Chapter 10

THE GROUP 1 ELEMENTS: THE ALKALI METALS

Exercises

10.1. (a) $2 \, Na(s) + 2 \, H_2O(l) \Rightarrow 2 \, NaOH(aq) + H_2(g)$

(b) $Rb(s) + O_2(g) \Rightarrow RbO_2(s)$

(c) $2 \, KOH(s) + CO_2(g) \Rightarrow K_2CO_3(s) + H_2O(l)$

(d) $2 \, NaNO_3(s) \Rightarrow 2 \, NaNO_2(s) + O_2(g)$

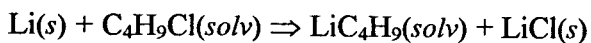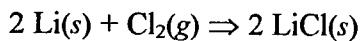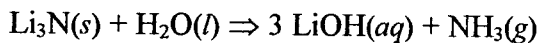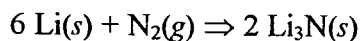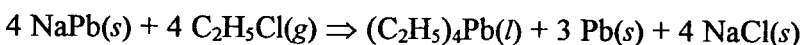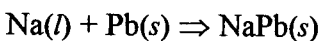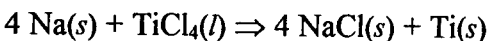10.3.   They resemble "typical" metals in that they are shiny and silvery and good conductors of heat and electricity. They differ from "typical" metals in that they are soft, extremely chemically reactive, and have low melting points and very low densities.

10.5.   Any three of the following:

All common chemical compounds are water-soluble.

They always form ions of +1 oxidation state.

Their compounds are almost always ionic.

The low charge density alkali metal ions stabilize large low-charge anions such as hydrogen carbonate.

Their compounds are rarely hydrated.

10.7.   The most likely argument is that the hydroxide ion can hydrogen bond with the surrounding water molecules whereas the chloride ion can only form ion-dipole attractions. This hydrogen bond formation would release more energy than the ion-dipole formation. Alternatively, we can simply argue that the smaller hydroxide ion will have a higher charge density and the ion-dipole attractions will be greater -- this is the same argument, just a different approach. In fact, the hydration enthalpy for the hydroxide ion is indeed much greater than that of the chloride ion.

10.9. (a) Because reduction of water requires a lesser potential than that for the reduction of sodium ion. Hence the following reaction would be preferred in aqueous solution:

$$2 H_2O(l) + 2 e^- \Rightarrow H_2(g) + 2 OH^-(aq)$$

(b) Adding calcium chloride lowers the melting point of the sodium chloride, making the process commercially feasible.

10.11. The diaphragm call has the advantages of a lower electrical consumption than the mercury process, and it can utilize less pure brine. Its disadvantage is that the sodium hydroxide product is dilute and the chloride ion contaminated.

10.13. (a) Potassium hydroxide; (b) sodium sesquicarbonate; (c) sodium hydroxide.

10.15. (a) The very electropositive alkali metals, where the properties of very high chemical reactivity and very low density are different to those of typical metals. (b) The absorption of water from the air by salts until the salts dissolve in the excess water (hygroscopic is the term used for salts that simply absorb water until they become hydrated).

10.17. Large low charge anions can be stabilized only by low charge density cations.

10.19. Five of the following:
Its hardness is closer to that of the alkaline earth metals.
Lithium forms a normal oxide.
It forms a dicarbide.
The carbonate, phosphate and fluoride salts have low solubilities.
Its compounds are more covalent than the other alkali metals.
Lithium's carbonate decomposes on heating.

10.21. Potassium dioxide(1–) has a lower molar mass than the equivalent cesium compound. For launch, minimum mass for the same oxygen-generating capacity is crucial. Also, the common potassium salts are much lower in cost than those of cesium.

10.23. Lithium:

$$6 \text{ Li}(s) + \text{N}_2(g) \Rightarrow 2 \text{ Li}_3\text{N}(s)$$

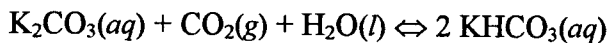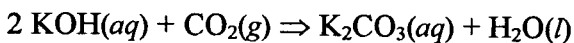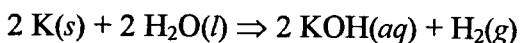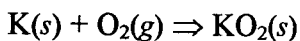$$\text{Li}_3\text{N}(s) + \text{H}_2\text{O}(l) \Rightarrow 3 \text{ LiOH}(aq) + \text{NH}_3(g)$$

$$2 \text{ Li}(s) + \text{Cl}_2(g) \Rightarrow 2 \text{ LiCl}(s)$$

$$\text{Li}(s) + \text{C}_4\text{H}_9\text{Cl}(solv) \Rightarrow \text{LiC}_4\text{H}_9(solv) + \text{LiCl}(s)$$

$$4 \text{ Li}(s) + \text{O}_2(g) \Rightarrow 2 \text{ Li}_2\text{O}(s)$$

$$2 \text{ Li}(s) + \text{H}_2\text{O}(l) \Rightarrow 2 \text{ LiOH}(aq) + \text{H}_2(g)$$

$$\text{Li}_2\text{O}(s) + \text{H}_2\text{O}(l) \Rightarrow 2 \text{ LiOH}(aq)$$

$$2 \text{ LiOH}(aq) + \text{CO}_2(g) \Rightarrow \text{Li}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)$$

Sodium:

$$2 \text{ Na}(s) + \text{Cl}_2(g) \Rightarrow 2 \text{ NaCl}(s)$$

$$2 \text{ Na}(s) + \text{H}_2\text{O}(l) \Rightarrow 2 \text{ NaOH}(aq) + \text{H}_2(g)$$

$$2 \text{ Na}(s) + \text{O}_2(g) \Rightarrow \text{Na}_2\text{O}_2(s)$$

$$\text{Na}_2\text{O}_2(g) + \text{H}_2\text{O}(l) \Rightarrow 2 \text{ NaOH}(aq) + \text{H}_2\text{O}_2(aq)$$

$$2 \text{ NaOH}(aq) + \text{CO}_2(g) \Rightarrow \text{Na}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)$$

$$\text{Na}_2\text{CO}_3(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \Leftrightarrow 2 \text{ NaHCO}_3(aq)$$

$$2 \text{ Na}(s) + 2 \text{ NH}_3(l) \Rightarrow 2 \text{ NaNH}_2(NH_3) + \text{H}_2(g)$$

$$4 \text{ Na}(s) + \text{TiCl}_4(l) \Rightarrow 4 \text{ NaCl}(s) + \text{Ti}(s)$$

$$\text{Na}(l) + \text{Pb}(s) \Rightarrow \text{NaPb}(s)$$

$$4 \text{ NaPb}(s) + 4 \text{ C}_2\text{H}_5\text{Cl}(g) \Rightarrow (\text{C}_2\text{H}_5)_4\text{Pb}(l) + 3 \text{ Pb}(s) + 4 \text{ NaCl}(s)$$

Potassium

$$\text{Na}(l) + \text{KCl}(l) \Leftrightarrow \text{K}(g) + \text{NaCl}(l)$$

$$2 \text{ K}(s) + \text{Cl}_2(g) \Rightarrow 2 \text{ KCl}(s)$$

$$\text{K}(s) + \text{O}_2(g) \Rightarrow \text{KO}_2(s)$$

$$2 \text{ KO}_2(s) + 2 \text{ H}_2\text{O}(l) \Rightarrow 2 \text{ KOH}(aq) + \text{H}_2\text{O}_2(aq) + \text{O}_2(g)$$

$$2 \text{ K}(s) + 2 \text{ H}_2\text{O}(l) \Rightarrow 2 \text{ KOH}(aq) + \text{H}_2(g)$$

$$2 \text{ KOH}(aq) + \text{CO}_2(g) \Rightarrow \text{K}_2\text{CO}_3(aq) + \text{H}_2\text{O}(l)$$

$$\text{K}_2\text{CO}_3(aq) + \text{CO}_2(g) + \text{H}_2\text{O}(l) \Leftrightarrow 2 \text{ KHCO}_3(aq)$$

Beyond the Basics

10.25. Mass of sodium = 1.00 t × $(10^6$ g)/(1 t) = $1.00×10^6$ g

Mole sodium = $(1.00×10^6$ g) × (1 mol)/(23.0 g) = $4.35×10^4$ mol

$Na^+(NaCl) + e^- \Rightarrow Na(l)$
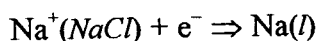
Thus mole electrons = $4.35×10^4$ mol

$$Current = (4.35×10^4 \text{ mol}) × \frac{(9.65×10^4 \text{ A} \cdot \text{V} \cdot \text{s})}{(1 \text{ mol})(7.0 \text{ V})(86400 \text{ s})} = 6.94×10^4 \text{ A}$$

10.27. In the series LiF to CsF, there is an increasing mismatch in ion sizes; thus the lattice energy will decrease more than otherwise expected. As a result, the enthalpies of formation will decrease. For the series LiI to CsI, there is a decreasing mismatch in ion sizes; thus the lattice energy will decrease to a lesser extent than otherwise expected. As a result the enthalpies of formation will increase.

10.29 Sodium fluoride will be the less soluble, as there is a close match in ion sizes resulting in a higher lattice energy (Na^+ = 116 pm; F^- = 117 pm). There is a mismatch in sizes with the tetrafluoroborate ion (which actually has a radius of 218 pm). Thus the hydration energy will more probably exceed the (lower) lattice energy, making the compound more soluble.

10.31. There are two possible answers: that there is appreciable covalent bonding in the lithium hydride, thus reducing the Li–H separation, or that the lithium ion is so small that the lattice consists of touching hydride ions with lithium ions "rattling around" in the lattice holes — this is certainly true of lithium iodide.