# Chapter 6

INORGANIC THERMODYNAMICS

Exercises

6.1 (a) A reaction that occurs without external "help," or a reaction for which $\Delta G°$ is negative.

(b) A measure of disorder.

(c) The enthalpy change when a mole of a substance is formed from its constituent elements in their standard phases at 298 K and 100 kPa.

6.3 The entropy change is probably negative, because according to the chemical equation, there is a decrease of one half mole of gas (gases have a much higher entropy than liquids and solids).

$$Ca(s) + \tfrac{1}{2} O_2(g) \rightarrow CaO(s)$$
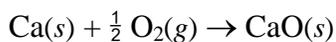
If the entropy change is negative, then for a spontaneous reaction, the enthalpy change must be negative.

6.5 $\Delta H_f° = -286$ kJ·mol^{-1};

$\Delta S_f°$ $= [1 \times (70) - 1 \times (131) - \tfrac{1}{2} \times (205)]$ J·mol^{-1}·K^{-1}

$= -163$ J·mol^{-1}·K^{-1} $= -0.163$ kJ·mol^{-1}·K^{-1}

$\Delta G_f°$ $= -286$ kJ·mol^{-1} $- (298K)(-0.163$ kJ·mol^{-1}·K$^{-1})$

$= -237$ kJ·mol^{-1}

The reaction is spontaneous at SATP.

6.7 $PCl_5(g) + SO_3(g) \rightarrow SO_2Cl_2(g) + POCl_3(l)$

$\Delta G° = \Sigma\Delta G_f°(products) - \Sigma\Delta G_f°(reactants)$

$\Delta G° = [1 \times (-314) + 1 \times(-521)] - [1 \times (-305) + 1 \times (-371)]$ kJ·mol^{-1}

$= -159$ kJ.mol^{-1}

This is only an approximate value of $\Delta G°$ because the $\Delta G_f°$ values are not those of the common phases at SATP.

6.9 The N=N bond will be stronger, because multiple bonds are stronger than single bonds between the same elements.

6.11   Bonds broken = 4(S–S) + 8(H–S) = [(4 × 266) + (8 × 363)] kJ·mol^{-1}

    = 3968 kJ·mol^{-1}

    Bonds formed = 8(S–S) + 4(H–H) = [(8 × 266) + (4 × 432)] kJ·mol^{-1}

    = 3856 kJ·mol^{-1}

    Approximate enthalpy of reaction = [3968 – 3856] kJ·mol^{-1} = +112 kJ·mol^{-1}

6.13   Sodium chloride, lithium fluoride, magnesium oxide. LiF will be higher than NaCl because LiF has smaller, higher charge density ions. MgO will be the highest because the charges (and thus charge densities) are higher.

6.15   The first two terms will be [8/(3)^{½} – 6/2] = 1.62. Again, more terms must be considered to approach the limiting value of 1.763.

6.17 $$U = -\frac{(6.02 \times 10^{23}\ \text{mol}^{-1}) \times 2.519 \times 2 \times 1 \times (1.602 \times 10^{-19}\ \text{C})^2}{4 \times 3.142 \times (8.854 \times 10^{-12}\ \text{C}^2 \cdot \text{J}^{-1} \cdot \text{m}^{-1})(2.31 \times 10^{-10}\ \text{m})}\left(1 - \frac{1}{8}\right)$$

    $$= -2649\ \text{kJ·mol}^{-1}$$

6.19
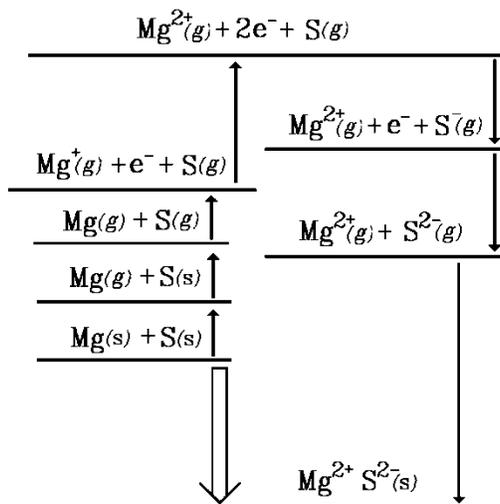
6.21 Na(s) sublimation = +107 kJ·mol^{-1}

$\frac{1}{2}$ H$_2$ bond energy = +216 kJ·mol^{-1}

Na(g) first ionization energy = +502 kJ·mol^{-1}

H(g) electron affinity (EA H) = to find

Na$^+$H$^-$ lattice energy = −782 kJ·mol^{-1}

$\Delta H_f°$(NaCl(s)) = −411 kJ·mol^{-1}

−411 kJ·mol^{-1} = [+107 + 216 + 502 + (EA H) − 782] kJ·mol^{-1}

(EA H) = −454 kJ·mol^{-1}

6.23 Because of the high charge density of the oxide, O^{2-}, ion, the lattice energy of oxides will be very high. This will more than compensate for the net electron affinity being positive. It is the importance of the lattice energy factor that results in oxides only being stable in the solid phase.

Beyond the Basics

6.25 The term "the permittivity of free space" is a constant that relates the attractive force between two point charges. The mathematical formula is known as Coulomb's law and it has the formula
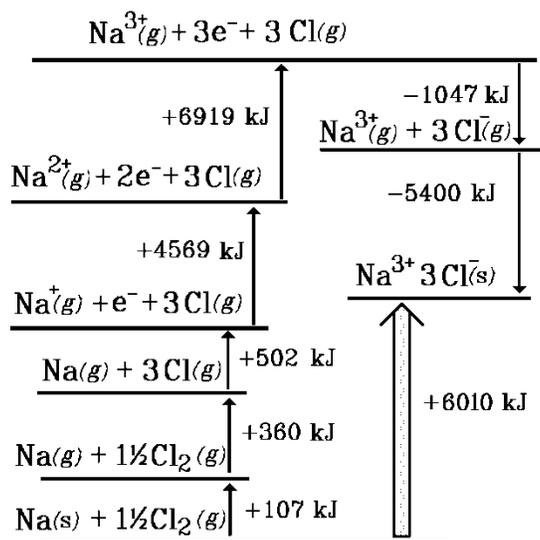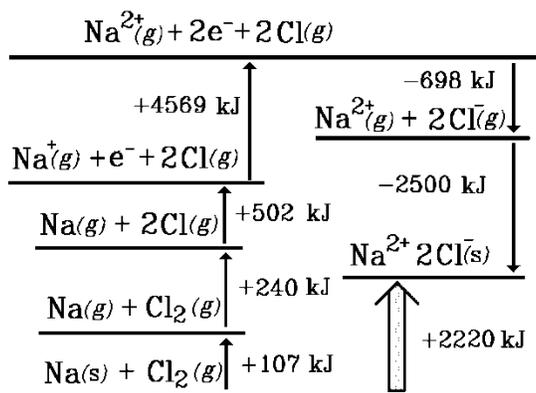
$$F = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r^2}$$

where F is the force, q_1 and q_2 are the magnitudes of the point charges, r is the distance between the charges, and ε_0 is the permittivity of free space. The permittivity of free space is an important constant throughout equations related to electric charge and electromagnetic waves. The most important relationship, perhaps, is

$$c^2 = \frac{1}{\varepsilon_0 \mu_0}$$

where c is the velocity of light and μ_0 is the permeability of free space. Thus the velocity of light is related to these two other physical constants.

6.27   As can be seen, the enthalpy of formation for both $NaCl_2$ and $NaCl_3$ are positive. Even though the lattice energies resulting from the more highly charged ions are much greater, they are not enough to compensate for the ionization of one or two $2p$ (inner) electrons.

$$Na^{2+}{}_{(g)} + 2e^- + 2\,Cl_{(g)}$$

+4569 kJ

$$-698\ kJ$$

$$Na^{2+}{}_{(g)} + 2\,Cl^-{}_{(g)}$$

$$Na^+{}_{(g)} + e^- + 2\,Cl_{(g)}$$

$$Na_{(g)} + 2\,Cl_{(g)} \quad +502\ kJ$$

$$-2500\ kJ$$

$$Na_{(g)} + Cl_{2\,(g)} \quad +240\ kJ$$

$$Na^{2+}\,2\,Cl^-{}_{(s)}$$

$$Na_{(s)} + Cl_{2\,(g)} \quad +107\ kJ$$

+2220 kJ

$$Na^{3+}{}_{(g)} + 3e^- + 3\,Cl_{(g)}$$

+6919 kJ

$$-1047\ kJ$$

$$Na^{3+}{}_{(g)} + 3\,Cl^-{}_{(g)}$$

$$Na^{2+}{}_{(g)} + 2e^- + 3\,Cl_{(g)}$$

$$-5400\ kJ$$

+4569 kJ

$$Na^{3+}\,3\,Cl^-{}_{(s)}$$

$$Na^+{}_{(g)} + e^- + 3\,Cl_{(g)}$$

$$Na_{(g)} + 3\,Cl_{(g)} \quad +502\ kJ$$

$$Na_{(g)} + 1\tfrac{1}{2}Cl_{2\,(g)} \quad +360\ kJ$$

+6010 kJ

$$Na_{(s)} + 1\tfrac{1}{2}Cl_{2\,(g)} \quad +107\ kJ$$

6.29   Magnesium oxide, being a 2+/2− ion combination, will have a higher lattice energy than the 2+/1− ion combination of magnesium chloride. This energy input must be greater than the energy released from the hydration of the ions.

6.31   From the energy diagram, $\Delta H_f° = -913$ kJ·mol^{-1}, while the tabulated value is -933 kJ·mol^{-1}.

$C(g) + 4\ F(g)$

$+310$ kJ

$C(g) + 2\ F_2(g)$

-1940 kJ

$+717$ kJ

$C(s) + 2\ F_2(g)$

-913 kJ

$C\ F_4(g)$
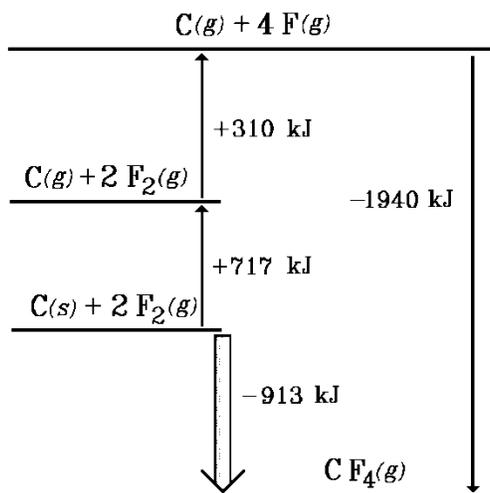
6.33   From the following energy diagram (using the $\Delta H_f°$ value from Appendix 2), the Cl−F bond energy is calculated to be 250 kJ·mol^{-1}.

$+78$ kJ

$Cl(g) + \frac{1}{2}F_2(g)$

-250 kJ

$+120$ kJ

$\frac{1}{2}Cl_2(g) + \frac{1}{2}F_2(g)$

-54 kJ

$ClF(g)$
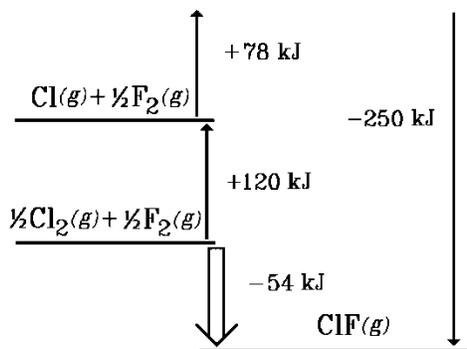
6.35   The lattice energy of the calcium chloride will also be much greater. This will negate the higher hydration energy.

6.37   For calcium sulfate:

-17.8 kJ·mol^{-1} = 2653 kJ·mol^{-1} − (1650 + $\Delta H_{hydr}(SO_4^{2-})$) kJ·mol^{-1}

$\Delta H_{hydr}(SO_4^{2-})$ = −1021 kJ·mol^{-1}

For strontium sulfate:

-8.7 kJ·mol^{-1} = 2603 kJ·mol^{-1} − (1480 + $\Delta H_{hydr}(SO_4^{2-})$) kJ·mol^{-1}

$\Delta H_{hydr}(SO_4^{2-})$ = −1132 kJ·mol^{-1}

For barium sulfate:

$+19.4$ kJ·mol^{-1} = 2423 kJ·mol^{-1} − (1360 + $\Delta H_{hydr}(SO_4^{2-})$) kJ·mol^{-1}

$\Delta H_{hydr}(SO_4^{2-})$ = −1044 kJ·mol^{-1}

The values are consistent, within the errors of the data.

6.39   The cycle is shown in the diagram.
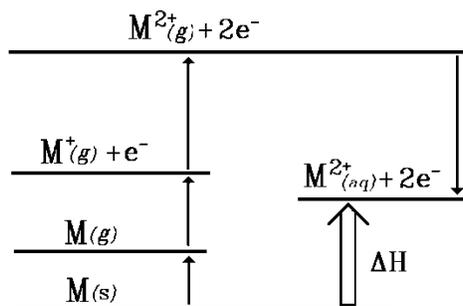
Using the values for magnesium:

ΔH = [+147 + 744 + 1457 − 1920] kJ·mol^{-1} = +428 kJ·mol^{-1}

Using the values for lead:

ΔH = [+196 + 722 + 1457 − 1477] kJ·mol^{-1} = +898 kJ·mol^{-1}

The only significant difference between the two ions is their hydration enthalpies. If we look at the charge densities, we see that the charge density for the magnesium ion is much greater than that of the lead(II) ion. Hence there will be a stronger attraction (more exothermic reaction) between the magnesium ion and the oxygen ends of water molecules than for the equivalent process with the lead(II) ion (you can also argue using comparative ionic radii because the charges are the same).

6.41   Using the Kapustinskii equation:

$$U = -\frac{1.202\times10^5 \times 2\times1\times1}{348}\left(1-\frac{34.5}{348}\right) = -622 \text{ kJ·mol}^{-1}$$

compared with -668 kJ·mol^{-1} experimentally and -636 kJ·mol^{-1} from the Born-Landé equation.

6.43   According to the Appendix, the NaCl-structure lattice energy of rubidium chloride is 693 kJ·mol^{-1}. We can calculate the theoretical CsCl lattice energy using the Born-Landé equation:
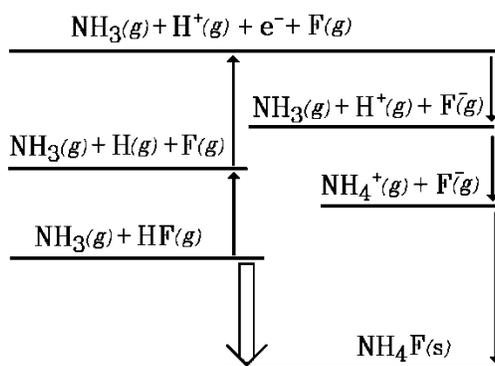
$$U = -\frac{(6.02\times10^{23} \text{ mol}^{-1})\times1.763\times1\times1\times(1.602\times10^{-19} \text{ C})^2}{4\times3.142\times(8.854\times10^{-12} \text{ C}^2\cdot\text{J}^{-1}\cdot\text{m}^{-1})(3.33\times10^{-10} \text{ m})}\left(1-\frac{1}{9.5}\right)$$

$$= -657 \text{ kJ·mol}^{-1}$$

Thus the approximate ΔH for the transformation $= [(-657)-(-693)]$
    kJ·mol^{-1}
    $= +36$ kJ·mol^{-1}

6.45   First, we have to calculate the lattice energy of NH$_4$F:

$$U = -\frac{(6.02\times10^{23} \text{ mol}^{-1})\times1.641\times1\times1\times(1.602\times10^{-19} \text{ C})^2}{4\times3.142\times(8.854\times10^{-12} \text{ C}^2\cdot\text{J}^{-1}\cdot\text{m}^{-1})(2.56\times10^{-10} \text{ m})}\left(1-\frac{1}{8}\right)$$

$$= -778 \text{ kJ·mol}^{-1}$$
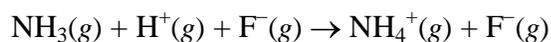
Then we can construct a Born-Haber type cycle:

ΔH reaction can be calculated from the difference in the enthalpies of formation:

$\Delta H = [(-464) - (-273) - (-46)] \text{ kJ·mol}^{-1} = -145 \text{ kJ·mol}^{-1}$

The ionization energy of hydrogen ($+1537 \text{ kJ·mol}^{-1}$) is provided in the question.

The other information needed to complete the cycle, except for

$NH_3(g) + H^+(g) + F^-(g) \rightarrow NH_4^+(g) + F^-(g)$

is found in the appendices:

Bond energy (H–F) $= +565 \text{ kJ·mol}^{-1}$

Electron affinity F $= -328 \text{ kJ·mol}^{-1}$

$-145 \text{ kJ·mol}^{-1} =$

$[(+565) + (+1537) + (-328) + (\text{proton affinity}) + (-778)] \text{ kJ·mol}^{-1}$

proton affinity $= -1141 \text{ kJ·mol}^{-1}$

6.47   Metals certainly do not "want to lose electrons," as is apparent from the high positive values of the ionization energies. It is generally but not always true that the electron affinities for nonmetals are negative, for example; the second electron affinity of oxygen is positive. Thus ionic bond formation is best considered as a competition for electrons.