10.2 **Trends of the fluorides and chlorides of the group 1 metals?**

	$-\Delta_f H^\circ$ /(kJ mol^{-1})		$-\Delta_f H^\circ$ /(kJ mol^{-1})
LiF	625	LiCl	470
NaF	535	NaCl	411
KF	564	KCl	466
RbF	548	RbCl	458
CsF	537	CsCl	456

See Figure 10.4, which plots the enthalpy of formation of the group I metals versus the halogens. Fluoride is a hard Lewis base and will form strong complexes with hard Lewis acids. The lithium cation is the hardest Lewis acid of the group I metals, so it makes sense that it has the largest enthalpy of formation with fluoride compared to the rest of the group I metals. However, the trends reverse for the chloride ion; since it is a softer Lewis base than the fluoride ion, it will form stronger bonds with the heavier group I metals.

10.3 **Synthesis of group 1 alkyls?** Most alkyl lithiums are made using elemental lithium with the corresponding alkyl chlorides. The formation of LiCl helps drive the reaction.

$$C_2H_5Cl + 2Li \rightarrow C_2H_5Li + LiCl$$

The sodium analogue can be made the same way.

$$C_2H_5Cl + 2Na \rightarrow C_2H_5Na + NaCl$$

10.4 **Which is more likely to lead to the desired result? (a) Cs^+ or Mg^{2+}, form an acetate complex?** The metal ion with the higher charge, Mg^{2+}, is more likely to form a complex with acetate ion than Cs^+. The reason is that the binding of ligands for these hard metal ions is governed by the electrostatic parameter, z^2/r. As stated in the text, the weakness with which *s*-block metal ions bind ligands explains why until recently very few *s*-metal complexes had been characterized.

(b) Be or Sr, dissolve in liquid ammonia? It is more likely that strontium will dissolve in liquid ammonia than beryllium. There are two ways to arrive at this conclusion. First of all, electropositive metals in low enthalpies of sublimation are prone to dissolve in liquid ammonia. Second, the Be^{2+}/Be reduction potential, -1.97 V, is less negative than E° for the Sr^{2+}/Sr potential, -2.89 V. Even though you were asked to focus on liquid ammonia solutions in this exercise, and E° values refer to redox reactions in *aqueous acid*, the principal steps are the same on going from $M^0 \rightarrow M^{2+}$, namely sublimation, ionization, and solvation. Therefore, you can expect a general agreement between E° values and a tendency to dissolve in liquid ammonia.

(c) Li^+ or K^+, form a complex with C2.2.2? Potassium ion is more likely to form a complex with the cryptate ligand C2.2.2 than Li^+. The difference has to do with the match between the interior size of the cryptate and the ionic radius of the alkali metal ion. According to Figure 10.7, K^+ forms a stronger complex, by about two orders of magnitude, with C2.2.2 than does Li^+.

10.5 **Identify the compounds?**

$$\mathbf{NaOH} \leftarrow H_2O + \textbf{Sodium metal} + O_2 \rightarrow \mathbf{Na_2O_2} + \text{heat} \rightarrow \mathbf{Na_2O}$$

$+ NH_3$

$\downarrow$

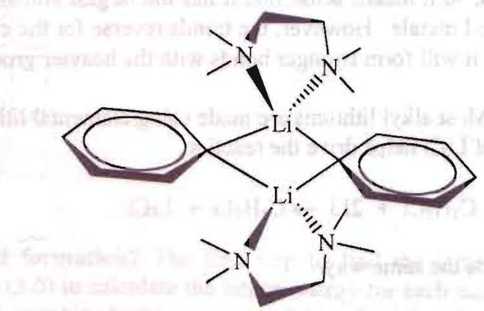
$\mathbf{NaNH_2}$

10.6 **Trends in solubility?** In LiF and CsI the cation and anion have similar radii. Solubility is lower if there is a large difference between radii of cation and anion, as in CsF and LiI.

10.7 **Thermal stability of hydrides versus carbonates?** Hydrides decompose to elements. Lattice energy decreases down the group as the radius of cation increases. Carbonates decompose to oxides. There is a difference in lattice energy between carbonate and oxide decreases down the group, which results in increased stability.

10.8 **The structures of CsCl and NaCl?** See Figures 3.28 and 3.30; 6-coordinate Na^+, 8-coordinate Cs^+; different r^+/r^-. Cesium is so large that the only way it can pack is in a body-centred cubic lattice.

10.9 **The effect of the alkyl group on the structure of lithium alkyls?** Whether a molecule is monomeric or polymeric is based on the streric size of the alkyl group. Less bulky alkyl groups lead to polymerization; methyl groups are tetrameric or hexameric, while a ^{t}Bu group yields a monomer. The larger aggregates can be broken down into dimmers and monomers using strong Lewis bases such as TMEDA. Below shows how phenyl lithium (which is normally polymeric) forms a dimmer with TMEDA.



10.10 **Predict the products of the following reactions? (a)** The driving force behind this reaction is the formation of lithium bromide (very large lattice energy). The same reasoning for reaction **(b)**. For reaction **(c)**, the driving force is the loss of ethane gas.

(a) $CH_3Br + Li \rightarrow Li(CH_3) + LiBr$

(b) $MgCl_2 + LiC_2H_5 \rightarrow Mg(C_2H_5)Br + LiBr$

(c) $C_2H_5Li + C_6H_6 \rightarrow LiC_6H_5 + C_2H_6$