8.1: Enthalpy

In Chapter 7, we introduce the enthalpy function, which we define as

$$H = E + PV$$

When the only form of work possible is pressure–volume work and a system change occurs at constant pressure, the enthalpy change is synonymous with the heat added to the system.

$H = q_P$ (only PV work)

Since we define $C_P = (\partial q/\partial T)_P$, it follows that $(\partial H/\partial T)_P = C_P$. Recalling our earlier discovery that $(\partial E/\partial T)_V = C_V$, we have the important parallel relationships:

$$C_P = \left(\frac{\partial q}{\partial T}\right)_P = \left(\frac{\partial H}{\partial T}\right)_P$$

and

$$C_V = \left(\frac{\partial q}{\partial T}\right)_V = \left(\frac{\partial E}{\partial T}\right)_V$$

We can find the enthalpy change for heating a substance at constant pressure by integrating its constant-pressure heat capacity, C_P, over the change in temperature. That is, $C_P = (\partial H/\partial T)_P$ implies that

$$\Delta H = \int_{T_1}^{T_2} C_P dT$$

Similarly, we have

$$\Delta E = \int_{T_1}^{T_2} C_V dT$$

for a process in which a substance is heated at constant volume.

One reason that the enthalpy function is useful in chemistry is that many processes are carried out at conditions (constant pressure, only PV work) where the enthalpy change is synonymous with the heat exchanged. The heat exchanged in a process is frequently an important consideration. If we want to carry out an endothermic process, we must provide means to add sufficient

heat. If we want to carry out an exothermic process, we may have to make special arrangements to safely transfer the heat evolved from the system to its surroundings.

One of our principal objectives is to predict whether a given process can occur spontaneously. We will see that the heat evolved in a process is ***not*** a generally valid predictor of whether or not the process can occur spontaneously; however, it is true that a very exothermic process is usually one that can occur spontaneously. (We will see that $\Delta H < 0$ is a rigorous criterion for whether the process can occur spontaneously if and only if the process is one for which both the entropy and the pressure remain constant.)