Group 1 (1A) - Alkali Metals

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

- Reactivity increases down the group as ionization energy decreases.

Element	IP (kJ/mol)	m.p. (ºC)	b.p. (ºC)	E^o (V)
Li	520	180.5	1347	–3.045
Na	496	97.8	881	–2.7109
K	419	63.2	766	–2.924
Rb	403	39.0	688	–2.925
Cs	376	28.5	705	−2.923
Fr	~400	27		~ −2.9

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

M^+	Li^+	Na^+	K^+	Rb^+	Cs^+	NH_4^+	Ag^+	Tl^+
r^+ (pm)	60	95	133	148	169	143	126	140

- 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.

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^\circ = -0.42\ \text{V (pH 7)}$$

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

Cathode: $M^+ + e^- \rightarrow M$

Anode: $Cl^- \rightarrow \tfrac{1}{2}Cl_2 + e^-$

Reactivity

- All react with halogens, hydrogen, and water.

  $M + ½X_2 \rightarrow MX$ X = F, Cl, Br, I

  $M + ½H_2 \xrightarrow{\Delta} MH$

  $M + H_2O \rightarrow MOH + ½H_2$

- Only Li reacts with $N_2(g)$ and is the only element that reacts with nitrogen at room temperature.

  $6Li + N_2 \xrightarrow{20 - 200°C} 2Li_3N$

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

$M + O_2 \rightarrow$	Li_2O	Na_2O_2	KO_2	RbO_2	CsO_2
Anion	oxide	peroxide	superoxide	superoxide	superoxide

- Sodium also produces some Na_2O along with Na_2O_2.

- 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 $NH_3(l)$

- All alkali metals dissolve in liquid ammonia to give blue solutions of solvated electrons.

$$M \xrightarrow[NH_3(l)]{} M^+[NH_3(l)] + e^-[NH_3(l)]$$

- With Fe^{3+} catalyst the amide is formed.

$$M + NH_3(l) \xrightarrow[NH_3(l)]{Fe^{3+}} MNH_2 + \frac{1}{2}H_2$$

  - An analogous reaction occurs with RNH_2 amines.

- $LiNH_2$ uniquely decomposes to the immide on heating.

$$2LiNH_2 \xrightarrow[\Delta]{} Li_2NH + NH_3$$

  - This is an example of *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.

$$NaNO_3 \xrightarrow[\Delta]{} NaNO_2 + \tfrac{1}{2}O_2$$

$$2LiNO_3 \xrightarrow[\Delta]{} Li_2O + N_2O_4 + \tfrac{1}{2}O_2$$

$$Pb(NO_3)_2 \xrightarrow[\Delta]{} PbO + N_2O_4 + \tfrac{1}{2}O_2$$

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.

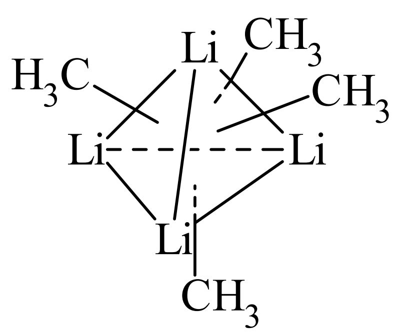
- LiR compounds are formed by reacting organic halides with metallic lithium.

$$RCl + 2Li \xrightarrow[C_6H_6]{} LiR + LiCl$$

- LiR compounds are spontaneously flammable in air, but addition of LiBr or LiI causes formation of stable complexes.

$$LiR + nLiBr \rightarrow LiR{\cdot}(LiBr)_n \qquad n = 1 - 6$$

- $LiCH_3$ and LiC_2H_5 are tetramers with a tetrahedral structure.



T_d

Group 2 (2A) Elements

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

Element	$IP_1 + IP_2$ (kJ/mol)	m.p. (ºC)	b.p. (ºC)	E^o (V)
Be	2656.6	1287	~2500	–1.847
Mg	2184.4	649	1105	–2.372
Ca	1735.2	839	1494	–2.868
Sr	1613.8	768	1381	–2.889
Ba	1468.2	727	~1850	–2.912
Ra	1488.5	~700	~1700	–2.8

- 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.

M^{2+}	Be^{2+}	Mg^{2+}	Ca^{2+}	Sr^{2+}	Ba^{2+}	Ra^{2+}	Eu^{2+}	Pb^{2+}
r^{2+} (pm)	31	65	99	113	135	140	112	120

  - 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 (β^-, $t_{1/2}$ = 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, $3BeO \cdot Al_2O_3 \cdot 6SiO_2 = Be_3Al_2(SiO_3)_6$ – gem forms emerald and aquamarine.
  - Phenacite – Be_2SiO_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, $Ca(OH)_2 \cdot Mg(OH)_2$.
  - Ca is found as gypsum, $CaSO_4 \cdot 2H_2O$; 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 (α, $t_{1/2}$ = 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.
  $Be(H_2O)_4^{2+} + H_2O \rightleftharpoons Be(H_2O)_3OH^+ + H_3O^+$ $\quad K_a \approx 10^{-5}$
  $Be(H_2O)_3OH^+ + H_2O \rightleftharpoons Be(H_2O)_2(OH)_2 + H_3O^+$ $\quad K_a \approx 10^{-14}$
  $Be(H_2O)_2(OH)_2 + H_2O \rightleftharpoons Be(H_2O)(OH)_3^- + H_3O^+$
  $Be(H_2O)(OH)_3^- + H_2O \rightleftharpoons Be(OH)_4^{2-} + H_3O^+$

  - These equilibria are complicated by a tendency to polymerize.
    $3Be^{2+}(aq) + 6H_2O \rightleftharpoons (BeOH)_3^{3+} + 3H_3O^+$ $\quad K = 4.6 \times 10^8$

- Amphoteric character of BeO is evident by its hydrolysis to give $Be(OH)_2$, typical of a metal oxide.

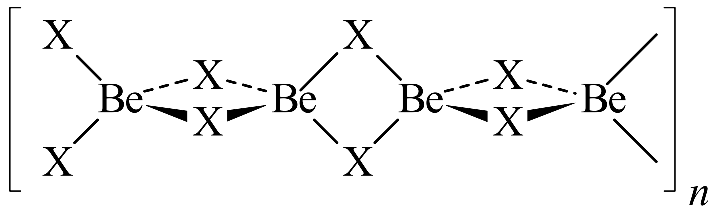
$$BeO + H_2O \rightarrow Be(OH)_2$$

- Strong coordination by water tends to make most Be^{2+} salts tetrahydrates; e.g., $BeSO_4 \cdot 4H_2O$.

Covalent Beryllium Compounds

- Covalent compounds of Be tend to be tetrahedrally coordinated; e.g., $BeCl_2(OEt_2)_2$, 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.



X = CH_3, Cl

  - In $Be(CH_3)_2$ the Be–C–Be bridges are 3*c*-2*e* bonds.
  - In $BeCl_2$ the Be–Cl–Be bridges are normal 2*c*-2*e* bonds.

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

$$Hg(CH_3)_2 + Be \xrightarrow{110^\circ C} Be(CH_3)_2 + Hg$$

  - 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.

$$2LiC_6H_5 + BeCl_2 \rightarrow Be(C_6H_5)_2 + 2\ LiCl\downarrow$$

☛ 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 CO_2 atmosphere.

$$2Mg + CO_2 \rightarrow 2MgO + C$$

- SrO and BaO can be converted to the peroxides with heat and pressure.

$$2BaO + O_2 \xrightarrow[\Delta]{P} 2BaO_2$$

- MgO is relatively inert, but the others readily form hydroxides and carbonates.

$$MO + H_2O \rightarrow M(OH)_2 \qquad M \neq Mg$$
$$MO + CO_2 \rightarrow MCO_3 \qquad M \neq Mg$$

- 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.

$Ca(OH)_2$ <	$Sr(OH)_2$ <	$Ba(OH)_2$ <	$Ra(OH)_2$
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.

$CaCO_3$	limestone, chalk, marble, calcite, aragonite
$CaSO_4$	anhydrite
$CaSO_4 \cdot 2H_2O$	gypsum
CaO	quicklime
$Ca(OH)_2$	slaked lime

- Plaster of Paris is the hemihydrate of $CaSO_4$, which forms gypsum on setting.

$$2CaSO_4 \cdot \tfrac{1}{2}H_2O + 3H_2O \rightleftharpoons 2CaSO_4 \cdot 2H_2O$$

- Hydration of quicklime is the basis of some traditional mortars.
  - Initial formation of slaked lime is followed by "curing", which forms $CaCO_3$.

slaking of lime $$CaO + H_2O \underset{\Delta}{\rightleftharpoons} Ca(OH)_2$$

curing $$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

- Portland cement is made by roasting CaO with clay, forming a complex mixture of silicates and aluminates.

- A suspension of $Ca(OH)_2$ (solubility ≈ 1 g/L hot H_2O), called "lime water" is reactive to acid gases and has been used as a test for such.

$$Ca(OH)_2(aq) + CO_2(g) \rightarrow CaCO_3(s) + H_2O(l)$$
$$Ca(OH)_2(aq) + SO_2(g) \rightarrow CaSO_3(s) + H_2O(l)$$
$$CaSO_3(s) + \tfrac{1}{2}O_2(g) \rightarrow CaSO_4(s)$$

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.

$$CaCO_3 \xrightarrow[750^{\circ}C]{} CaO + CO_2$$ calcination

$$CaO + 3C \xrightarrow[\Delta]{} CaC_2 + CO$$

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$$

$$CaC_2 + N_2 \xrightarrow[1000^{\circ}C]{} CaCN_2 + C$$ cyanamide reaction

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3$$

- $CaCO_3$ 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.

$$Mg + RX \xrightarrow{Et_2O} RMgX \xrightarrow[\text{evap.}]{} RMgX{\cdot}2Et_2O$$