

Greenwood & Earnshaw

2nd Edition

Chapter 4

**Lithium, Sodium, Potassium,
Rubidium, Caesium and Francium**

The Alkali Metals – Trends

- Alkali Metals are soft, low melting, low density, low: ΔH_{fus} , ΔH_{vap} , ΔH_{subl} .
- mp: $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ $\text{mp}_{\text{Cs}} = 28.5^\circ \text{C}$, $\text{mp}_{\text{Li}} = 180.5^\circ \text{C}$
- bp: $\text{Li} > \text{Na} > \text{K} > \text{Rb} > \text{Cs}$ $\text{bp}_{\text{Cs}} = 671^\circ \text{C}$, $\text{bp}_{\text{Li}} = 1342^\circ \text{C}$
- density: $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ $\rho_{\text{Li}} 0.534 \text{ g/cm}^3$, $\rho_{\text{Cs}} 1.90 \text{ g/cm}^3$
- sodium best electrical and heat conductor, low neutron cross section (coolant in high flux nuclear reactors).
- lithium has marked covalency in compounds.
- lithium has very high enthalpy of hydration.
- lithium has lowest density of any known solid.

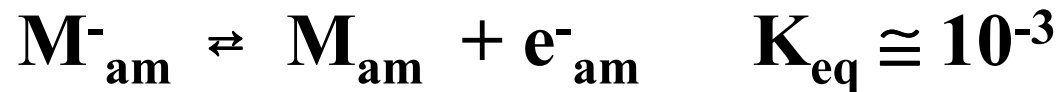
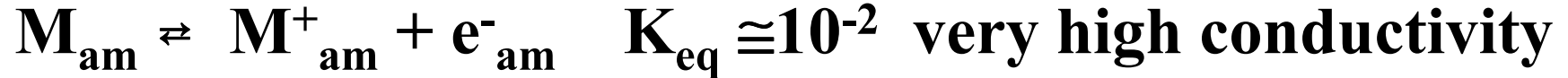
Metal Ammonia Solutions

Cs, Li, K, Na, Ba, Sr, Ca are very soluble in liquid NH₃.

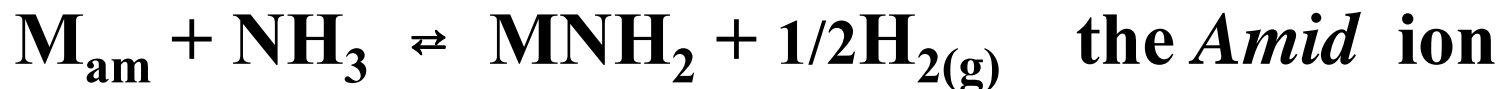
Species present in metal-liquid ammonia systems:

M, M₂, M⁺, M⁻ and e⁻ are all solvated.

Equilibria:



Presence of TM catalyst



Metal Ammonia Solutions

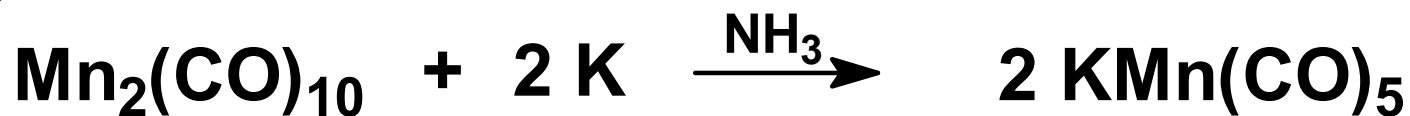
SOLUBILITY OF METAL IONS: moles NH₃/moles M

Li	Na	K	Cs
3.75	5.37	4.95	2.34
grams M/ kilogram NH₃			
108.7	251.4	463.7	333.5
-33.2°	-33.5°	-33.2°	-50°

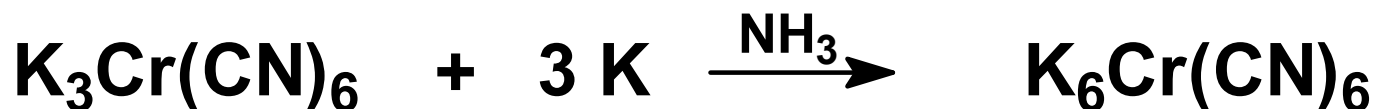
Lithium has a higher molar solubility than sodium!

Metal Ammonia Solutions - Uses

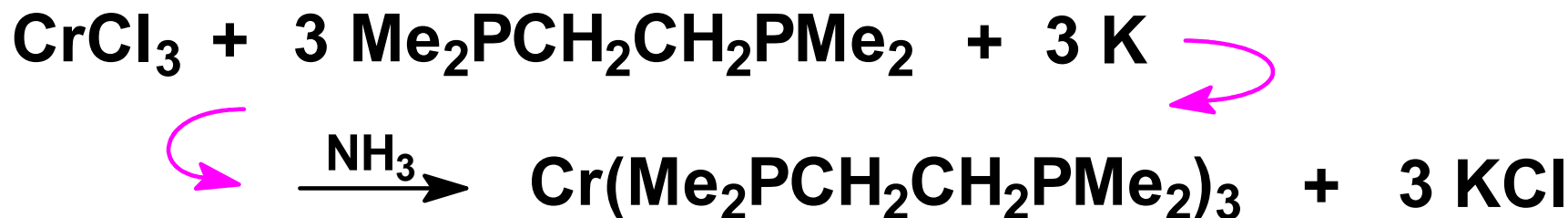
Cleavage of Metal-Metal Bonds:



Reduction of Complex Ions:



Synthesis of low oxidation state coordination compounds:

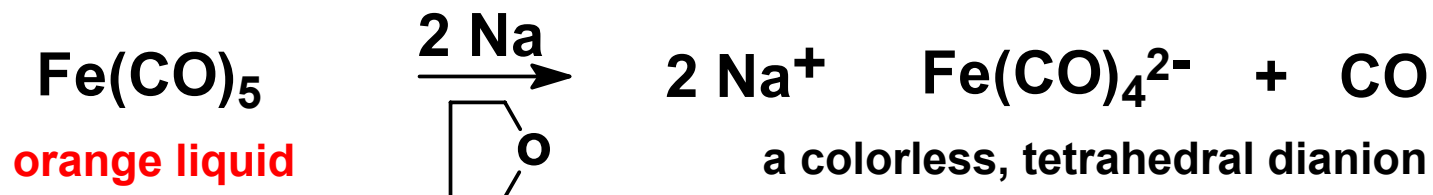
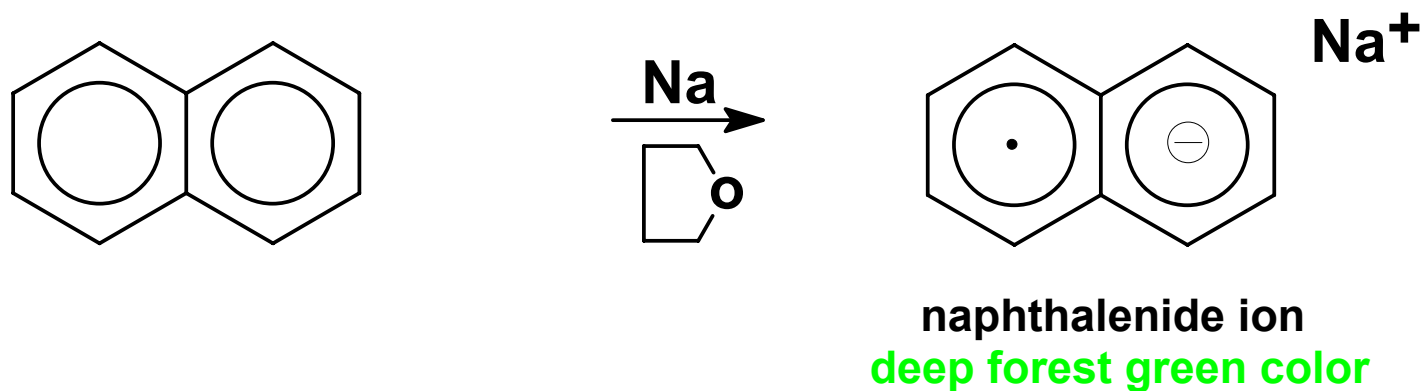
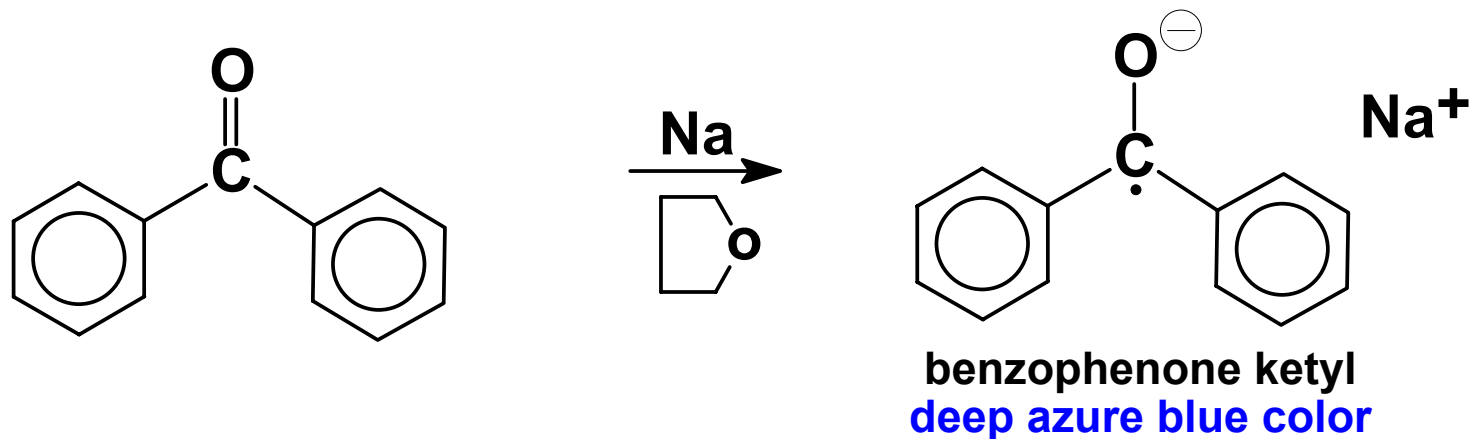


Sodium metal ammonia systems are very versatile reducing agents and metalation agents in industrial synthesis where the high cost of lithium agents and the hazard of ethers mitigates against their use.

Other Electron Carriers

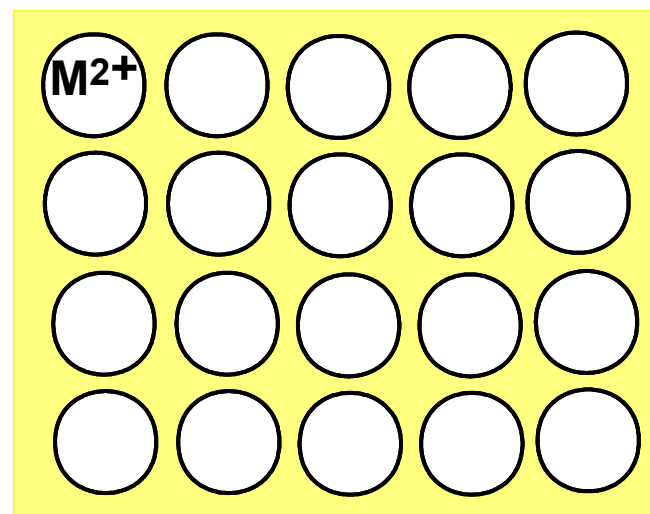
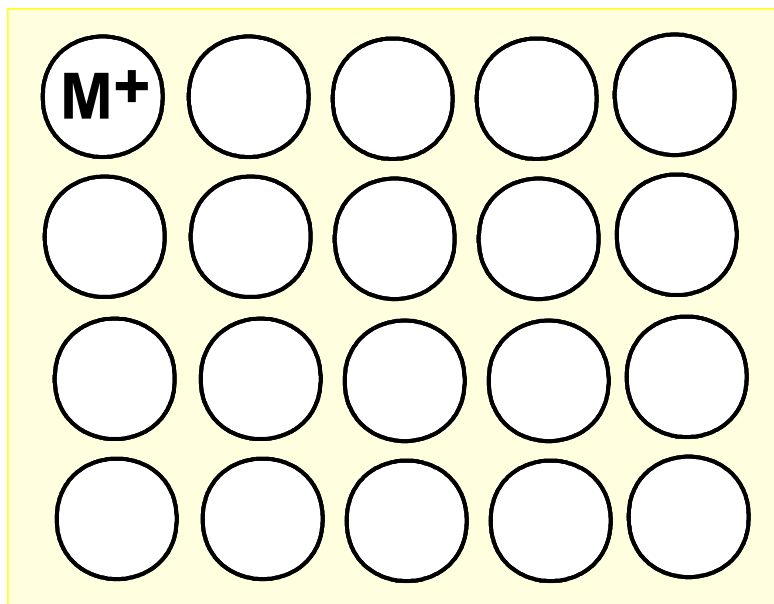
Aliphatic amines and $\text{P}(\text{NH}_2)_3$ will also stabilize solvated electrons.

Other electron carriers useful in synthesis are:



Metal-Metal Bonding

Electron Sea Model: An Electrostatic (Ionic) Model - Metal Cation Spheres are close packed and immersed in a “sea” of mobile delocalized electrons.



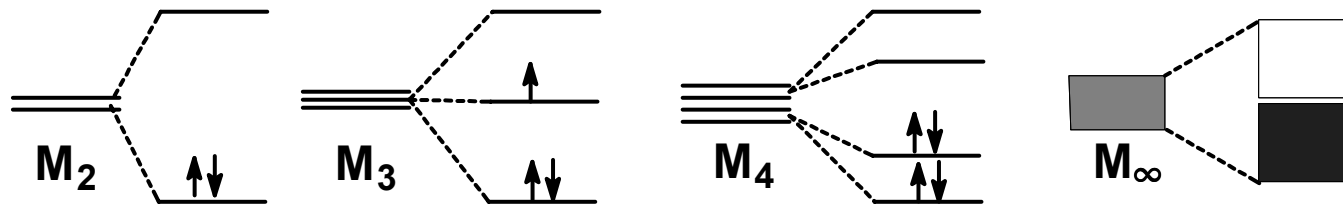
Metal-Metal Bonding

Band Theory: A Covalent Bonding Model - Atomic Orbitals (s, p, d) overlap to create an equal number of “molecular orbitals”. As the number of metal atoms becomes very large, the bonding molecular orbitals coalesce into a lower “valence band” and the anti-bonding molecular orbitals coalesce into a “conduction band” which comprise a continuum due to negligibly small energy separations. For a metallic conductor the separation between the two bands is $\ll kT$. Electrons may be excited at normal temperatures into the conduction band allowing electrical conduction to occur in both the conduction and valence bands.

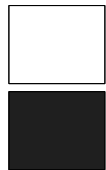
Metallic Bonding – Band Theory

Overlap of metal atomic orbitals to form molecular orbitals:

Example: Li metal $2s^1$ electron configuration



The overlap of a very large number of metal atoms produces a two band structure. The upper band is "empty" but is separated from the lower, "filled" band by a *band gap* $\Delta E \ll kT$.



A metallic conductor has a *band gap* $\Delta E \ll kT$.

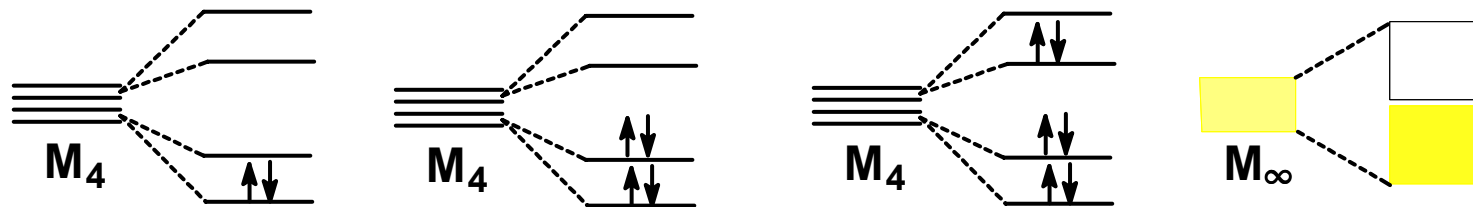
The electron population in the upper band, and the "hole" population in the lower band is optimum. Electron and "hole" conduction is limited only by thermal disorder.

- Thermal energies continually create "holes" and a fuzzy cut-off energy called the "Fermi Level".
- Electron motion is random when no electric field is applied.
- An electric field destabilizes orbitals having electrons migrating toward the negative pole, stabilizes electrons migrating toward the positive pole. A net transfer of electrons in the bulk metal, an induced current.

Electron Filling - The Properties of Metals

The mp, bp, ΔH_{fus} , ΔH_{vap} , ΔH_{subl} , strength, ductility and many other properties of metals can be related to participation of atomic orbitals in bonding and electron filling of the resulting molecular orbitals. The highest values occur near the middle of the periodic chart.



Overlap of transition metal d atomic orbitals to form molecular orbitals:



The overlap of a very large number of metal atoms produces a two band structure. The picture looks more complex as p and d metal atomic orbitals are introduced. Incomplete filling of d atomic orbitals allows for wide variation in bond strength.

 Early transition metals have low valence band filling.


 Mid-period transition metals have filled valence band.


 Late period transition metals have a filled valence band and partially filled conduction band.


Electron Filling - The Properties of Metals

Metals having few participating orbitals and few participating electrons are soft and malleable. Metals with many participating orbitals and electrons sufficient to fill the valence band (and actually a little higher) will be hard and refractory with less ductility at lower temperatures. Metals with filled subshells and filling reaching significantly into the conduction band will be soft, ductile and commonly good electrical conductors. The “d” atomic orbitals, especially higher periods, bond most effectively. Very strong metal-metal bonding may reduce electrical conductivity by localizing electrons. Metallic *clusters* may also reduce delocalization in the bulk.

Ionic Bonding Model – A Useful Model

Unitary Electron Transfer gives rise to the formation of *spherical cations* and anions whose binding is purely electrostatic. The notion of “*hard sphere*” ions gives rise to the concepts of *Ionic Radii* and simplistic concepts of coordination numbers based on hard-sphere radius ratios.

The "ionic model" has even been computationally successful with metallic alloys and covalent networks. It is computationally self compensating and the enthalpies usually calculated are notoriously insensitive to bonding model.

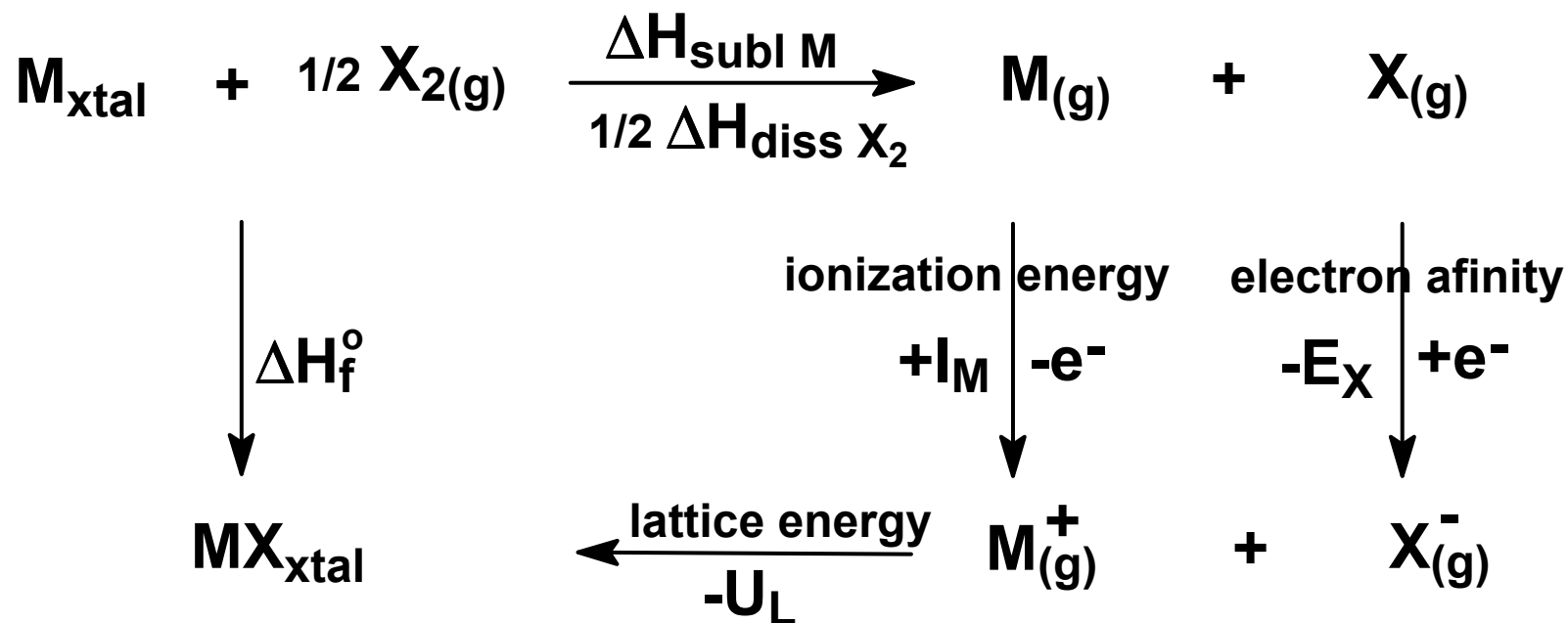
Ionic Bonding Model – An Oversimplification

Careful X-ray diffraction electron-density maps show that complete electron transfers and nodes of electron densities at ionic radii are not consistent with experiment. In all cases anions are smaller, cations are larger. Even the most ionic of species involve only about 97% transfer. Electron density minima vary considerably from ionic radii and vary significantly from compound to compound.

Consider that cations, especially non-rare gas cations, have vacant and appropriately placed orbitals relative to filled electron rich and in most cases deformable anion orbitals of appropriate symmetry. Excluding covalency from "ionic" compounds is a conceptual and computational over simplification removed significantly from reality.

The Born-Haber Cycle

Formation of a Metal Halide



$$\Delta H_{\text{f}}^{\circ} = \Delta H_{\text{subl M}} + 1/2 \Delta H_{\text{diss X}_2} + I_{\text{M}} - E_{\text{X}} - U_{\text{L}}$$

**lattice energy
is defined as:**

$$U_{\text{L}} = \frac{N_{\text{o}} A e^2}{4\pi\epsilon_{\text{o}} r_{\text{o}}} \left(1 - \frac{\rho}{r_{\text{o}}} \right)$$

The Lattice Energy Equation

$$U_L = \frac{N_o A e^2}{4\pi\epsilon_o r_o} \left(1 - \frac{\rho}{r_o} \right)$$

N_o : Avogadro's Number

A : Madlung Constant - A summation of electrostatic repulsions and attractions related by 3D geometry of a crystal. It is usually calculated. Available from tables.

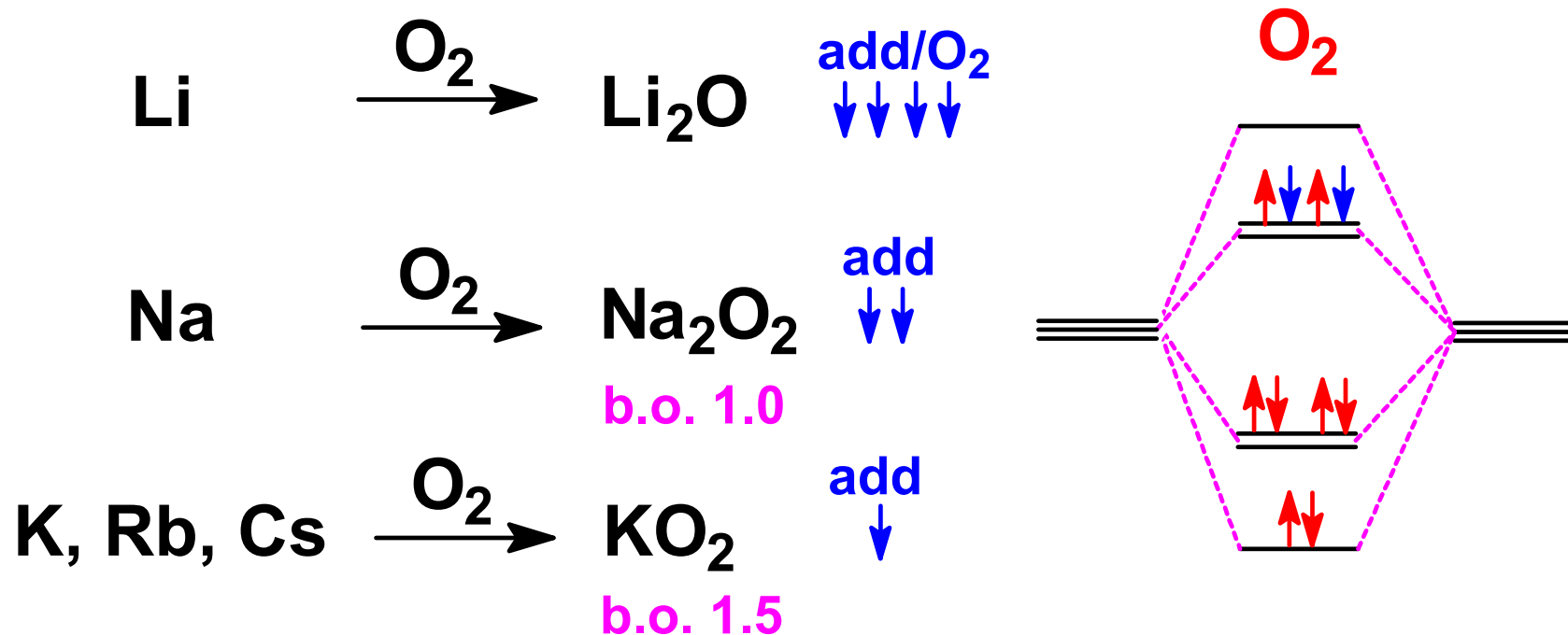
r_o : shortest cation Anion internuclear distance

ρ : close range repulsion force, i.e. "hard sphere repulsion force"

e : charge on electron

ϵ_o : permittivity in vacuum.

Alkali Metal Oxides by “Free Burning”

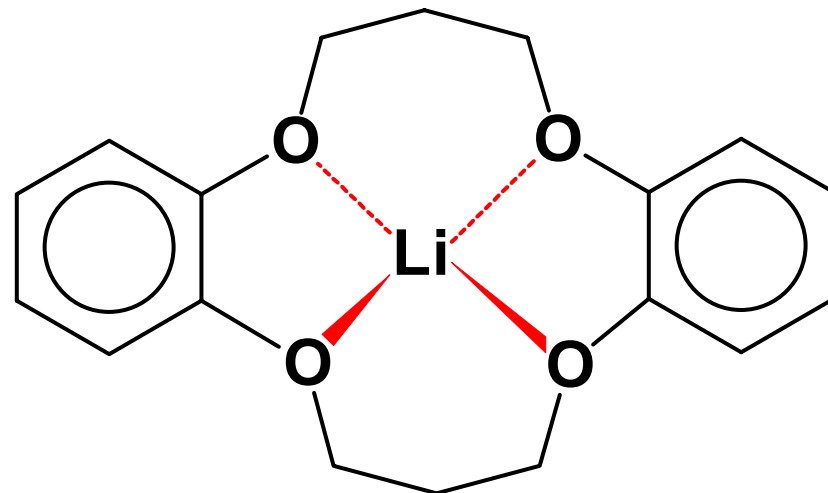


Rb and Cs form many suboxides: Rb₉O₂, Rb₆O, Cs₁₁O₃, Cs₇O
 These are metal clusters with delocalized metallic bonding.

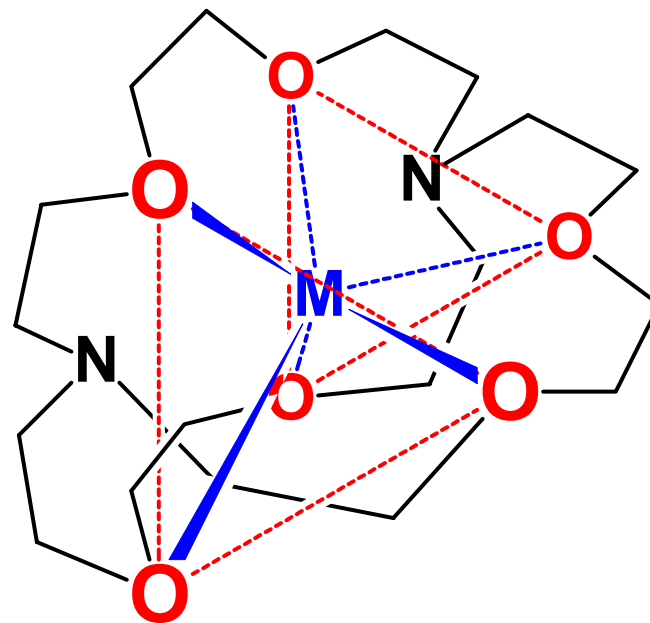
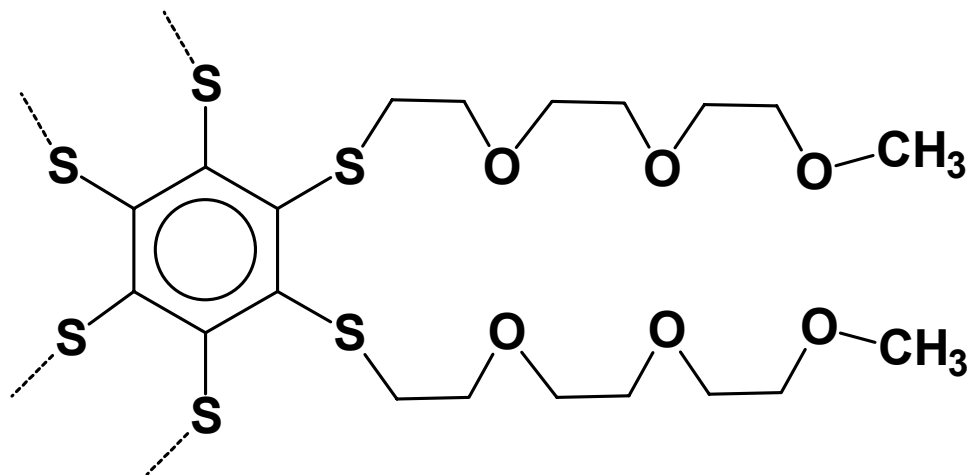
The oxide species formed by free burning is determined by the relative sizes of the cations formed.

Crowns, Crypts and Octopi

<u>Ionic Diameter</u>	<u>Crown</u>	<u>Hole Size</u>
152	Li	14-crown-4 120-150
204	Na	15-Crown-5 170-220
276	K	18-Crown-6 260-320
304	Rb	21-Crown-7 340-430



Make alkali salts soluble in less polar
(i.e. ether) solvents - "Naked Anions"



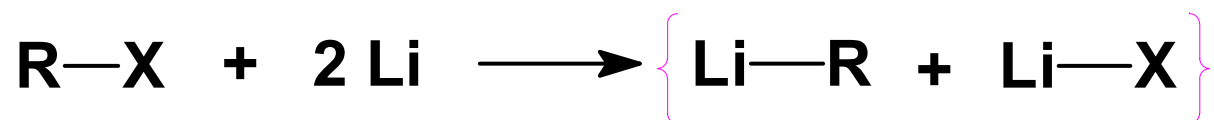
Organometallics – Lithium & Sodium



Sodium alkyls are cheaper for industry.



A way to make pure alkyl-lithium compounds.



form a "complex"

$(\text{CH}_3\text{Li})_4$ Methyl lithium is a tetramer, a cluster.

