

## 16.15: Maximum Useful Work

The Gibbs free energy has another very useful property. When a spontaneous chemical reaction occurs, the decrease in free energy,  $-\Delta G$  corresponds to the maximum possible quantity of useful work,  $w_{max}$ , which can be obtained. Symbolically,

$$-\Delta G = w_{max}$$

For a reaction which is not spontaneous  $\Delta G$  is positive and  $w_{\text{max}}$  is negative. This means that work must be done on the system (through some outside intervention) to force the nonspontaneous reaction to occur. The minimum work that must be done is given by  $\Delta G$ . As an example of the utility of this interpretation of  $\Delta G$ , consider the recovery of Al from Al<sub>2</sub>O<sub>3</sub> ore:

$$\mathrm{Al_2O_3} 
ightarrow 2\,\mathrm{Al} + rac{3}{2}\mathrm{O_2} \qquad \Delta G_m^\circ(298\;\mathrm{K}) = 1576.4 rac{\mathrm{kJ}}{\mathrm{mol}}$$

The positive  $\Delta G$  tells us that at least 1576.4 kJ of work must be done on 1 mol Al<sub>2</sub>O<sub>3</sub> to effect this change. In a modern aluminum manufacturing plant this work is supplied electrically, and the electricity is often provided by burning coal. Assuming coal to be mainly carbon, we can write

$$\mathrm{C(s)} + \mathrm{O_2(g)} \rightarrow \mathrm{CO_2(g)} \qquad \Delta G_m^{\circ}(298 \; \mathrm{K}) = -394.4 \frac{\mathrm{kJ}}{\mathrm{mol}}$$

Thus 1 mol C can do almost exactly one-quarter the work required to decompose 1 mol  $Al_2O_3$  and we must burn at least 4 mol C to process each 1 mol  $Al_2O_3$  ore. (In practice the aluminum smelting process is only 17 percent efficient, so it is necessary to burn nearly 6 times the theoretical 4 mol C.)

In the context we have just described, *free* energy is energy that is *available to do useful work*, not energy that we can get for nothing. When a spontaneous process occurs and there is a free energy decrease, it is the *availability of useful energy* which decreases. According to the first law of thermodynamics, energy *cannot* be consumed in any process, but according to the second law, free (or available) energy is *always* consumed in a spontaneous process.

When we talk about consuming energy resources by burning fossil fuels, it is the availability of energy that is used up. The energy originally stored in a fuel is converted to heat energy and dispersed to the surroundings. Once this has happened its usefulness is lost. There is no way of abstracting this energy from the surroundings and using it to lift a weight or do other useful work, because that would correspond to the reversal of a spontaneous process. The second law thus adds a very important qualification to the first law. While the first law tells us that we cannot destroy energy, the second law tells as that we cannot recycle it either.

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