

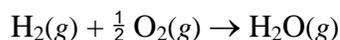
Chapter 6

INORGANIC THERMODYNAMICS

Exercises

- 6.2 (a) The heat content of a substance.
(b) The energy needed to break one mole of that covalent bond.
(c) The energy released when a mole of gaseous ions is surrounded by the shell of water molecules to form the hydrated ion.

- 6.4 The reaction



is spontaneous in the conventional range of temperature. However, there is a decrease of one half mole of gas; thus the entropy is decreasing and it must be the enthalpy factor (exothermic reaction) that drives the process to the right. Because the free energy is given by

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

at a high enough temperature, the negative entropy factor will “overwhelm” the enthalpy term and result in a positive free energy. At this point it will be the reverse process, the decomposition of water, that will become spontaneous.

- 6.6 Using data from Appendix 1:

$$\Delta H_f^\circ = +33 \text{ kJ}\cdot\text{mol}^{-1};$$

$$\begin{aligned} \Delta S_f^\circ &= [1 \times (240) - \frac{1}{2} \times (192) - 1 \times (205)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \\ &= -61 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -0.061 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_f^\circ &= +33 \text{ kJ}\cdot\text{mol}^{-1} - (298 \text{ K})(-0.061 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= +51 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The reaction is nonspontaneous at SATP.

- 6.8 $\Delta G^\circ = \Sigma \Delta G_f^\circ(\text{products}) - \Sigma \Delta G_f^\circ(\text{reactants})$

$$\begin{aligned} \Delta G^\circ &= [1 \times (-1119) + 4 \times (-95)] - [1 \times (-305) + 4 \times (-237)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -246 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

This is only an approximate value of ΔG° because the ΔG_f° values are not those of the common phases at SATP.

6.10 The triple bond in carbon monoxide might be stronger than that in dinitrogen because the former is a polar molecule and there might be an added electrostatic contribution to the bonding.

$$6.12 \quad \text{Bonds broken} = 4(\text{C-H}) + 4(\text{F-F}) = [(4 \times 411) + (4 \times 155)] \text{ kJ}\cdot\text{mol}^{-1} \\ = 2264 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{Bonds formed} = 4(\text{C-F}) + 4(\text{H-F}) = [(4 \times 485) + (4 \times 565)] \text{ kJ}\cdot\text{mol}^{-1} \\ = 4200 \text{ kJ}\cdot\text{mol}^{-1}$$

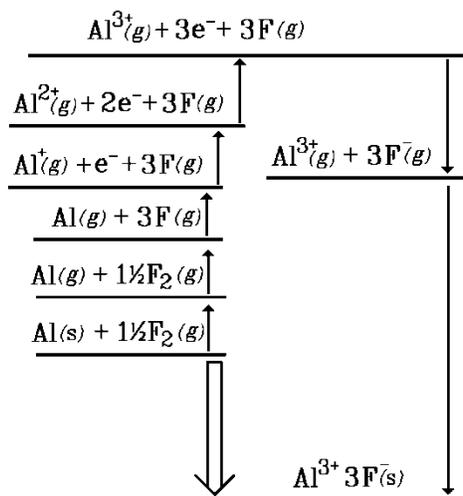
$$\text{Approximate enthalpy of reaction} = [2264 - 4200] \text{ kJ}\cdot\text{mol}^{-1} \\ = -1936 \text{ kJ}\cdot\text{mol}^{-1}$$

We can ignore entropy factors because both reactants and products involve four moles of gas. Note that the very exothermic nature of the reaction is primarily a result of the weak F-F bond and the strong H-F bond.

6.14 The first three terms will be $[6/(1) - 12/(2)^{1/2} + 8/(3)^{1/2}] = 2.13$. We must consider more terms to approach the limiting value of 1.748.

$$6.16 \quad U = -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.763 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1}) (3.48 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{10.5}\right) \\ = -636 \text{ kJ}\cdot\text{mol}^{-1}$$

6.18



- 6.20 Cu(s) sublimation = +337 kJ·mol⁻¹
 $\frac{1}{2}$ F₂ bond energy = +77 kJ·mol⁻¹
 Cu(g) first ionization energy = +752 kJ·mol⁻¹
 F(g) electron affinity = -328 kJ·mol⁻¹

Lattice energy =

$$-\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.638 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.08 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8}\right)$$

$$= -957 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H_f^\circ = -119 \text{ kJ} \cdot \text{mol}^{-1}$$

- 6.22 (a) Not significantly; in the first reaction the moles of gas increase from 7 to 8, while in the second, they increase from 9 to 10.
 (b) If the free energy change for the second reaction is less negative, and the major difference between the two equations is the formation of nitrogen monoxide rather than dinitrogen (for which by definition $\Delta H_f^\circ = 0$), then the enthalpy of formation of nitrogen monoxide must be positive.

6.24 $\Delta H_{\text{soln}}(\text{MX}) = U - [\Delta H(\text{hydration } \text{M}^+) + \Delta H(\text{hydration } \text{X}^-)]$

Let $\Delta H(\text{hydration } \text{X}^-) = x$

Then $\Delta H(\text{hydration } \text{M}^+) = 1.5x$

$$-90 = +1205 - 2.5x$$

$$x = 518$$

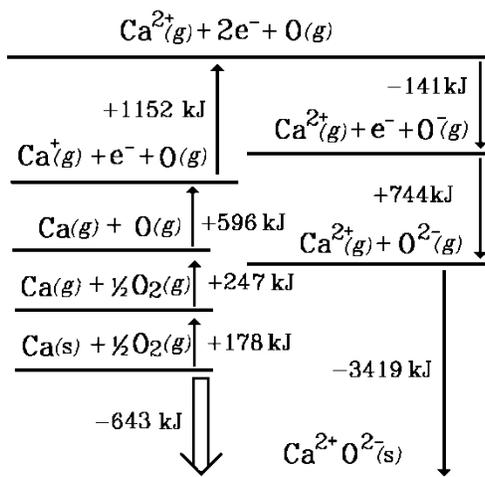
$$\Delta H(\text{hydration } \text{X}^-) = -518 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H(\text{hydration } \text{M}^+) = -777 \text{ kJ} \cdot \text{mol}^{-1}$$

Note that we had to insert the minus sign to indicate that ion hydration is an exothermic step. Alternatively, we could have written the equation as the sum of the lattice energies and the enthalpies of hydration, in which case the minus sign would have appeared from the calculation.

Beyond the Basics

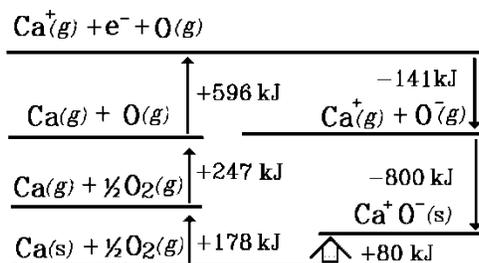
6.26 For $\text{Ca}^{2+}\text{O}^{2-}(s)$, ΔH_f from the Born-Haber cycle is $-643 \text{ kJ}\cdot\text{mol}^{-1}$ (see the diagram, and note that the second electron affinity of oxygen is endothermic). This compares with the tabulated value of $-635 \text{ kJ}\cdot\text{mol}^{-1}$.



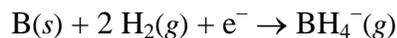
For $\text{Ca}^{+}\text{O}^{-}(s)$, ΔH_f is estimated to be approximately $+80 \text{ kJ}\cdot\text{mol}^{-1}$.

Though the cycle does not require the input of the second ionization energy of calcium

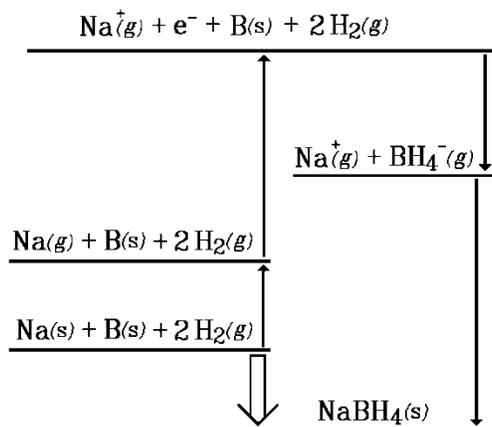
($+1152 \text{ kJ}\cdot\text{mol}^{-1}$), there is not the high lattice energy release that occurs with a divalent cation/anion combination. Thus the net effect is to provide a less favorable ΔH_f .



6.28 We need to find the enthalpy of formation for



This can be obtained from a Born-Haber type cycle:



$$-189 \text{ kJ}\cdot\text{mol}^{-1} = [(+107) + (+502) + \Delta H_{\text{f}}(\text{BH}_4^-(\text{g})) + (-703)] \text{ kJ}\cdot\text{mol}^{-1}$$

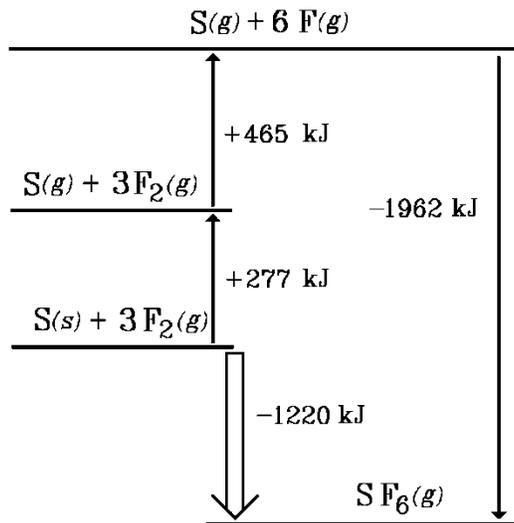
$$\Delta H_{\text{f}}(\text{BH}_4^-(\text{g})) = -95 \text{ kJ}\cdot\text{mol}^{-1}$$

6.30 $\Delta H_{\text{soln}}(\text{LiCl}) = [+862 + (-519 + -364)] \text{ kJ}\cdot\text{mol}^{-1} = -21 \text{ kJ}\cdot\text{mol}^{-1}$

$$\Delta H_{\text{soln}}(\text{MgCl}_2) = [+2523 + (-1920 + 2 \times -364)] \text{ kJ}\cdot\text{mol}^{-1} = -125 \text{ kJ}\cdot\text{mol}^{-1}$$

Magnesium chloride has a much higher lattice energy than lithium chloride as a result of the higher cation charge. Similarly, the dipositive magnesium ion has a much higher hydration energy than the monopositive lithium ion. We can rationalize the effect by arguing that the MgCl_2 lattice energy is only three times greater than that of LiCl , while the cation hydration energy is over four times greater. Hence the negative terms have increased and the solution process for magnesium chloride is exothermic, while that for lithium chloride is endothermic.

- 6.32 From the energy diagram, $\Delta H_f^\circ = -1220 \text{ kJ}\cdot\text{mol}^{-1}$, while the tabulated value is $-1209 \text{ kJ}\cdot\text{mol}^{-1}$.



- 6.34 For sulfur dioxide:

$$\Delta H_f^\circ = -297 \text{ kJ}\cdot\text{mol}^{-1};$$

$$\begin{aligned} \Delta S_f^\circ &= [1 \times (248) - 1 \times (32) - (205)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \\ &= +11 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = +0.011 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_f^\circ &= -297 \text{ kJ}\cdot\text{mol}^{-1} - (298 \text{ K})(+0.011 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= -300 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

For sulfur trioxide:

$$\Delta H_f^\circ = -396 \text{ kJ}\cdot\text{mol}^{-1};$$

$$\begin{aligned} \Delta S_f^\circ &= [1 \times (257) - 1 \times (32) - \frac{3}{2} \times (205)] \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \\ &= -82 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} = -0.082 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta G_f^\circ &= -396 \text{ kJ}\cdot\text{mol}^{-1} - (298 \text{ K})(-0.082 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= -372 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

- (a) The entropy change is negative because there is a one-half mole decrease in the number of moles of gas from reactants to products.
 (b) The formation of sulfur trioxide is thermodynamically preferred.
 (c) Sulfur dioxide.

(d) If sulfur dioxide is commonly formed even though sulfur trioxide is thermodynamically preferred, then kinetic factors must be involved, that is, the reaction to form sulfur trioxide has a high activation energy and hence sulfur dioxide is kinetically preferred.

6.36 (a) Because $\Delta G_{\text{soln}} = \Delta H_{\text{soln}} - T\Delta S_{\text{soln}}$, the more positive ΔH for the silver chloride would suggest that compound to be less soluble. The assumption is that the ΔS_{soln} for the two compounds is similar.

(b) For sodium chloride:

$$+4 \text{ kJ}\cdot\text{mol}^{-1} = + \text{L.E.} - (406 + 364) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{L.E.} = 766 \text{ kJ}\cdot\text{mol}^{-1}$$

For silver chloride:

$$+65 \text{ kJ}\cdot\text{mol}^{-1} = + \text{L.E.} - (464 + 364) \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{L.E.} = 763 \text{ kJ}\cdot\text{mol}^{-1}$$

(c) For sodium chloride:

$$\begin{aligned} U &= -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.748 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.83 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{8}\right) \\ &= -751 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

For silver chloride:

$$\begin{aligned} U &= -\frac{(6.02 \times 10^{23} \text{ mol}^{-1}) \times 1.748 \times 1 \times 1 \times (1.602 \times 10^{-19} \text{ C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12} \text{ C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.96 \times 10^{-10} \text{ m})} \left(1 - \frac{1}{9.5}\right) \\ &= -734 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

The value for silver chloride is significantly less than the value derived from the Born-Landé equation. Probably the bonding in silver chloride has a significant covalent component (as Fajans' rules would predict for a d^{10} electron configuration for the Ag^+ ion).

$$\begin{aligned} 6.38 \quad \Delta H_{\text{soln}}(\text{Ca}_3(\text{PO}_4)_2) &= [3(-543) + 2(-1277) - (-4121)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -62 \text{ kJ}\cdot\text{mol}^{-1} \end{aligned}$$

$$\begin{aligned} \Delta S_{\text{soln}}(\text{Ca}_3(\text{PO}_4)_2) &= [3(-56) + 2(-220) - (+236)] \text{ kJ}\cdot\text{mol}^{-1} \\ &= -884 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \end{aligned}$$

$$\begin{aligned}\Delta G_{\text{soln}}(\text{Ca}_3(\text{PO}_4)_2) &= (-62 \text{ kJ}\cdot\text{mol}^{-1}) - (293 \text{ K})(-0.884 \text{ kJ}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}) \\ &= +197 \text{ kJ}\cdot\text{mol}^{-1}\end{aligned}$$

The very positive value of ΔG indicates that the compound is very insoluble.

- 6.40 For all the lanthanoids, the first three ionization energies are quite low—low enough to be compensated by the higher lattice energy resulting from a 3+ ion. The fourth ionization energy is too high to be similarly compensated by the corresponding increase in lattice energy.

- 6.42 For TlF:

$$U = -\frac{1.202 \times 10^5 \times 2 \times 1 \times 1}{281} \left(1 - \frac{34.5}{281}\right) = -750 \text{ kJ}\cdot\text{mol}^{-1}$$

For TlF₃:

$$U = -\frac{1.202 \times 10^5 \times 4 \times 3 \times 1}{219} \left(1 - \frac{34.5}{219}\right) = -5549 \text{ kJ}\cdot\text{mol}^{-1}$$

- 6.44 $\Delta H = \Delta H_{\text{f}}(\text{Al}_2\text{O}_3(\text{s})) - \Delta H_{\text{f}}(\text{Fe}_2\text{O}_3(\text{s})) = [(-1676) - (-824)] \text{ kJ}\cdot\text{mol}^{-1} = -852 \text{ kJ}\cdot\text{mol}^{-1}$. Note that we have to assume that $\Delta H_{\text{melting}}(\text{Fe}(\text{s}))$ is negligible—this is the case as its value is only $15 \text{ kJ}\cdot\text{mol}^{-1}$. Enthalpies of phase change are usually very small compared to enthalpies of reaction.

- 6.46 Step 1: $\Delta G^\circ = [1(-603) + 2(-53) - 1(-664) - 1(-229)] \text{ kJ}\cdot\text{mol}^{-1} = +184 \text{ kJ}\cdot\text{mol}^{-1}$

$$\text{Step 2: } \Delta G^\circ = [1(-153) - 2(-53)] \text{ kJ}\cdot\text{mol}^{-1} = -47 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{Step 3: } \Delta G^\circ = [1(-59) + 1(-664) - 1(153) - 1(-603)] \text{ kJ}\cdot\text{mol}^{-1} = +33 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\text{Step 4: } \Delta G^\circ = [1(0) + \frac{1}{2}(0) - 1(-59)] = +59 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta G^\circ(\text{overall}) = +229 \text{ kJ}\cdot\text{mol}^{-1}$$

This, of course, is the free energy for the decomposition of water because the cycle terms all cancel each other out.

Spontaneity requires $\Delta G \leq 0$, thus high temperatures will be needed for the first and last steps to make them free-energy favorable. The heat energy required would be far more easily employed to generate electricity and electrolyze the water.

In addition, there will be the environmental concerns of a process that utilizes large quantities of mercury.

