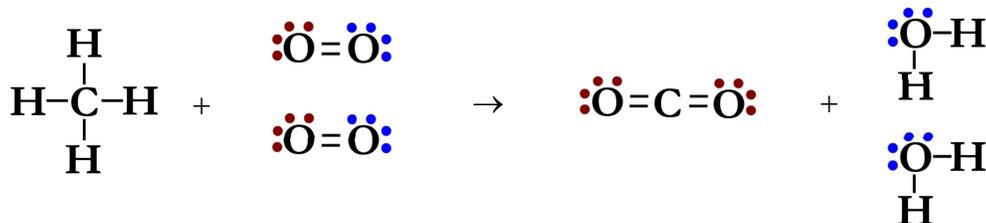


Solutions to the Extra Problems for Chapter 14

1. The $\Delta H = -670$ kJ. To use bond energies, we have to figure out what bonds are being broken and what bonds are being made, so we need to make Lewis structures for everything:



We have to break four C–H bonds (each of which is worth 410 kJ/mole) and two O=O bonds (each of which is worth 498 kJ/mole). We then have to make two C=O bonds (each of which is worth 732 kJ/mole) and four O–H bonds (each of which is worth 460 kJ/mole).

$$\Delta H = (\text{Energy for breaking bonds}) - (\text{Energy from making bonds})$$

$$\Delta H = (4 \text{ moles}) \cdot (410 \frac{\text{kJ}}{\text{mole}}) + (2 \text{ moles}) \cdot (498 \frac{\text{kJ}}{\text{mole}}) - (2 \text{ moles}) \cdot (732 \frac{\text{kJ}}{\text{mole}}) - (4 \text{ mole}) \cdot (460 \frac{\text{kJ}}{\text{mole}})$$

$$\Delta H = -670 \text{ kJ}$$

2. The bond energy is 840 kJ/mole. We have bond energies for all the bonds except the C≡C bond. That means we can set up the ΔH equation and solve for the energy of the C≡C bond. The Lewis structures tell us we have to break two C–H bond (which is worth 410 kJ/mole), one C≡C bond (which is not known), and two H–H bonds (each of which is worth 436 kJ/mole). We then have to make six C–H bonds (each of which is worth 410 kJ/mole), one C–C bond (which is worth 350 kJ/mole).

$$\begin{aligned} \Delta H = & (2 \text{ moles}) \cdot (410 \frac{\text{kJ}}{\text{mole}}) + (1 \text{ mole}) \cdot (\text{C} \equiv \text{C bond}) + (2 \text{ moles}) \cdot (436 \frac{\text{kJ}}{\text{mole}}) - (6 \text{ moles}) \cdot (410 \frac{\text{kJ}}{\text{mole}}) \\ & - (1 \text{ mole}) \cdot (350 \frac{\text{kJ}}{\text{mole}}) \end{aligned}$$

$$\Delta H = -1,120 \text{ kJ} + (1 \text{ mole}) \cdot (\text{C} \equiv \text{C bond})$$

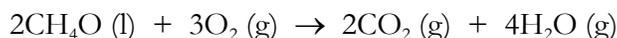
Remember, we are treating these like addition/subtraction problems, and least precise numbers (410 and 350) require us to report our answer to the tens place.

We know what ΔH is. The problem gave it to us. So we can put that into the equation and solve for the energy of the C≡C bond.

$$-280 \text{ kJ} = -1,120 \text{ kJ} + (1 \text{ mole}) \cdot (\text{C} \equiv \text{C bond})$$

$$\text{C} \equiv \text{C bond} = \frac{-280 \text{ kJ} + 1,120 \text{ kJ}}{1 \text{ mole}} = 840 \frac{\text{kJ}}{\text{mole}}$$

3. The $\Delta H = -1,276.8 \text{ kJ}$. To use Hess's Law, we need the chemical equation and the standard enthalpies of formation. You learned complete combustion in Chapter 6:



The standard enthalpies of formation are: -393.5 kJ/mole for $\text{CO}_2 (\text{g})$, -241.8 kJ/mole for $\text{H}_2\text{O} (\text{g})$, -238.7 kJ/mole for $\text{CH}_4\text{O} (\text{l})$, and 0 for $\text{O}_2 (\text{g})$, since it's an element in its natural phase.

$$\Delta H = (2 \text{ moles}) \cdot (-393.5 \frac{\text{kJ}}{\text{mole}}) + (4 \text{ moles}) \cdot (-241.8 \frac{\text{kJ}}{\text{mole}}) - (2 \text{ moles}) \cdot (-238.7 \frac{\text{kJ}}{\text{mole}}) = -1,276.8 \text{ kJ}$$

4. The $\Delta H_f^\circ = 91.3 \text{ kJ/mole}$. The table of standard enthalpies of formation doesn't have $\text{NO} (\text{g})$, but since we know ΔH , we can calculate it. The standard enthalpy of formation for $\text{H}_2\text{O} (\text{g})$ is -241.8 kJ/mole . For $\text{NH}_3 (\text{g})$, it is -45.9 kJ/mole , and for $\text{O}_2 (\text{g})$, it is zero, since it is an element in its natural phase.

$$\Delta H = (4 \text{ moles}) \cdot \Delta H_f^\circ[\text{NO}(\text{g})] + (6 \text{ moles}) \cdot (-241.8 \frac{\text{kJ}}{\text{mole}}) - (4 \text{ moles}) \cdot (-45.9 \frac{\text{kJ}}{\text{mole}}) - (5 \text{ moles}) \cdot (0 \frac{\text{kJ}}{\text{mole}})$$

$$\Delta H = (4 \text{ moles}) \cdot \Delta H_f^\circ[\text{NO}(\text{g})] + -1,267.2 \text{ kJ}$$

Since we are given ΔH , we can plug it into that equation and solve for $\Delta H_f^\circ[\text{NO} (\text{g})]$:

$$-902.0 \text{ kJ} = (4 \text{ moles}) \cdot \Delta H_f^\circ[\text{NO} (\text{g})] + -1,267.2 \text{ kJ}$$

$$\Delta H_f^\circ[\text{NO} (\text{g})] = \frac{-902.0 \text{ kJ} + 1,267.2 \text{ kJ}}{4 \text{ moles}} = 91.3 \frac{\text{kJ}}{\text{mole}}$$

5. 89,000 kJ will be released. Since ΔH is negative (you calculated it to be $-1,276.8 \text{ kJ}$ in problem 3), the reaction releases energy, so energy is a product. We can put it right into the equation:



Now we can just do stoichiometry:

$$\text{Mass of CH}_4\text{O} = 12.01 \text{ amu} + 4 \times 1.01 \text{ amu} + 1 \times 16.00 \text{ amu} = 32.05 \text{ amu}$$

Since this tells us the number of grams in one mole, we need to convert 4.5 kg to 4,500 g.

$$\frac{4,500 \text{ g } \cancel{\text{CH}_4\text{O}}}{1} \times \frac{1 \text{ mole CH}_4\text{O}}{32.05 \text{ g } \cancel{\text{CH}_4\text{O}}} = 140 \text{ moles CH}_4\text{O}$$

The chemical equation tells us:



We can use that to convert moles of CH₄O into kJ of energy released:

$$\frac{140 \text{ moles } \cancel{\text{CH}_4\text{O}}}{1} \times \frac{1,276.8 \text{ kJ}}{2 \text{ moles } \cancel{\text{CH}_4\text{O}}} = 89,000 \text{ kJ}$$

6. a. Reaction II is the endothermic reaction, since the energy of the products is higher than that of the reactants.

b. The $\Delta H = -100 \text{ kJ}$. ΔH is the difference between the energy of the products and that of the reactants. It is negative because the products are lower in energy than the reactants.

c. The $\Delta H = 100 \text{ kJ}$. ΔH is the difference between the energy of the products and that of the reactants. It is positive because the products are higher in energy than the reactants.

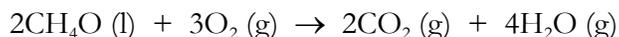
d. Reaction I has the highest activation energy. The activation energy is the difference in energy between the top of the “hill” and the reactants. For Reaction I, that’s about 270 kJ. For Reaction II, it is only about 190 kJ.

7. a. ΔS is negative ($\Delta S < 0$). There are only gases on the reactants side, but there is a solid on the products side. Also, there are fewer molecules on the products side. This means the products side has lower entropy, so ΔS is negative.

b. ΔS is positive ($\Delta S > 0$). There is only a solid on the reactants side. However, there is a gas on the products side as well as more molecules on the products side. That makes ΔS positive.

c. ΔS is negative ($\Delta S < 0$). There are only gases on both sides of the equation, but there are more molecules on the reactants side (five as opposed to four). That means ΔS is negative.

8. ΔS is 313.6 J/mole·K. You already determined the equation:

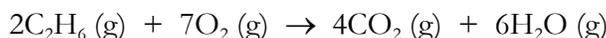


The absolute entropies are: 213.7 J/mole·K for CO₂ (g), 188.7 J/mole·K for H₂O (g), 126.8 J/mole·K for CH₄O (l), and 205.0 J/mole·K for O₂ (g).

$$\Delta S = (2 \text{ moles}) \cdot (213.7 \frac{\text{J}}{\text{mole} \cdot \text{K}}) + (4 \text{ moles}) \cdot (188.7 \frac{\text{J}}{\text{mole} \cdot \text{K}}) - (2 \text{ moles}) \cdot (126.8 \frac{\text{J}}{\text{mole} \cdot \text{K}}) - (3 \text{ moles}) \cdot (205.0 \frac{\text{J}}{\text{mole} \cdot \text{K}})$$

$$\Delta S = 313.6 \text{ J/K}$$

9. The reaction is spontaneous, with a ΔG of -2,883.4 kJ. The complete combustion of C_2H_6 (g) is:



The ΔG_f° 's are: -394.4 kJ/mole for CO_2 (g), -228.6 kJ/mole for H_2O (g), -32.9 kJ/mole for C_2H_6 (g), and 0 for O_2 (g), since it's an element in its natural phase.

$$\Delta G = (4 \text{ moles}) \cdot (-394.4 \frac{\text{kJ}}{\text{mole}}) + (6 \text{ moles}) \cdot (-228.6 \frac{\text{kJ}}{\text{mole}}) - (2 \text{ moles}) \cdot (-32.9 \frac{\text{kJ}}{\text{mole}}) = -2,883.4 \text{ kJ}$$

Since ΔG is negative, the reaction is spontaneous.

10. a. This reaction is spontaneous at $T < 986.3 \text{ K}$. In this one, we can't make a statement for all temperatures, so we need to use Equation (14.5), remembering that we have to convert kJ to J to make the units consistent:

$$\Delta G = \Delta H - T \cdot \Delta S = -115,600 \text{ J} - T \cdot (-117.2 \frac{\text{J}}{\text{K}})$$

To be spontaneous, $\Delta G < 0$:

$$-115,600 \text{ J} - T \cdot (-117.2 \frac{\text{J}}{\text{K}}) < 0$$

Solving for T:

$$-T \cdot (-117.2 \frac{\text{J}}{\text{K}}) < 115,600 \text{ J}$$

The negatives cancel, so when we divide by 117.2 J/K we get:

$$T < \frac{115,600 \text{ J}}{117.2 \frac{\text{J}}{\text{K}}}$$

$$T < 986.3 \text{ K}$$

b. In this case, ΔG will always be positive, because Equation (14.5) has us adding something to a positive number, so this reaction is never spontaneous no matter what the temperature.

c. This reaction is spontaneous at $T > 1,532 \text{ K}$. In this case, we have to use Equation (14.5), remembering to convert kJ to J to make the units consistent. To be spontaneous, $\Delta G < 0$:

$$203,100 \text{ J} - T \cdot (132.6 \frac{\text{J}}{\text{K}}) < 0$$

Solving for T:

$$-T \cdot (132.6 \frac{\text{J}}{\text{K}}) < -203,100 \text{ J}$$

We need to divide by -132.6, but that means switching the direction of the sign:

$$T > \frac{203,100 \text{ J}}{132.6 \frac{\text{J}}{\text{K}}}$$

$$T > 1,532 \text{ K}$$

d. In this case, ΔG will always be negative, because Equation (14.5) has us subtracting something from a negative number, so this reaction is spontaneous no matter what the temperature.