8.9: Calorimetry

Calorimetry is the experimental science of measuring the heat changes that accompany chemical or physical changes. The accurate measurement of small amounts of heat is experimentally challenging. Nevertheless, calorimetry is an area in which great experimental sophistication has been achieved and remarkably accurate measurements can be made. Numerous devices have been developed to measure heat changes.

Some of these devices measure a (usually small) temperature change. Such devices are calibrated by measuring how much their temperature increases when a known amount of heat is introduced. This is usually accomplished by passing a known electric current through a known resistance for a known time. Other calorimeters measure the amount of some substance that undergoes a phase change. The ice calorimeter is an important example of the latter method. In an ice calorimeter, the heat of the process is transferred to a mixture of ice and water. The amount of ice that melts is a direct measure of the amount of heat released by the process. The amount of ice melted can be determined either by direct measurement of the increase in the amount of water present or by measuring the change in the volume of the ice–water mixture. (Since ice occupies a greater volume than the same mass of water, melting is accompanied by a decrease in the total volume occupied by the mixture of ice and water.)

The processes that can be investigated accurately using calorimetry are limited by two important considerations. One is that the process must go to completion within a relatively short time. No matter how carefully it is constructed, any calorimeter will exchange thermal energy with its environment at some rate. If this rate is not negligibly small compared to the rate at which the process evolves heat, the accuracy of the measurement is degraded. The second limitation is that the process must involve complete conversion of the system from a known initial state to a known final state. When the processes of interest are chemical reactions, these considerations mean that the reactions must be quantitative and fast.

Combustion reactions and catalytic hydrogenation reactions usually satisfy these requirements, and they are the most commonly investigated. However, even in these cases, there can be complications. For a compound containing only carbon, hydrogen, and oxygen, combustion using excess oxygen produces only carbon dioxide and water. For compounds containing heteroatoms like nitrogen, sulfur, or phosphorus, there may be more than one heteroatom-containing product. For example, combustion of an organosulfur compound might produce both sulfur dioxide and sulfur trioxide. To utilize the thermochemical data obtained in such an experiments, a chemical analysis must be done to determine the amount of each oxide present.