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.

Li\(^+\) salts are used to treat manic depressive disorders.

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

$$\text{NaCl}_\text{(s)} \xrightarrow{\text{Electrolysis}} \text{Na}_\text{(s)} + \frac{1}{2} \text{Cl}_2\text{(g)}$$
Reactivity Comparisons

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

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

\[
\text{K}_\text{(s)} + \text{H}_2\text{O} \xrightarrow{\text{flames}} \text{KOH} + \frac{1}{2} \text{H}_2 \quad 25 \degree \text{C}
\]

\[
\text{Rb}_\text{(s)} \text{ or Cs}_\text{(s)} + \text{H}_2\text{O} \xrightarrow{\text{explodes}} \text{MOH} + \frac{1}{2} \text{H}_2 \quad 25 \degree \text{C}
\]

\[
6\text{Li} + \text{N}_2 \xrightarrow{\text{slow}} 2\text{Li}_3\text{N} \quad \text{ruby-red crystals unique among the alkali metals}
\]

25 \degree \text{C}
A Fundamental Difference Can Be Observed in O₂ Reactions

(main products in bold)

(1) Li + O₂ → Li₂O + trace Li₂O₂
(2) Na + O₂ → Na₂O₂ → you get NaO₂ (if you force it)
(3) K, Rb or Cs + O₂ → MO₂

<table>
<thead>
<tr>
<th>M₂O</th>
<th>M₂O₂</th>
<th>MO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxide</td>
<td>peroxide</td>
<td>superoxide</td>
</tr>
<tr>
<td>O²⁻</td>
<td>O=O⁻ (O₂²⁻)</td>
<td>O₂⁻</td>
</tr>
</tbody>
</table>

Q  Why differences?

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

Solutions of Alkali Metals in Ammonia NH₃(1)

Naₐ(s) (finely divided) ⇌ Na (in NH₃ solution)

↑ ↓
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) 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.

\[
\text{Na} + \text{NH}_3(1) \rightleftharpoons \text{Na}^+ + \text{e}^-
\]
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 – \(\text{M}_2\text{O}, \text{M}_2\text{O}_2, \text{MO}_2\)
hydroxides – \(\text{MOH}\) (not really binary but these are viewed as metal oxides as well)
salts – \(\text{MX}\) (\(X = \text{halide}\) for example)

Oxides, Peroxides and Superoxides of Alkali Metals are Easily Hydrolyzed
\[
\text{M}_2\text{O} + \text{H}_2\text{O} \rightleftharpoons 2\text{M}^+ + 2 \text{OH}^- \\
\text{M}_2\text{O}_2 + 2\text{H}_2\text{O} \rightleftharpoons 2\text{M}^+ + 2 \text{OH}^- + \text{H}_2\text{O}_2 \\
2\text{MO}_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{O}_2 + 2\text{M}^+ + 2\text{OH}^- + \text{H}_2\text{O}_2
\]

Hydroxides
- \(\text{NaOH}\) 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
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) LiH stable to 900 °C
    NaH decomposes at 350 °C
(2) Li$_3$N stable
    Na$_3$N does not exist at 25 °C
(3) LiOH $\xrightarrow{\Delta}$ Li$_2$O 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) Li$_2$CO$_3$ $\xrightarrow{\Delta}$ Li$_2$O + 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. \[ \text{Li(H}_2\text{O)}_4^+ \text{ is considered the first coordination sphere (found in the solid state).} \]

\[ \text{Li(H}_2\text{O)}_4^+ + 21 \text{ H}_2\text{O} \]

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!
<table>
<thead>
<tr>
<th></th>
<th>Li⁺</th>
<th>Na⁺</th>
<th>K⁺</th>
<th>Rb⁺</th>
<th>Cs⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic Radii (Å)</td>
<td>0.90</td>
<td>1.16</td>
<td>1.52</td>
<td>1.66</td>
<td>1.81</td>
</tr>
<tr>
<td>Approximate Hydrated Radii (Å)</td>
<td>3.40</td>
<td>2.76</td>
<td>2.32</td>
<td>2.28</td>
<td>2.28</td>
</tr>
<tr>
<td>Approximate Hydration Numbers (# of H₂O)</td>
<td>25.3</td>
<td>16.6</td>
<td>10.5</td>
<td>10.0</td>
<td>9.9</td>
</tr>
<tr>
<td>Hydration Enthalpies (kJ/mol)</td>
<td>519</td>
<td>406</td>
<td>322</td>
<td>293</td>
<td>264</td>
</tr>
</tbody>
</table>

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!

**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.

![Chemical structures](image)

18-crown-6 2,2,2-crypt
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

Li⁺ < Na⁺, Cs⁺ < Rb⁺ < K⁺

Binding is less than

Best size match!
Cryptates

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.

Rb⁺(2,2,2-crypt)

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:

![Valinomycin](image)

valinomycin

![Nonactin](image)

nonactin

$K^+$

*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.]
Alkali Metal Organometallics

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

organolithium reagent

\( \text{Li}^+\text{R}^- \)  \( \text{R} = \text{Me, Bu, etc.} \), 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.

Other Common Compounds Often Used In Organometallic Chemistry

Alcohols, amines, and other X-H bonds are highly reactive towards the neutral alkali metals \( \text{M} \).

**Alkoxides**  \( \text{M}^+\text{(OR)}^- \)

\[ \text{M} + \text{ROH} \rightarrow \text{MOR} + \frac{1}{2} \text{H}_2 \]

Same type of reaction as \( \text{Li} + \text{H}_2\text{O} \rightarrow \text{LiOH} + \frac{1}{2} \text{H}_2 \)

**Amides**  \( \text{M} + \text{NR}_2\text{H} \rightarrow \text{M}^+\text{(NR}_2\text{)}^- \)

(from amines)  \( \text{M} + \text{NRH}_2 \rightarrow \text{M}^+\text{(NRH)}^- \)

\[ \text{M} + \text{NH}_3 \rightarrow \text{M}^+\text{(NH}_2\text{)}^- \]

What is happening here? Redox chemistry of course. \( \text{M} \) is oxidized, \( \text{H}^+ \) is reduced
Chapter 11
Group IIA (2) Elements
Alkaline Earth Elements

Beryllium, Magnesium, Calcium, Strontium, Barium, Radium

Be is an important element in a negative sense – very toxic if its compounds are inhaled (destroys lungs) 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 CaCO₃
dolomite which is CaCO₃ ∙ MgCO₃

Ra all isotopes of this element are radioactive
<table>
<thead>
<tr>
<th>Property</th>
<th>Group IA</th>
<th>→</th>
<th>Group IIA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radii</td>
<td>larger</td>
<td>→</td>
<td>smaller (increased effective</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>nuclear charge)</td>
</tr>
<tr>
<td>Melting and boiling point</td>
<td>lower</td>
<td>→</td>
<td>higher</td>
</tr>
<tr>
<td></td>
<td>density</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ionization energies</td>
<td>lower</td>
<td>→</td>
<td>higher</td>
</tr>
<tr>
<td></td>
<td>energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydration energies</td>
<td>lower</td>
<td>→</td>
<td>higher</td>
</tr>
<tr>
<td></td>
<td>energy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice energies</td>
<td>lower</td>
<td>→</td>
<td>higher</td>
</tr>
<tr>
<td></td>
<td>energy</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Chemistry of Group IIA (some highlights)

Be very small ionic radius
\[
\text{Be}^{2+} \quad 0.31 \text{ Å} \quad \text{compared to:}
\]
\[
\text{Li}^+ \text{ is } 0.60 \text{ Å}; \quad \text{Na}^+ \text{ is } 0.96 \text{ Å}; \quad \text{K}^+ \text{ is } 1.33 \text{ Å}; \quad \text{Mg}^{2+} \text{ is } 0.65 \text{ Å}; \quad \text{Ca}^{2+} \text{ is } 0.99 \text{ Å}; \quad \text{etc.}
\]

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.

\[
\text{F}^- \quad \text{Be} \quad \text{F}^-
\]
- linear
- coordinatively unsaturated
- exists only in the gas phase
Polymerization of BeX$_2$ compounds is common [BeF$_2$]$_n$, [BeCl$_2$]$_n$, etc.,

\[
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl} \\
\end{array}
\begin{array}{c}
\text{Cl} \\
\text{Be} \\
\text{Cl} \\
\end{array}
\]

\[2^-\]

a portion of [BeCl$_2$]$_n$ is above

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

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

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

(ether)

assumes tetrahedral coordination