PRE-TRANSITION METAL NOTES

The Ionic Model

Groups 1 & 2, plus the Lanthanides (f-contraction ➔ little covalency). Provides simple equations for calculation of interaction energies between ions (ΔH_L) and dipolar molecules (e.g. ΔH_{hyd}).

Evidence for the existence of ions:
Electrical conductivity when molten or dissolved in polar solvents.
Electronic Spectra (charge transfer) – similarity between spectra of gas phase/solutions and solid compounds.
Magnetic – unpaired electrons. Similarity between gas/solid again.
Electron-density measurements – x-ray diffraction data along the internuclear axis.
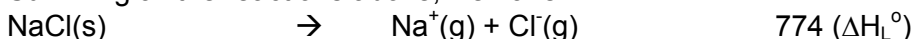
Lattice Enthalpy

ΔH_L of a compound MX is the enthalpy change when:
$$MX_{(s)} ➔ M^+_{(g)} + X^-_{(g)}$$
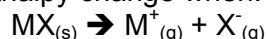
Can be found by using Born-Haber Cycles (Enthalpy is a state function).

For NaCl: ΔH^o / kJ mol^{-1}
(2)	$NaCl(s)$	➔	$Na(s) + ½ Cl_2 (g)$	411
(3)	$Na(s)$	➔	$Na(g)$	107
(4)	$Na(g)$	➔	$Na^+(g) + e^-(g)$	502
(5)	$½ Cl_2(g)$	➔	$Cl(g)$	122
(6)	$Cl(g) + e^-$	➔	$Cl^-(g)$	-368

Summing all the reactions above, we have:
$NaCl(s)$ ➔ $Na^+(g) + Cl^-(g)$ 774 (ΔH_L^o)

Notes:
- the reverse of equation (2) is the definition of the standard enthalpy of formation of solid NaCl.
- Equations (3) and (4) together define the standard enthalpy of formation of $Na^+(g)$.
- Equations (5) and (6) together define the standard enthalpy of formation of $Cl^-(g)$. Notice that the enthalpy change (5) is half the bond enthalpy of the chlorine molecule.

Thus,
$$\Delta H_L [NaCl_{(s)}] = \Delta H_f [Na^+_{(g)}] + \Delta H_f [Cl^-_{(g)}] - \Delta H_f [NaCl_{(s)}]$$
$$\Delta H_f [NaCl_{(s)}] = \Delta H_f [Na^+_{(g)}] + \Delta H_f [Cl^-_{(g)}] - \Delta H_L [NaCl_{(s)}]$$

Electrostatic Interactions –
It is known that:
$$E = -\frac{z^+ z^- e^2}{4\pi\varepsilon_0 r} \text{ (Coulomb)}$$

So for NaCl, each Na has 6 Cl ions as nearest neighbours distance r away, then 12 Na ions as next nearest neighbours distance $r\sqrt{2}$ away, and so on.

Summing the attractive and repulsive terms, the total electrostatic interaction can thus be expressed as:

$$E = -\frac{Nz^+z^-e^2}{4\pi\varepsilon_0 r}(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - ...)$$

The series in brackets converges to a constant, the Madelung Constant, A. It is entirely geometric in origin.

When considering the short-range repulsive interactions, it can also be suggested that $E = B/r^n$, where B is a constant and n is the Born-Exponent.

Then by differentiation we obtain the Born-Lande Equation for the total Energy:

$$U_0 = -\frac{NAz^+z^-e^2}{4\pi\varepsilon_0 r}(1 - \frac{1}{n})$$

Similarly, if $E = ae^{-r/p}$ for short range repulsive interaction instead, then we get the Born-Mayer Equation for lattice energy:

$$U_0 = -\frac{NAz^+z^-e^2}{4\pi\varepsilon_0 r}(1 - \frac{\rho}{r})$$

These equations imply that ionic attractions are a long range force (1/r), compared to covalent (nearest neighbour) and van der Waals ($1/r^6$).

They depend only on the radius of the ions, which implies that same radius = same behaviour. Properties independent of nature of ions.

The degree of packing in the structures depends on the Madelung Constant (not Radius/Ratio Rules! - unreliable).

The Kapustinskii Equation

Ratio of Madelung Constant to total number of ions per formula unit (ν) for a series of compounds are very similar. Thus, the variation of $A/\nu r$ between structures is very small. The following approximations are made:

a) replace A with 0.87ν.
b) internuclear distance taken as sum of ionic radii.
c) Value of n=9 for NaCl can be taken as average for all structures.

This gives:

$$\Delta H_L = -\frac{1.08\times10^5 z^+z^-\nu}{(r^+ + r^-)}$$ where r is in pm, and H in kJ mol^{-1}.

Needs only ionic radii. Accurate to within 10% of experimental values.

Estimating Ionic Radii –

Lande:

Suggested that in LiI, with a small cation and a large anion, the large I$^-$ are in contact and hence from the unit cell parameter an ionic radius of I$^-$ can be derived. By examining other metal halides a table of ionic radii could be drawn up.

Pauling:

Theoretical basis: in many-electron atoms and ions, screening and penetration effects result in the electrons experiencing an effective nuclear charge, $Z_{eff} = Z - \sigma$, where σ is the screen constant calculated using Slater's Rules. Pauling therefore propose that:
$R_{ionic} = C_n/Z_{eff} = C_n/(Z-\sigma)$, where C_n is a constant depending on the principal quantum number n. For isoelectronic ions such as Na^+/F^-, K^+/Cl^-, Mg^{2+}/O^{2-}, the C_n values for the pairs should be the same. Thus,
$r(Na^+)/r(F^-) = [Z(F^-) - \sigma] / [Z(Na^+) - \sigma]$.
Knowing $r(Na^+) + r(F^-)$ from crystallographic data, the ionic radii can be calculated.

Shannon and Prewitt:

Compiled unit cell data for more than 1000 compounds and evaluated a set of self-consistent ionic radii which can best reproduce the experimentally observed internuclear distances. They based their data set on $r(O^{2-}) = 140pm$ and $r(F^-) = 133pm$. The values they obtained were in good agreement with those from other methods. The Shannon-Prewitt ionic radii are the most commonly used data set.

Thermochemical Radii:

Ionic radii for complex ions such as NO_3^-, CO_3^{2-}, SO_4^{2-}, NH_4^+. Use a Born-Haber cycle to calculate the lattice enthalpy, then the Kapustinskii equation to calculate $(r^{a+}+r^{b-})$, knowing r^{a+} one can calculate r^{b-}.

Trends in Ionic Radii

1. For isoelectronic pairs, the cation is smaller than the anion.
2. Across a row, radii of isoelectronic cations decrease rapidly, but the change in anionic radii is less pronounced. Electrons added to the same shell (Z_{eff} increases).
3. Down a group the radii increase. Electrons are added to extra shells, and penetration (increase Z_{eff}) not as dominant as increasing n.
4. Ionic radii depend on coordination number. Increase slightly with CN. This is due to increased anion repulsion around the cation.
5. d/f contractions. Thus Group 11 & 12 ions are smaller than Group 1 and 2. 3d/4f orbitals are non-penetrating and so poor shielders, which causes Z_{eff} to rise.

"Diagonal Relationship" – $r(Li^+) \approx r(Mg^{2+})$, and similarly $r(Na^+) \approx r(Ca^{2+})$. This is due to points 2 and 3, and often leads to similar chemistry (e.g. isostructural compounds).

Covalency

This effect causes lattice enthalpy and solvation energy to increase (not expected from the Ionic Model).

Covalence should be considered for polarisable anions (large, low electronegativity) and polarising cations (Z^2/r, i.e. small or highly charged, e.g. Be^{2+}, Zn^{2+}).

Formation of Ionic Compounds by the Alkali and Alkaline Earth Metals

| Reaction	Product	Anion	Comments
$M + \frac{1}{2} X_2 \rightarrow MX$	Halide	X^-	Group 1 elements also form polyhalides, e.g. $K^+[ICl_4]^-$
$2M + \frac{1}{2} O_2 \rightarrow M_2O$	Oxide	O^{2-}	Normal product of combustion in air for Li, Mg, Ca. Suboxides also formed by Rb and Cs, e.g. Rb_6O, Rb_9O_2, $Cs_{11}O_3$. Basic: $M_2O + H_2O \rightarrow 2MOH$.
$2M + O_2 \rightarrow M_2O_2$	Peroxide	O_2^{2-}	Normal product of combustion in air for Na, Ba
$M + O_2 \rightarrow MO_2$	Superoxide	O_2^-	Normal product of combustion in air for K, Rb, Cs
$3M + \frac{1}{2} N_2 \rightarrow M_3N$	Nitride	N^{3-}	Only formed by Li in Group 1, Mg $\rightarrow$ Ba (M_3N_2) in Group 2. Basic: $Li_3N + H_2O \rightarrow LiOH + NH_3$.
$2M + 2C \rightarrow M_2C_2$	Carbide	C_2^{2-}	Readily with Li, Ca, Sr, etc at elevated temperature. Basic: $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$.
$M + \frac{1}{2} H_2 \rightarrow MH$	Hydride	H^-	Formed at high temperature (Mg requires high pressure), saline hydrides. Basic: $MH + H_2O \rightarrow MOH + H_2$.
$M + H_2O \rightarrow MOH + \frac{1}{2} H_2$	Hydroxide	OH^-	Oxides and hydroxides strong bases. Absorb atmospheric CO_2 to give M_2CO_3 and $MHCO_3$ (Na and K).
$M + NH_2 \rightarrow MNH_2 + \frac{1}{2} H_2$	Amide	NH_2^-	Reaction with gaseous NH_3 at high temperature, or the metal with liquid NH_3 and a transition metal ion such as Fe^{3+} as a catalyst.

[M = 1 mole of a Group 1 metal or ½ mole of a Group 2 metal].

Solid Compounds of G1 & 2

All form stable binary halides, oxides and hydroxides with the group oxidation state.
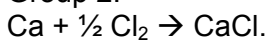+1 state of Group 2 is unstable wrt disproportionation.
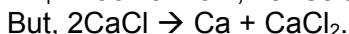
Disproportionation

Group 1:

$$CsF_2 \xrightarrow{\Delta H_d} CsF + \frac{1}{2} F_2$$

$\Delta H_f(-138)$ $\Delta H_f(-555)$

$$Cs + F_2$$
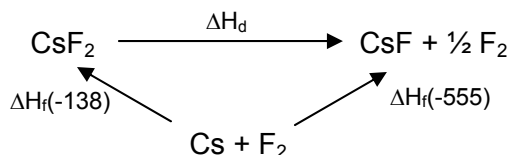
$\Delta H_d = +138 - 555 = -417$ kJ mol^{-1}
Actually unstable wrt CsF, even though stable wrt elements (see below).

Group 2:
$Ca + \frac{1}{2} Cl_2 \rightarrow CaCl$.
$\Delta H_f = -93$ kJ mol^{-1}, i.e. CaCl is stable wrt the elements.
But, $2CaCl \rightarrow Ca + CaCl_2$.

ΔH_d = -610 kJ mol^{-1}. Unstable wrt disproportionation. Common in Group 2 for M$^+$.

Stability of compounds with small anions (F$^-$, H$^-$) decrease down the groups, while stability increases for large anions. Exception is Mg.
Stability of halides decreases down the halide group, but the decrease is less severe for large cations.
Only Li of Group 1 forms stable nitride. All Group 2 form nitrides.

Structural Chemistry
(SEE TUTORIAL 1 FOR MORE DETAIL)

All hydrides, halides and hydroxides of Group 1 have Rock Salt structure except CsCl, CsBr, CsI. All oxides have anti-fluorite structure except Cs_2O. Superoxides (MO_2) have pyrite structure.

Group 2 Oxides except BeO have Rock Salt structure. Most of the fluorides are fluorite structures, except BeF_2 / BeF_4 which are tetrahedral chains, and MgF_2 which is rutile. Other halides are difficult to predict and tend to adopt distorted/layered structures due to polarisability. CN > 8 for some Barium compounds.

As cations increase in size, the thermal stability of compounds with large complex ions increases. For example, heating Li in air gives the oxide, Na on the other hand forms peroxide, while the other Group 1 elements for superoxide. Rb and Cs also form a series of sub-oxides with unusual structures based on OM_6 octahedra.

Heating the nitrates of Group 1 gives nitrites, except Li which forms the oxide. Stability of carbonates, sulphates, etc. increase down the group.

The ionic model can also predict the course of reactions using lattice enthalpies. For example,

$$LiI + NaF \rightarrow LiF + NaI$$
$$2NaF + CaCl_2 \rightarrow 2NaCl + CaF_2$$
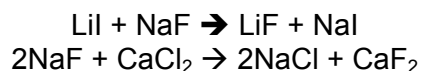
These occur because the lattice enthalpy of LiF and CaF_2 is very high (the latter despite $r(Na^+) \approx r(Ca^{2+})$).

But there are notable exceptions, especially those involving complex ion salts:
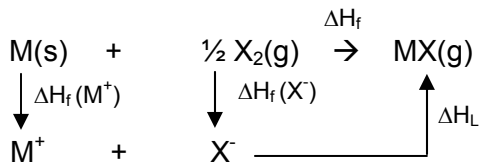
$$NaNO_3 + KCl \rightarrow NaCl + KNO_3$$
$$NaNO_3 + LiCl \rightarrow NaCl + LiNO_3$$
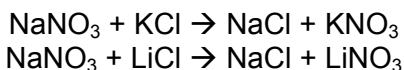
Both reactions found to be thermodynamically favourable even though $r(Cl^-) < r(NO_3^-)$. Here we expect the combination of the smaller Na$^+$ and Cl$^-$ to provide the lattice enthalpy driving force for the first reaction, but on these grounds the second reaction should not proceed. Apparently, there is stronger than expected interaction between the small Li$^+$ and the non-spherical nitrate ion.

Also the following reactions:

$$AgF + KCl \rightarrow AgCl + KF$$
$$HgF_2 + 2KCl \rightarrow HgCl_2 + 2KF$$
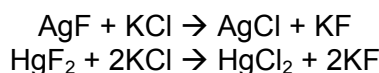
In these two reactions, the substantial non-ionic contributions to the lattice enthalpies of AgCl and $HgCl_2$ provide the driving force.

Trends in Stability

$$M(s) \quad + \quad \tfrac{1}{2} X_2(g) \quad \xrightarrow{\Delta H_f} \quad MX(g)$$

$$\downarrow \Delta H_f(M^+) \qquad \downarrow \Delta H_f(X^-) \qquad \uparrow \Delta H_L$$

$$M^+ \quad + \quad X^-$$

$$\Delta H_f = \Delta H_f(M^+) + \Delta H_f(X^-) - \Delta H_L$$

For a given anion:
1) $\Delta H_f (M^+)$ decreases down the group. Both ΔH_{atom} & E_I decrease.

2) $\Delta H_L \propto \dfrac{1}{r^+ + r^-}$ so ΔH_L decreases down the group.

Thus, have to look at which factors change by the greatest amounts to determine stability.

ΔH_L can be controlled. If r^- is small, then the proportional decrease in ΔH_L is large (by differentiation). If r^- is large, the ΔH_L decreases slowly.

Nitrides:

For Group 1, only Li is sufficiently small to form Li_3N. All other M_3N compounds are endothermic. This is because ΔH_L is large with the small Li^+ ion, whereas Na^+ is too large.
For Group 2, $z^+ = +2$, and $\nu = 5$, gives a very large ΔH_L. All form M_3N_2.
Both Group 1 and Group 2 trends can be justified by the Kapustinskii Equation.

Hydrides:

Much less stable than F/O compounds. Not due to polarisability of H^- though. The ΔH_f of H^- is +140 kJ mol^{-1}, compared to -271 kJ mol^{-1} for F^-. H-H bond is very strong, while the F-F is weak (due to lone pair repulsions).

Halides:

For halides in general, the stability increases down the group as it gets easier to form the metal ions due to the valence electron being in a higher energy orbital. This term dominates.
However, with fluorides, the small radii means that the lattice enthalpy term is quite large and is responsive to changes in cation size, and so with increasing cation size, the lattice enthalpy is very small and so they are less favourable down the group.

Oxides:

For group 2 the stability of the oxides decreases as the lattice enthalpy term is getting much smaller.
For group 1, the situation is complex as there are many types of oxides besides O^{2-} that can form, and so the stability isn't simply with respect to the elements. With respect to the elements the stability decreases down the group. It should be noted however, that compounds such as Na_2O_2 and NaO_2 are formed as well as Na_2O.
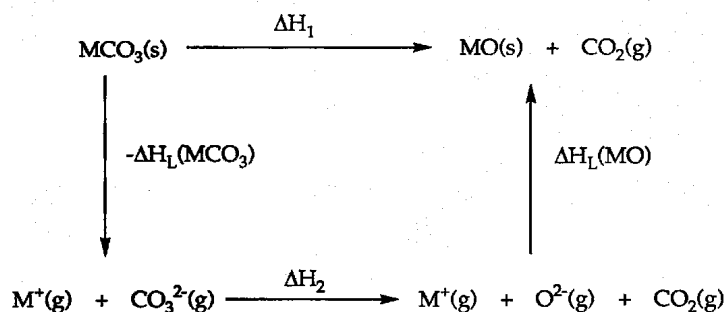
Oxy acid salts:

In general, stability with respect to elements falls down the group, but the stability with respect to the oxide increases. With a large cation, there is very little change in lattice enthalpy on decomposition (i.e. $BaCO_3 \rightarrow BaO$) and so decomposition is not very favourable. But if you have a small cation like Mg, the large change makes the oxy acid salt unstable.

Thermodynamics of Ionic Systems

Useful for explaining stability, e.g. $CaCO_3$ decomposes at 900^oC, but $MgCO_3$ decomposes at 400^oC.

Start by drawing the cycle:

$$MCO_3(s) \xrightarrow{\Delta H_1} MO(s) + CO_2(g)$$

with $-\Delta H_L(MCO_3)$ (downward) and $\Delta H_L(MO)$ (upward)

$$M^+(g) + CO_3^{2-}(g) \xrightarrow{\Delta H_2} M^+(g) + O^{2-}(g) + CO_2(g)$$

i.e. $\Delta H_1 = \Delta H_2 + \Delta H_L(MO) - \Delta H_L(MCO_3)$

Also, always define the decomposition temperature.

Decomposition occurs when ΔG for the reaction is negative. In this case, the ΔS_{decomp} term is dominated by the gas produced (CO_2) and so is positive and effectively constant. Note that T_{decomp} is proportional to ΔH_{decomp}, i.e. when ΔH is positive (endothermic), higher temperatures of decomposition are expected.

The thermodynamic driving force is a gain in lattice energy with smaller anion. This implies it is more important for small cations, i.e. smaller M^{2+} carbonates have lower decomposition temperatures. Hence, large cations stabilise large anions, but this is NOT because of packing.
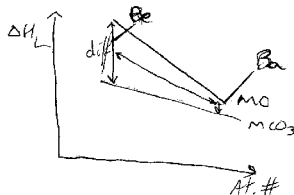
This can be explained by using the cycle above:
MCO_3: $\Delta H_L = (A.2.2.2)/(r^{2+}+r(CO_3^{2-}))$.
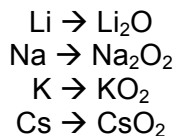MO: $\quad \Delta H_L = (A.2.2.2)/(r^{2+}+r(O^{2-}))$.
$\Delta H_1 = [(8A/(r^{2+}+r(CO_3^{2-}))) - (8A/(r^{2+}+r(O^{2-})))] + \Delta H_2$
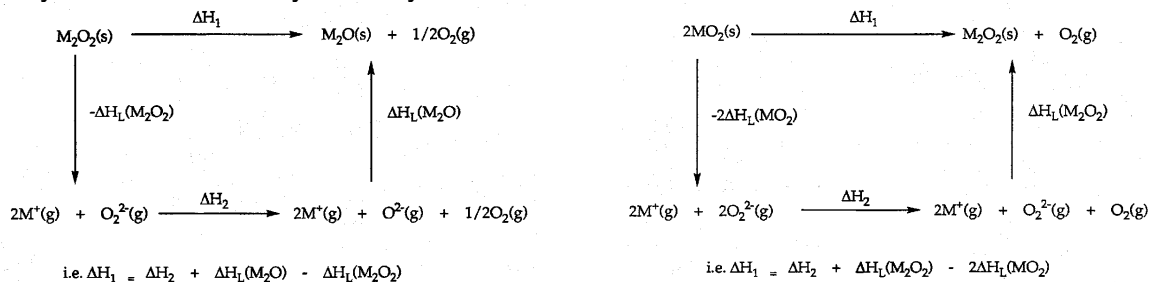
i.e. to stabilise MCO_3 want to minimise difference in ΔH_L:

As another example, consider the Group 1 Oxides.
Burning in excess O_2 gives:

$$Li \rightarrow Li_2O$$
$$Na \rightarrow Na_2O_2$$
$$K \rightarrow KO_2$$
$$Cs \rightarrow CsO_2$$

Why? Look at thermodynamic cycles.

e.g. for $Rb^+O_2^-$ superoxide.
$$U_L = 1.08 \times 0^5 \times 2 \times 1 \times 1 / (166+181) = 622.5 \text{ kJ mol}^{-1}.$$

Similarly for $Rb^+_2O_2^{2-}$.
$$U_L = 1825 \text{ kJ mol}^{-1}.$$

$$\Delta H_{dec} = 2\Delta H_L(RbO_2) - \Delta H_L(Rb_2O_2) + \Delta H_f(O_2^{2-}) - 2\Delta H_f(O_2^-).$$
$$\Delta H_{dec} = 2(622.5) - 1825 + 520 - 2(-105) = 150 \text{ kJ mol}^{-1}.$$

Assume entropy of any solid is identical and insignificant, compared with entropy of gas.

$$\Delta S_{dec} = S^o(g) = 205 \text{ J K}^{-1} \text{ mol}^{-1}.$$

This then allows the decomposition temperature to be calculated.
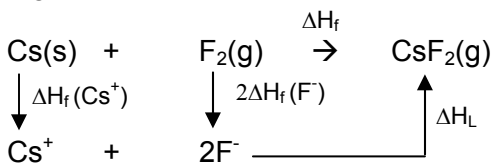
Comparison of Properties of Group 1 and Group 2

All are soft light metals.
Very reactive. Strong reducing agents.
Group 2 tend to be more stable with respect to elements (e.g. Nitrides). This is due mainly to higher charge, which gives a higher lattice enthalpy:

Comparing Cs and Ca compounds – CsF_2 / CaCl both stable wrt elements.

e.g. $CsF_2(s)$:

$$\Delta H_f = 2694 - 2(-271) - \Delta H_L$$
$$\Delta H_L = (c.2.1.3)/(r^+ +133)$$

$$r(Cs^{2+}) < r(Cs^+) \text{ (167pm)}$$
$$r(Cs^{2+}) > r(Ba^{2+}) \text{ (135pm)}$$
Hence, predict $r(Cs^{2+}) \approx 150$pm.
Thus, $\Delta H_L = -138 \text{ kJ mol}^{-1}.$

Negative ΔH_L ➔ stable wrt the elements.

Similar calculations show that CaCl is also stable wrt to the elements.

Stability of Oxidation States:
2nd Ionisation Energies vs. Difference in Lattice Enthalpy.
For Cs, difference in ionic radii is small (167 vs. 150pm), whereas much larger difference for Ca (170 vs. 100pm), due to loss of a subshell.

Generalising, Al^{2+} unstable ($\rightarrow Al^{3+}$). Also, no Tl^{2+}, Pb^+, Pb^{3+}, etc.

The change in radii is the key point (from the Kapustinskii Equation).

Similarly, Transition Metals can occupy various oxidation states because the change in radius is small from electrons lost within d-subshell.

Also, for small ions, $\Delta H_L \propto \dfrac{1}{r^+ + r^-}$ ➔ ΔH_L is large.

Solutions in Liquid Ammonia

Alkali Metals – all look bright blue in liquid ammonia.
High concentrations gives a bronze colour, and the conductivity increases to that of molten metals.
Thus, the metals must give rise to the same species to cause the same colour, and the actual metal does not matter. This occurs because the metal breaks down to $M^+ + e^-$. This electron is then trapped in the linked NH_3 molecules (H-bonding as a liquid). The gaps in the NH_3 occur as when 2-3 displace, and gives a cavity 300-350pm wide.
This is known from the absorption spectra, which is centred around the infrared region. Thus, it appears blue, irrespective of metal.
The bronze colour appears when the concentration of M^+ is so high that this electride (electron coordinated by ammonium ions) associates with the M^+ as well.

NB: these solutions require anhydrous conditions and minimal impurities to be stable, otherwise amide formation results.

Also of note, the electride is understandably a powerful reducing agent:
$$RCH=CH_2 + 2e_{am} \xrightarrow{2NH_3} RCH\text{-}CH_2^{2-} \rightarrow RCH_2CH_3 + 2NH_2^-$$
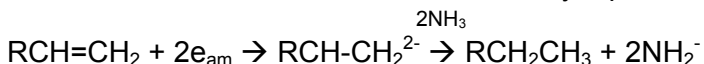
Stability of Complexes

Neutral ligands:
Few stable. Dependent on desolvation of the ions and also metal-ligand attraction. It is the latter which is a problem, since a charged ligand is held more tightly. As it is, the M-L depends on polarity, and water is extremely polar, as shown:
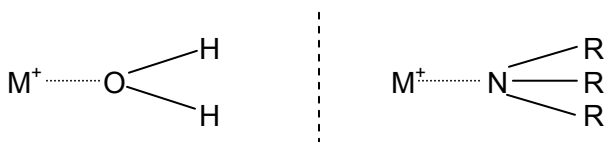

The O of the water is very electronegative, and draws e away from the H, making the +/- attraction of MO stronger. This is not the case with the amine on the right. Thus, the amine is incapable of displacing the more stable H_2O ligands.

Charged ligands:
$$M^+ + L^- \rightarrow ML + nH_2O$$

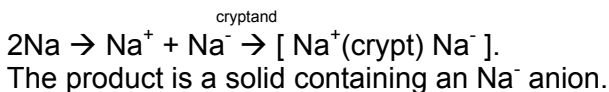This is now favourable, since the attraction of $M^+ + L^-$ is much greater than a dipole attraction.

Considering whether enthalpy or entropy drives this reaction, we note that $M^+ + X^-$ is good from an enthalpy point of view, but also the loss of ΔH_{solv} is bad. Thus, $\Delta H_{complexation} \approx 0$. However, $\Delta S \gg 0$ due to release of H_2O from M^+ and X^-, so entropy is the driving force for these reactions. This is especially shown by polydentate ligands, where it is possible to free 6 water molecules for one ligand.

An extreme example of this is with crown ethers. These are in fact uncharged, but the entropy gain is so high that it is possible. A Crown Ether such as 18-crown-6 looks like the diagram on the right.
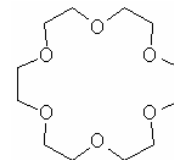
Unlike the amine ligand above, which can rotate and invert, this crown ether has few degrees of freedom – it is preorganised. Thus, ΔS is much more positive.

Also worth noting is the specificity of these ligands. For example, the 2.2.1 cryptand binds to Na^+, while the 2.2.2 cryptand prefers K^+. This is useful for isolation purposes. Another isolation effect is:

$$2Na \xrightarrow{} Na^+ + Na^- \xrightarrow{cryptand} [\, Na^+(crypt)\, Na^- \,].$$

The product is a solid containing an Na^- anion.

See **Coordination Chemistry Notes** for more info on the Chelate and Macrocyclic Effects.

Organometallics

Most heavy metals form very reactive ionic compounds with alkyls, and so don't last very long. However, the strong polarising nature of Li, Be and Mg mean that covalently bonded structures are possible.
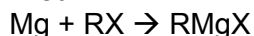
Synthesis:
$$2\,Li + RX \rightarrow LiR + LiX$$
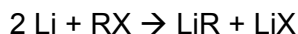
This is carried out in ether, and is otherwise in inert conditions. The yield is often poor due to a reaction between LiX and LiR again. Careful choice of RX is required. HgR_2 works well.
$$LiBu + PhI \rightarrow PhLi + BuI$$
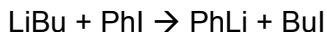
Also, Grignard Reagents can be formed:
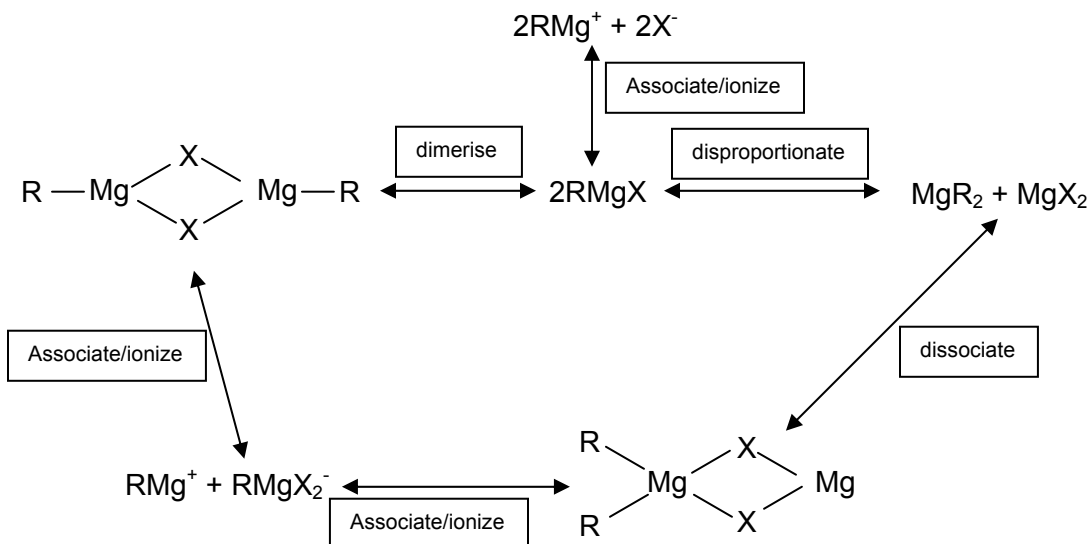$$Mg + RX \rightarrow RMgX$$

Structures:
Most lithium alkyls exist as hexameric structures, and have similar properties to most covalent structures. The extended structures means they are usually soluble in organic solvents.
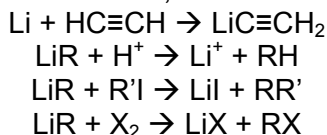
Solution Equilibria:
From the point of view of Grignard Reagents, a series of equilibrium structures are possible. The following diagram shows this:

$$2RMg^+ + 2X^-$$

Associate/ionize

dimerise   disproportionate

$$R-Mg \underset{X}{\overset{X}{\diamond}} Mg-R \longleftrightarrow 2RMgX \longleftrightarrow MgR_2 + MgX_2$$

Associate/ionize

dissociate

$$RMg^+ + RMgX_2^- \longleftrightarrow \underset{R}{\overset{R}{>}}Mg\underset{X}{\overset{X}{\diamond}}Mg$$

Associate/ionize

Reactions:

Reactions are those expected of carbanions, such as:

$$Li + HC\equiv CH \rightarrow LiC\equiv CH_2$$
$$LiR + H^+ \rightarrow Li^+ + RH$$
$$LiR + R'I \rightarrow LiI + RR'$$
$$LiR + X_2 \rightarrow LiX + RX$$
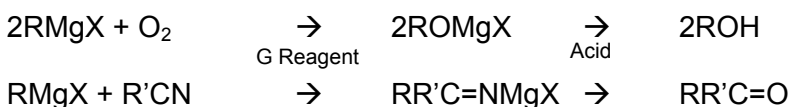
LiR + ether yields alkenes and LiOR.

In water, $LiPh + CO_2 \rightarrow PhCO_2Li \rightarrow PhCOOH + LiOH$

Grignard Reagents are very useful in Organic Synthesis. These usually involve the formation of an unstable product, which then decomposes with acid to the desired product. The G Reagents form RH as they are hydrolysed by water.
Examples:

$$2RMgX + O_2 \underset{G\ Reagent}{\rightarrow} 2ROMgX \underset{Acid}{\rightarrow} 2ROH$$

$$RMgX + R'CN \rightarrow RR'C=NMgX \rightarrow RR'C=O$$

Biological Roles of Pre-Transition Metals

No redox chemistry, which would be problematic in biological systems. This is because there is no variable oxidation state. For example, the presence of Cu^+ could cause O_2 to form OH radicals, which then damage DNA.

Other advantages are that they are often not strong Lewis Acids (preventing Acid catalysis, or harmful pH conditions). This usually means they are poor catalysts. Also, since they are highly soluble, they can behave as electrolytes, and aid charge balance (particularly Na and K).

Na⁺

Important in nerve function in animals. Sodium channels carry an impulse along a nerve fibre, due to solubility and charge balance. Also used to balance concentration gradients in extracellular fluid.

K⁺

Similar to Na. Intracellular fluid concentration maintenance. Essential for nerve impulse transmission and cardiac function.

Mg²⁺

Essential for chlorophyll function, so all green plants depend on it. Also has enzyme activating properties in all animals.

Ca²⁺

Structural component – shells, bones, cell walls. Involved in blood clotting – enzyme activator. Also essential in muscles and nerve synapses.

Similarities between Groups – Li and Be

These elements have properties which often don't fit well with the others in their groups, because of their small size.

For example, LiF is very insoluble compared with other alkali metal fluorides. This is due to very high lattice enthalpy. As noted earlier, Li is the only G1 element capable of forming a solid with N^{3-}, again because of its tendency to form structures with high lattice enthalpies.

Be is even more unlike its relatives. In fact, as is true with many periodic arrangements, the properties of Li are related to Mg (diagonally down to the right). Be is similar to Al in that respect, and this is true when noting that Be forms mainly covalent structures. A good example is $[Be_4O(acetate)_6]$, a large covalent complex structure which solvates in organic solvents. The Be_4O is tetrahedrally arranged, with Be continuing its extended covalent bonding around a central O atom.