

## 1.3: Classical Thermodynamics

One goal of chemical thermodynamics is to predict whether a particular chemical reaction can occur. We say can, not will, because chemical thermodynamics is unable to make predictions about reaction rates. If we learn from our study of chemical thermodynamics that a particular reaction can occur, we still do not know whether it will occur in a millisecond—or so slowly that no change is detectable. The science of thermodynamics builds on the idea that a particular chemical system can be characterized by the values of certain **thermodynamic functions**. These **state functions** include such familiar quantities as **pressure**, **temperature**, **volume**, **concentrations**, and **energy**, as well as some that are not so well known, notably **enthalpy**, **entropy**, **Gibbs free energy**, **Helmholtz free energy**, **chemical potential**, **fugacity**, and **chemical activity**. We can think of a state function as a quasi-mathematical function whose argument is a physical system. That is, a state function maps a real system onto a real number. When we insert a thermometer into a mixture, the measurement that we make maps the state of the mixture onto the real number that we call temperature.

The word “thermodynamics” joins roots that convey the ideas of heat and motion. In general, motion involves kinetic energy and mechanical work. The interconversion of heat and mechanical work is the core concern of the science of thermodynamics. We are familiar with the idea that kinetic energy can be converted into work; given a suitable arrangement of ropes and pulleys, a falling object can be used to lift another object. Kinetic energy can also be converted—or, as we often say, degraded—into heat by the effects of friction. We view such processes as the conversion of the kinetic energy of a large object into increased kinetic energy of the atoms and molecules that comprise the warmed objects. We can say that easily visible mechanical motions are converted into invisible mechanical motions. The idea that heating an object increases the kinetic energy of its component atoms is called **the kinetic theory of heat**.

It is often convenient to use the term **microscopic process** to refer to an event that occurs at the atomic or molecular level. We call a process that occurs on a larger scale a **macroscopic process**, although the usual connotation is that a macroscopic process is observable in a quantity of bulk matter. When friction causes the degradation of macroscopic motion to heat, we can say that macroscopic motion is converted to microscopic motion.

While this terminology is convenient, it is not very precise. Changes visible under an optical microscope are macroscopic processes. Of course, all macroscopic changes are ultimately attributable to an accumulation of molecular-level processes. The Brownian motion of a colloidal particle suspended in a liquid medium is noteworthy because this relationship is visible. Viewed with an optical microscope, a suspended, macroscopic, colloidal particle is seen to undergo a rapid and random jiggling motion. Each jiggle is the accumulated effect of otherwise invisible collisions between the particle and the molecules of the liquid. Each collision imparts momentum to the particle. Over long times, the effects average out; momentum transfer is approximately equal in every direction. During the short time of a given jiggle, there is an imbalance of collisions such that more momentum is transferred to the particle in the direction of the jiggle than in any other.

We are also familiar with the idea that heat can be converted into mechanical motion. In an earlier era, steam engines were the dominant means by which heat was converted to work. Steam turbines remain important in large stationary facilities like power plants. For applications we encounter in daily life, the steam engine has been replaced by the internal-combustion engine. When we want to create mechanical motion (do work) with a heat engine, it is important to know how much heat we need in order to produce a given quantity of work. Sadi Carnot was the first to analyze this problem theoretically. In doing so, he discovered the idea that we call the second law of thermodynamics.

The interconversion of heat and work involves an important asymmetry. We readily appreciate that the conversion of kinetic energy to heat can be complete, because we have seen countless examples of objects coming to a complete standstill as the result of frictional forces. However, ordinary experience leaves us less prepared to deal with the question of whether heat can be completely converted into work. Possibly, we remember hearing that it cannot be done and that the reason has something to do with the second law of thermodynamics. If we have heard more of the story, we may remember that it is slightly more complicated. Under idealized circumstances, heat can be converted into work completely. If we confine an ideal gas in a frictionless piston and arrange to add heat to the gas while increasing the volume of the piston in a coordinated way, such that the temperature of the gas remains constant, the expanding piston will do work on some external entity, and the amount of this work will be just equal to the thermal energy added to the gas. We call this process a reversible isothermal expansion. This process does not involve a cycle; the volume of the gas at the end of the process is greater than its volume at the start.

What Carnot realized is that an engine must operate in a cyclic fashion, and that no device—not even an idealized frictionless device—operating around a cycle can convert heat to work with 100% efficiency. Carnot analyzed the process of converting heat

into work in terms of an ideal engine that accepts thermal energy (heat) at a high temperature, uses some of this thermal energy to do work on its surroundings, and rejects the rest of its thermal-energy intake to the surroundings in the form of thermal energy at a lower temperature. Carnot's analysis preceded the development of our current ideas about the nature of thermal energy. He expressed his ideas using a now-abandoned theory of heat. In this theory, heat is considered to be a fluid-like quantity—called **caloric**. Transfers of heat comprise the flow of caloric from one object to another. Carnot's ideas originated as an analogy between the flow of caloric through a steam engine and the flow of water through a water wheel. In this view, the temperature of the steam, entering and leaving the engine, is analogous to the altitude of the water entering and leaving the wheel<sup>1</sup>.

Such considerations are obviously relevant if we are interested in building engines, but we are interested in chemical reactivity. How does chemical change relate to engines and the conversion of heat into work? Well, rather directly, actually; after all, a chemical reaction usually liberates or absorbs heat. If we can relate mechanical work to heat, and we can relate the amount of heat liberated to the extent of a chemical reaction, then we can imagine allowing the reaction to go to equilibrium in a machine that converts heat to work. We can expect that the amount of work produced will have some relationship to the extent of the reaction. The nature of this relationship is obscure at this point, but we can reasonably expect that one exists.

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