

## Chapter 11

### THE GROUP 1 ELEMENTS: THE ALKALI METALS

#### Exercises

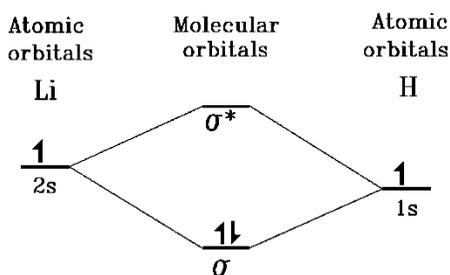
- 11.2 (a)  $6 \text{Li}(s) + \text{N}_2(g) \rightarrow 2 \text{Li}_3\text{N}(s)$   
(b)  $2 \text{CsO}_2(s) + 2 \text{H}_2\text{O}(l) \rightarrow 2 \text{CsOH}(aq) + \text{H}_2\text{O}_2(aq) + \text{O}_2(g)$   
(c)  $2 \text{NaHCO}_3(s) \rightarrow \text{Na}_2\text{CO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(g)$   
(d)  $\text{NH}_4\text{NO}_3(s) \rightarrow \text{N}_2\text{O}(g) + 2 \text{H}_2\text{O}(g)$
- 11.4 Lithium. This metal has the most negative standard reduction potential; that is, it is the most strongly reducing of any element. Its low chemical reactivity must indicate a higher activation energy of reaction than that of the other alkali metals and hence a slower reaction.
- 11.6 Sodium. Hydration is favored by high charge density cations; and of the two monovalent ions, sodium is the smaller and will have the higher charge density.
- 11.8 (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:  
$$2 \text{H}_2\text{O}(l) + 2 e^- \rightarrow \text{H}_2(g) + 2 \text{OH}^-(aq)$$
  
(b) Adding calcium chloride lowers the melting point of the sodium chloride, making the process commercially feasible.
- 11.10 The diaphragm cell has the advantages of a lower electrical consumption than the mercury process, and it can use less pure brine. Its disadvantage is that the sodium hydroxide product is dilute and the chloride ion is contaminated.
- 11.12 (a) Potassium hydroxide; (b) sodium sesquicarbonate; (c) sodium hydroxide.

11.14 (a) The very electropositive alkali metals, where the properties of very high chemical reactivity and very low density are different from 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).

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

11.18 There will be a single covalent bond.



11.20 The very large tetraphenylborate ion is more likely to give a precipitate with the large low-charge ammonium ion.

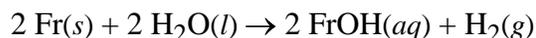
11.22 Potassium ion is inside and sodium ion is outside of cells.

### Beyond the Basics

11.24 Francium would be predicted to be a liquid at room temperature; the most reactive of the alkali metals; the most ionic of the series (that is, the most electropositive element); the largest atom and cation of the series. It should rapidly form a dioxide (1-) on exposure to air:



and it should react explosively with water:



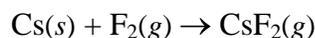
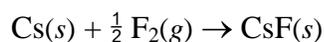
The large cation should form the least soluble salts of the alkali metals with large anions. The salts of the very low charge density francium are

unlikely to be hydrated. Other reactions common to the alkaline earth metals should be expected.

11.26 The  $\text{PtF}_6^-$  ion must be a very large, low charge anion. Lithium is the smallest of the alkali metal cations. It will not stabilize the large anion; instead it abstracts the fluoride ion. Cesium or any of the other lower alkali metals should form stable compounds, such as  $\text{CsPtF}_6$ .

11.28 Lithium consists of two isotopes, lithium-6 (7 percent) and lithium-7 (93 percent). The higher average atomic mass must be due to the sample being depleted of lithium-6. Lithium-6 is used in nuclear weapons and the remaining lithium, enriched in lithium-7, is sold to chemical suppliers. Samples of commercial lithium compounds have been analyzed that contain as little as 3.75 percent lithium-6.

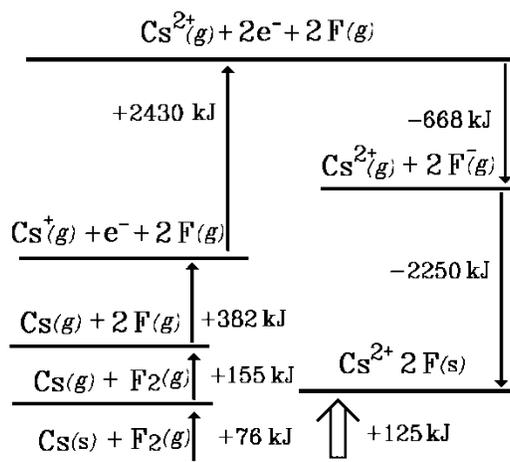
11.30 We can solve the problem once we know the enthalpies of formation of the two compounds



Reversing the second equation and summing gives



The enthalpy of formation of  $\text{CsF}$  is  $-554 \text{ kJ}\cdot\text{mol}^{-1}$ , while that for  $\text{CsF}_2$  can be found from the Born-Haber cycle as  $+125 \text{ kJ}\cdot\text{mol}^{-1}$ :



Thus the enthalpy change for the decomposition will be:

$$[(-554) - (+125)] \text{ kJ}\cdot\text{mol}^{-1} = -679 \text{ kJ}\cdot\text{mol}^{-1}$$

Because  $\frac{1}{2}$  mol of gas is produced in the decomposition, the entropy change will be positive.

Because  $\Delta G = \Delta H - T\Delta S$ ,  $\Delta G$  will be negative and the decomposition thermodynamically spontaneous.

### 11.32 $[\text{HCl}_2]^-$

A large low-charge cation (low charge density) is needed to stabilize this large low-charge anion.

11.34 We do not know the free energies of the two organic species, but the change in entropy must be close to zero (same number of moles of gas on each side) and the bond energy will favor reaction because the breaking C–Cl has an energy of  $327 \text{ kJ}\cdot\text{mol}^{-1}$  while the forming C–F bond has an energy of  $485 \text{ kJ}\cdot\text{mol}^{-1}$ . Thus the organic component will provide the necessary free energy or driving force for the reaction.

Focusing on the inorganic component, the free energies of formation are as follows:

NaF	-544	KF	-538
NaCl	-384	KCl	-409

$$\Delta G^\circ = \sum \Delta G_f^\circ(\text{inorganic product}) - \sum \Delta G_f^\circ(\text{inorganic reactant})$$

for the sodium system,  $\Delta G^\circ = +160 \text{ kJ}\cdot\text{mol}^{-1}$ ;

while for the potassium system,  $\Delta G^\circ = +129 \text{ kJ}\cdot\text{mol}^{-1}$ .

Thus the potassium system will not lead to as great a free energy increase as the sodium system.