Group 1 (1A) - Alkali Metals

- All are soft, lustrous, reactive metals with low melting points.

- Reactivity increases down the group as ionization energy decreases.

<table>
<thead>
<tr>
<th>Element</th>
<th>IP (kJ/mol)</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>$E^o$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>520</td>
<td>180.5</td>
<td>1347</td>
<td>−3.045</td>
</tr>
<tr>
<td>Na</td>
<td>496</td>
<td>97.8</td>
<td>881</td>
<td>−2.7109</td>
</tr>
<tr>
<td>K</td>
<td>419</td>
<td>63.2</td>
<td>766</td>
<td>−2.924</td>
</tr>
<tr>
<td>Rb</td>
<td>403</td>
<td>39.0</td>
<td>688</td>
<td>−2.925</td>
</tr>
<tr>
<td>Cs</td>
<td>376</td>
<td>28.5</td>
<td>705</td>
<td>−2.923</td>
</tr>
<tr>
<td>Fr</td>
<td>~400</td>
<td>27</td>
<td></td>
<td>~ −2.9</td>
</tr>
</tbody>
</table>

- Almost all compounds are ionic, except for some Li and Na organometallic compounds.

<table>
<thead>
<tr>
<th>$r^+$ (pm)</th>
<th>M$^+$</th>
<th>Li$^+$</th>
<th>Na$^+$</th>
<th>K$^+$</th>
<th>Rb$^+$</th>
<th>Cs$^+$</th>
<th>NH$_4^+$</th>
<th>Ag$^+$</th>
<th>Tl$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>95</td>
<td>133</td>
<td>148</td>
<td>169</td>
<td>143</td>
<td>126</td>
<td>140</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

- Same charge and similar size of NH$_4^+$, Ag$^+$, and Tl$^+$ result in similar compounds, often isomorphous with alkali metal analogs.
Electrolysis

- Reduction potentials are so negative that the metals cannot be obtained by electrolysis from aqueous solutions; water reduction occurs instead.
  \[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \quad E^o = -0.42 \text{ V (pH 7)} \]

- All can be obtained by electrolysis of their molten salts.

  Cathode: \[ \text{M}^+ + e^- \rightarrow \text{M} \]

  Anode: \[ \text{Cl}^- \rightarrow \frac{1}{2}\text{Cl}_2 + e^- \]
Reactivity

- All react with halogens, hydrogen, and water.
  \[ M + \frac{1}{2}X_2 \rightarrow MX \quad X = F, Cl, Br, I \]
  \[ M + \frac{1}{2}H_2 \xrightarrow[\Delta]{} MH \]
  \[ M + H_2O \rightarrow MOH + \frac{1}{2}H_2 \]

- Only Li reacts with \( N_2(g) \) and is the only element that reacts with nitrogen at room temperature.
  \[ 6Li + N_2 \xrightarrow{20-200^\circ C} 2Li_3N \]

- When burned in air, alkali metals form either the oxide, peroxide, or superoxide as the principal product, depending on the size of the cation.

<table>
<thead>
<tr>
<th>M + O₂ →</th>
<th>Li₂O</th>
<th>Na₂O₂</th>
<th>KO₂</th>
<th>RbO₂</th>
<th>CsO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anion</td>
<td>oxide</td>
<td>peroxide</td>
<td>superoxide</td>
<td>superoxide</td>
<td>superoxide</td>
</tr>
</tbody>
</table>

- Sodium also produces some Na₂O along with Na₂O₂.

- Peroxides contain \( O_2^{2-} \) ions, whose MO configuration is \((\sigma)^2(\pi)^4(\pi^*)^4\).

- Superoxides contain \( O_2^- \) ions, whose MO configuration is \((\sigma)^2(\pi)^4(\pi^*)^3\).

- The superoxide compounds are a rare example of a paramagnetic binary non-transition element compound.
Alkali Metals in NH₃(ℓ)

- All alkali metals dissolve in liquid ammonia to give blue solutions of solvated electrons.
  \[
  M \xrightarrow{\text{NH}_3(ℓ)} M^+[\text{NH}_3(ℓ)] + e^-[\text{NH}_3(ℓ)]
  \]

- With Fe³⁺ catalyst the amide is formed.
  \[
  M + \text{NH}_3(ℓ) \xrightarrow{\text{Fe}^3+_{\text{NH}_3(ℓ)}} \text{MNH}_2 + \frac{1}{2}\text{H}_2
  \]
  
  - An analogous reaction occurs with RNH₂ amines.

- LiNH₂ uniquely decomposes to the immide on heating.
  \[
  2\text{LiNH}_2 \xrightarrow{Δ} \text{Li}_2\text{NH} + \text{NH}_3
  \]
  
  - This is an example of \textit{first-element uniqueness}. 

First-Element Uniqueness

- First elements of the main groups tend to show some unique chemistry not shown by the heavier elements of the group.

- Lithium is the smallest of the alkali metals and has the highest charge density.
  - Lithium compounds tend to be more covalent than comparable alkali metal compounds.

- Thermal decomposition of ionic nitrates gives nitrites, but more covalent lithium nitrate decomposes to the oxide, similar to lead(II) nitrate.
  
  \[
  \begin{align*}
  \text{NaNO}_3 & \xrightarrow{\Delta} \text{NaNO}_2 + \frac{1}{2}\text{O}_2 \\
  2\text{LiNO}_3 & \xrightarrow{\Delta} \text{Li}_2\text{O} + \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2 \\
  \text{Pb(NO}_3)_2 & \xrightarrow{\Delta} \text{PbO} + \text{N}_2\text{O}_4 + \frac{1}{2}\text{O}_2
  \end{align*}
  \]
Group 1 Organometallic Compounds

- Li and Na organometallic compounds are important in organic synthesis.
  - Lithium organometallic compounds are more covalent and more soluble in organic solvents.

- LiR compounds are formed by reacting organic halides with metallic lithium.
  \[ \text{RCI} + 2\text{Li} \xrightarrow{C_{d}H_{6}} \text{LiR} + \text{LiCl} \]

- LiR compounds are spontaneously flammable in air, but addition of LiBr or LiI causes formation of stable complexes.
  \[ \text{LiR} + n\text{LiBr} \rightarrow \text{LiR} \cdot (\text{LiBr})_{n} \quad n = 1 - 6 \]

- LiCH\text{3} and LiC\text{2}H\text{5} are tetramers with a tetrahedral structure.
Group 2 (2A) Elements

- Compared to group 1 elements, these are harder, have higher melting points and boiling points, and are less reactive.

<table>
<thead>
<tr>
<th>Element</th>
<th>IP$_1 +$ IP$_2$ (kJ/mol)</th>
<th>m.p. (°C)</th>
<th>b.p. (°C)</th>
<th>$E^\circ$ (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Be</td>
<td>2656.6</td>
<td>1287</td>
<td>~2500</td>
<td>−1.847</td>
</tr>
<tr>
<td>Mg</td>
<td>2184.4</td>
<td>649</td>
<td>1105</td>
<td>−2.372</td>
</tr>
<tr>
<td>Ca</td>
<td>1735.2</td>
<td>839</td>
<td>1494</td>
<td>−2.868</td>
</tr>
<tr>
<td>Sr</td>
<td>1613.8</td>
<td>768</td>
<td>1381</td>
<td>−2.889</td>
</tr>
<tr>
<td>Ba</td>
<td>1468.2</td>
<td>727</td>
<td>~1850</td>
<td>−2.912</td>
</tr>
<tr>
<td>Ra</td>
<td>1488.5</td>
<td>~700</td>
<td>~1700</td>
<td>−2.8</td>
</tr>
</tbody>
</table>

- All can be obtained by electrolysis of their fused chlorides, but LiCl must be added to BeCl$_2$ to increase conductivity.

- Cations are much smaller than group 1 cations, and with a +2 charge have much higher charge densities.

<table>
<thead>
<tr>
<th>M$^{2+}$</th>
<th>Be$^{2+}$</th>
<th>Mg$^{2+}$</th>
<th>Ca$^{2+}$</th>
<th>Sr$^{2+}$</th>
<th>Ba$^{2+}$</th>
<th>Ra$^{2+}$</th>
<th>Eu$^{2+}$</th>
<th>Pb$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r^{2+}$ (pm)</td>
<td>31</td>
<td>65</td>
<td>99</td>
<td>113</td>
<td>135</td>
<td>140</td>
<td>112</td>
<td>120</td>
</tr>
</tbody>
</table>

- Eu$^{2+}$ and Pb$^{2+}$ have similar size and charge density to Sr$^{2+}$ and Ba$^{2+}$ and form similar compounds with similar chemistry.

- Radioactive $^{90}$Sr ($\beta^-$, $t_{1/2} = 28.1$ yr) from fallout is a problem because it can substitute for Ca (e.g., in milk).
Charge Density and Group 2 Chemistry

- Be\(^{2+}\) has high charge density, which makes its compounds appreciably covalent.

- High charge density of Be\(^{2+}\) is largely responsible for its first-element unique chemistry.

- Because beryllium's chemistry is so different from the other group 2 elements, the term "alkaline earth" is usually restricted to Mg, Ca, Sr, Ba, Ra.

- Mg\(^{2+}\) has a similar charge density to Li\(^{+}\), so the two elements show some similar chemistry (e.g., tendency to form useful organometallic compounds).
  - The similar chemistries of Li and Mg are an example of a diagonal relationship, also seen with other diagonally related period 2 and period 3 elements.
Group 2 Elements – Beryllium

- Beryllium is a light, brittle metal obtained from the mineral beryl.
  - Because of its low absorptivity, Be is used as a window material in x-ray tubes.
  - Added in small amounts to Cu, Ni, etc. it adds strength and corrosion resistance.
  - Be metal is fairly inert in air due to a BeO coating.

- All beryllium compounds, except certain minerals, are highly toxic and require extraordinary precautions when used!

- Non-toxic minerals:
  - Beryl, $3\text{BeO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 = \text{Be}_3\text{Al}_2(\text{SiO}_3)_6$ – gem forms emerald and aquamarine.
  - Phenacite – $\text{Be}_2\text{SiO}_4$
Group 2 Elements - The Alkaline Earths

- Ca and Mg are the 5th and 6th most abundant elements by mass in the earth's crust.
  - Found together in dolomite, Ca(OH)$_2$·Mg(OH)$_2$.
  - Ca is found as gypsum, CaSO$_4$·2H$_2$O; calcite, aragonite, chalk, CaCO$_3$; and many other minerals.

- Sr and Ba are much less abundant.
  - Found as their sulfates and carbonates.
  - Sr and Eu compounds and Ba and Ra compounds are often found together, due to similarities in sizes.

- All isotopes of Ra are radioactive.
  - Most stable isotope is $^{226}$Ra ($\alpha$, $t_{\frac{1}{2}} = 1600$ yr)
  - First isolated by Pierre and Marie Curie from uranium ore pitchblende in 1898.

- Metal reactivity with water increases with atomic weight.
  \[ M + 2H_2O \rightarrow M(OH)_2 + H_2 \]
  - Mg does not react appreciably except in acid.
    \[ Mg + 2H_3O^+ \rightarrow Mg^{2+} + H_2 + 2H_2O \]
  - Ca does not react unless freshly polished, owing to a protective coating of CaO.
Beryllium Aqueous Chemistry

- Be\(^{2+}\) has such high charge density that its hydrated ions are acidic, and both oxide and hydroxide are amphoteric.

- Be\(^{2+}(aq)\) acts as a polyprotic acid.
  \[
  \begin{align*}
  &\text{Be(H}_2\text{O)}_4^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{Be(H}_2\text{O)}_3\text{OH}^+ + \text{H}_3\text{O}^+ \quad K_a \approx 10^{-5} \\
  &\text{Be(H}_2\text{O)}_3\text{OH}^+ + \text{H}_2\text{O} \rightleftharpoons \text{Be(H}_2\text{O)}_2(\text{OH})_2 + \text{H}_3\text{O}^+ \quad K_a \approx 10^{-14} \\
  &\text{Be(H}_2\text{O)}_2(\text{OH})_2 + \text{H}_2\text{O} \rightleftharpoons \text{Be(H}_2\text{O})(\text{OH})_3^- + \text{H}_3\text{O}^+ \\
  &\text{Be(H}_2\text{O})(\text{OH})_3^- + \text{H}_2\text{O} \rightleftharpoons \text{Be(OH)}_4^{2-} + \text{H}_3\text{O}^+ \\
  \end{align*}
  \]

- These equilibria are complicated by a tendency to polymerize.
  \[
  3\text{Be}^{2+}(aq) + 6\text{H}_2\text{O} \rightleftharpoons (\text{BeOH})_3^{3+} + 3\text{H}_3\text{O}^+ \quad K = 4.6 \times 10^8
  \]

- Amphoteric character of BeO is evident by its hydrolysis to give Be(OH)\(_2\), typical of a metal oxide.
  \[
  \text{BeO} + \text{H}_2\text{O} \rightarrow \text{Be(OH)}_2
  \]

- Strong coordination by water tends to make most Be\(^{2+}\) salts tetrahydrates; e.g., BeSO\(_4\)\(\cdot 4\text{H}_2\text{O}\).
Covalent Beryllium Compounds

- Covalent compounds of Be tend to be tetrahedrally coordinated; e.g., BeCl$_2$(OEt)$_2$, BeF$_4^{2-}$.

- Although BeCl$_2$ and Be(CH$_3$)$_2$ exist as discreet, linear molecules in the gas phase, in the solid they are polymerized as tetrahedrally coordinated Be atoms forming infinite chains.

\[
\begin{array}{c}
\text{X} \quad \text{Be} \quad \text{X} \quad \text{Be} \quad \text{X} \quad \text{Be} \\
\text{X} \quad \text{Be} \quad \text{X} \quad \text{Be} \quad \text{X} \quad \text{Be} \\
\end{array}
\]

\[X = \text{CH}_3, \text{Cl}\]

- In Be(CH$_3$)$_2$ the Be–C–Be bridges are 3c-2e bonds.
- In BeCl$_2$ the Be–Cl–Be bridges are normal 2c-2e bonds.

- Beryllium alkyls are best made by reacting the metal with mercury dialkyl, followed by vacuum sublimation/distillation.

\[\text{Hg(CH}_3\text{)}_2 + \text{Be} \xrightarrow{110^\circ C} \text{Be(CH}_3\text{)}_2 + \text{Hg}\]

- Beryllium alkyls are liquids or solids of high reactivity that spontaneously flame in air and violently hydrolyze in water.

- Beryllium aryls are made by reacting a lithium aryl in a hydrocarbon with BeCl$_2$ in diethyl ether, in which the byproduct LiCl is insoluble.

\[2\text{LiC}_6\text{H}_5 + \text{BeCl}_2 \rightarrow \text{Be(C}_6\text{H}_5\text{)}_2 + 2 \text{LiCl}\]

Given the toxicity, organoberyllium compounds are of little practical value in most laboratory settings.
Alkaline Earth Oxygen Compounds

- When burned, all give the normal oxide.
  \[ M + \frac{1}{2}O \rightarrow MO \]

- Mg is used in incendiary bombs, because the reaction is very exothermic (–602 kJ/mol) and it is difficult to extinguish.
  - Mg will continue to burn in a \( \text{CO}_2 \) atmosphere.
    \[ 2\text{Mg} + \text{CO}_2 \rightarrow 2\text{MgO} + \text{C} \]

- SrO and BaO can be converted to the peroxides with heat and pressure.
  \[ 2\text{BaO} + \text{O}_2 \xrightarrow{\Delta} 2\text{BaO}_2 \]

- MgO is relatively inert, but the others readily form hydroxides and carbonates.
  \[ \text{MO} + \text{H}_2\text{O} \rightarrow \text{M(OH)}_2 \quad \text{M} \neq \text{Mg} \]
  \[ \text{MO} + \text{CO}_2 \rightarrow \text{MCO}_3 \quad \text{M} \neq \text{Mg} \]

- In base, Mg\(^{2+}(aq)\) solutions precipitate relatively insoluble Mg(OH)\(_2\) \( (K_sp = 1.1 \times 10^{-11}) \).

- Solubility of the other hydroxides increases down the group.
  \[ \text{Ca(OH)}_2 < \text{Sr(OH)}_2 < \text{Ba(OH)}_2 < \text{Ra(OH)}_2 \]
  sl. soluble soluble soluble soluble
  \[ K_sp = 1.3 \times 10^{-6} \]

- All the carbonates are insoluble
Important Ionic Calcium Compounds

- Many simple ionic compounds of calcium have been commercially important throughout history.
  - \( \text{CaCO}_3 \) - limestone, chalk, marble, calcite, aragonite
  - \( \text{CaSO}_4 \) - anhydrite
  - \( \text{CaSO}_4 \cdot 2\text{H}_2\text{O} \) - gypsum
  - \( \text{CaO} \) - quicklime
  - \( \text{Ca(OH)}_2 \) - slaked lime

- Plaster of Paris is the hemihydrate of \( \text{CaSO}_4 \), which forms gypsum on setting.
  \[
  2\text{CaSO}_4 \cdot \frac{1}{2}\text{H}_2\text{O} + 3\text{H}_2\text{O} \rightleftharpoons 2\text{CaSO}_4 \cdot 2\text{H}_2\text{O}
  \]

- Hydration of quicklime is the basis of some traditional mortars.
  - Initial formation of slaked lime is followed by “curing”, which forms \( \text{CaCO}_3 \).
    - slaking of lime: \( \text{CaO} + \text{H}_2\text{O} \rightleftharpoons \Delta \text{Ca(OH)}_2 \)
    - curing: \( \text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} \)

- Portland cement is made by roasting \( \text{CaO} \) with clay, forming a complex mixture of silicates and aluminates.

- A suspension of \( \text{Ca(OH)}_2 \) (solubility \( \approx 1 \text{ g/L hot H}_2\text{O} \)), called “lime water” is reactive to acid gases and has been used as a test for such.
  \[
  \text{Ca(OH)}_2(\text{aq}) + \text{CO}_2(\text{g}) \rightarrow \text{CaCO}_3(\text{s}) + \text{H}_2\text{O(\text{l})}
  \]
  \[
  \text{Ca(OH)}_2(\text{aq}) + \text{SO}_2(\text{g}) \rightarrow \text{CaSO}_3(\text{s}) + \text{H}_2\text{O(\text{l})}
  \]
  \[
  \text{CaSO}_3(\text{s}) + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CaSO}_4(\text{s})
  \]
Calcite Cycle

- The calcite cycle, which uses CaCO$_3$ from oyster shells, has long been an important industrial process for obtaining useful calcium compounds, acetylene, and ammonia.

  \[
  \text{CaCO}_3 \xrightarrow{750^\circ\text{C}} \text{CaO} + \text{CO}_2 \quad \text{calcination}
  \]

  \[
  \text{CaO} + 3\text{C} \xrightarrow{\Delta} \text{CaC}_2 + \text{CO}
  \]

  \[
  \text{CaC}_2 + 2\text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2 + \text{C}_2\text{H}_2
  \]

  \[
  \text{CaC}_2 + \text{N}_2 \xrightarrow{1000^\circ\text{C}} \text{CaCN}_2 + \text{C} \quad \text{cyanamide reaction}
  \]

  \[
  \text{CaCN}_2 + 3\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + 2\text{NH}_3
  \]

- CaCO$_3$ formed with the hydrolysis of CaCN$_2$ is recycled for use in the first step.
Organometallic Compounds

- Both Be and Mg form organometallic compounds, but only the Mg compounds are of practical importance, given the toxicity of Be.

- Tendency of Mg to form organometallic compounds is similar to that of Li (diagonal relationship).

- The Grignard reagents are the best known magnesium organometallic compounds.

\[
\text{Mg} + \text{RX} \xrightarrow{E_tO} \text{RMgX} \xrightarrow{\text{evap.}} \text{RMgX} \cdot 2E_tO
\]