{NaNH}_2 \text{ (sodium amide)} + \frac{1}{2} \text{H}_2
\]
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 – $MX$ ($X = \text{halide for example}$)

**Oxides, Peroxides and Superoxides of Alkali Metals are Easily Hydrolyzed**

$M_2O + H_2O \rightleftharpoons 2M^+ + 2 OH^-$

$M_2O_2 + 2H_2O \rightleftharpoons 2M^+ + 2 OH^− + H_2O_2$

$2MO_2 + 2H_2O \rightleftharpoons O_2 + 2M^+ + 2OH^− + H_2O_2$

**Hydroxides**
- NaOH etc., white, very hygroscopic (deliquescent) solids (means they literally dissolve in the moisture from the air)
- solids also absorb CO₂ 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!

**compare:**
(1) \( \text{LiH} \) stable to 900 °C
    \( \text{NaH} \) decomposes at 350 °C
(2) \( \text{Li}_3\text{N} \) stable
    \( \text{Na}_3\text{N} \) does not exist at 25 °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) \( \text{Li}_2\text{CO}_3 \overset{\Delta}{\longrightarrow} \text{Li}_2\text{O} + \text{CO}_2 \), 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 M\(^+\) alkali metal ions**  
issues:
- first coordination sphere  
  (How many waters are directly bound to M\(^+\)?)
- total coordination sphere  
  (How many total water molecules?)

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

\( \text{Li(H}_2\text{O)}^+ + 21 \text{H}_2\text{O} \)
additional water in the solvation shell
In other words Li$^+$ in H$_2$O exerts an influence on 25 H$_2$O molecules!

<table>
<thead>
<tr>
<th>Ionic Radii (Å)</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.90</td>
<td>1.16</td>
<td>1.52</td>
<td>1.66</td>
<td>1.81</td>
</tr>
</tbody>
</table>

| Approximate Hydrated Radii (Å) | 3.40 | 2.76 | 2.32 | 2.28 | 2.28 |

| Approximate Hydration Numbers (# of H$_2$O) | 25.3 | 16.6 | 10.5 | 10.0 | 9.9  |

| Hydration Enthalpies (kJ/mol) | 519  | 406  | 322  | 293  | 264  |

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 H\(_2\)O molecules, will not associate with anions in ion-exchange resins very well!

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**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\(_2\)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 and 2,2,2-crypt](image)

The most common and most important cryptand is N[CH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)OCH\(_2\)CH\(_2\)]\(_3\)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**

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

`Cryptating binding is less`

Best size match!

More potent and selective 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.

**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

\[ 2\text{Li}^+ + \text{RCl} \rightarrow \text{Li}^+\text{Cl}^- + \text{R}^-\text{Li}^+ \]

organolithium reagent

\[ \text{Li}^+\text{R}^- \quad \text{R} = \text{Me}, \text{Bu}, \text{etc.}, \] 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.

Other Common Compounds Often Used In Organometallic Chemistry

Alcohols, amines, and other \( \text{X-H} \) bonds are highly reactive towards the neutral alkali metals \( \text{M} \).
Alkoxides  \[ M^+(OR)^- \]
\[ M + ROH \rightarrow MOR + \frac{1}{2} H_2 \]
Same type of reaction as \[ Li + H_2O \rightarrow LiOH + \frac{1}{2} H_2 \]

Amides \[ M + NR_2H \rightarrow M^+(NR_2)^- \]
(from amines) \[ M + NRH_2 \rightarrow M^+(NRH)^- \]
\[ M + NH_3 \rightarrow M^+ (NH_2)^- \]

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 CaCO$_3$ $\cdot$ MgCO$_3$ or CaMg(CO$_3$)$_2$
Ra all isotopes of this element are radioactive

<table>
<thead>
<tr>
<th>Group IA</th>
<th>→</th>
<th>Group IIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkali Metals</td>
<td>→</td>
<td>Alkaline Earth Metals</td>
</tr>
<tr>
<td>larger atomic radii</td>
<td>→</td>
<td>smaller atomic radii (increased effective nuclear charge)</td>
</tr>
<tr>
<td>lower melting and boiling point</td>
<td>→</td>
<td>higher melting and boiling point</td>
</tr>
<tr>
<td>lower densities</td>
<td>→</td>
<td>higher densities</td>
</tr>
<tr>
<td>lower ionization energies</td>
<td>→</td>
<td>higher ionization energies</td>
</tr>
<tr>
<td>lower hydration energies</td>
<td>→</td>
<td>higher hydration energies</td>
</tr>
</tbody>
</table>
lower lattice energies $\rightarrow$ higher lattice energies

Chemistry of Group IIA (some highlights)

Be very small ionic radius
Be$^{2+}$ 0.31 Å compared to:
(Li$^+$ is 0.60 Å; Na$^+$ is 0.96 Å; K$^+$ is 1.33 Å; Mg$^{2+}$ is 0.65 Å; Ca$^{2+}$ is 0.99 Å; etc.)

Due to the very small size of Be$^{2+}$, it cannot exist as a simple cation in its compounds. Consequently, even BeF$_2$ and BeO are more covalent than they are ionic unlike other M$^{2+}$ species.

$:\ddot{F} \text{Be} \ddot{F}$ - linear
- coordinatively unsaturated
- exists only in the gas phase
Polymerization of BeX₂ compounds is common [BeF₂]ₙ, [BeCl₂]ₙ, etc.,

\[
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \\
\text{Be} \quad \text{Be} \quad \text{Be} \quad \text{Be} \\
\text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl} \quad \text{Cl}
\]

a portion of [BeCl₂]ₙ is above

Since BeX₂ compounds are so coordinatively unsaturated, they are useful as Lewis acids in many reactions

\[
\text{BeF}_2 + 2\text{F}^- \rightarrow [\text{BeF}_4]^{2-}
\]

\[
\text{BeCl}_2 + 2\text{R}_2\text{O} \rightarrow \text{BeCl}_2(\text{OR}_2)_2
\]

(ether)

adopts tetrahedral coordination