4.6: Applications

The lengthy derivation in Secs. 4.3–4.5 is based on the Kelvin–Planck statement describing the impossibility of converting completely into work the energy transferred into the system by heat from a single heat reservoir. The derivation has now given us all parts of the mathematical statement of the second law shown in the box in Sec. 4.2. The mathematical statement includes an equality, $dS = đq/T_b$, that applies to an infinitesimal *reversible* change, and an inequality, $dS > đq/T_b$, that applies to an infinitesimal *irreversible* change. It is convenient to combine the equality and inequality in a single relation that is a general mathematical statement of the second law:

$$dS \geq \frac{đq}{T_b}$$

$$\left(\begin{smallmatrix} \text{irrev} \\ \text{rev} \end{smallmatrix}, \text{closed system}\right)$$

(4.6.1)

The inequality refers to an irreversible change and the equality to a reversible change, as indicated by the notation $\begin{smallmatrix} \text{irrev} \\ \text{rev} \end{smallmatrix}$ in the conditions of validity. The integrated form of this relation is

$$\Delta S \geq \int \frac{đq}{T_b}$$

$$\left(\begin{smallmatrix} \text{irrev} \\ \text{rev} \end{smallmatrix}, \text{closed system}\right)$$

(4.6.2)

During a reversible process, the states are equilibrium states and the temperature is usually uniform throughout the system. The only exception is if the system happens to have internal adiabatic partitions that allow phases of different temperatures in an equilibrium state. When the process is reversible and the temperature is uniform, we can replace $dS = đq/T_b$ by $dS = đq/T$.

The rest of Sec. 4.6 will apply Eqs. 4.6.1 and 4.6.2 to various reversible and irreversible processes.

4.6.1 Reversible heating

The definition of the heat capacity C of a closed system is given by Eq. 3.1.9: $C \overset{\text{def}}{=} đq/dT$. For reversible heating or cooling of a homogeneous phase, $đq$ is equal to $T\,dS$ and we can write

$$\Delta S = \int_{T_1}^{T_2} \frac{C}{T}\,dT$$

(4.6.3)

where C should be replaced by C_V if the volume is constant, or by C_p if the pressure is constant (Sec. 3.1.5). If the heat capacity has a constant value over the temperature range from T_1 to T_2, the equation becomes

$$\Delta S = C \ln \frac{T_2}{T_1}$$

(4.6.4)

Heating increases the entropy, and cooling decreases it.

4.6.2 Reversible expansion of an ideal gas

When the volume of an ideal gas, or of any other fluid, is changed reversibly and *adiabatically*, there is of course no entropy change.

When the volume of an ideal gas is changed reversibly and *isothermally*, there is expansion work given by $w = -nRT \ln(V_2/V_1)$ (Eq. 3.5.1). Since the internal energy of an ideal gas is constant at constant temperature, there must be heat of equal magnitude and opposite sign: $q = nRT \ln(V_2/V_1)$. The entropy change is therefore

$$\Delta S = nR \ln \frac{V_2}{V_1}$$

(4.6.5)

(reversible isothermal volume
change of an ideal gas)

Isothermal expansion increases the entropy, and isothermal compression decreases it.

Since the change of a state function depends only on the initial and final states, Eq. 4.6.5 gives a valid expression for ΔS of an ideal gas under the less stringent condition $T_2 = T_1$; it is not necessary for the intermediate states to be equilibrium states of the same temperature.

4.6.3 Spontaneous changes in an isolated system

An isolated system is one that exchanges no matter or energy with its surroundings. Any change of state of an isolated system that actually occurs is spontaneous, and arises solely from conditions within the system, uninfluenced by changes in the surroundings—the process occurs by itself, of its own accord. The initial state and the intermediate states of the process must be nonequilibrium states, because by definition an equilibrium state would not change over time in the isolated system.

Unless the spontaneous change is purely mechanical, it is irreversible. According to the second law, during an infinitesimal change that is irreversible and adiabatic, the entropy increases. For the isolated system, we can therefore write

$$\mathrm{d}S > 0 \tag{4.6.6}$$
$$\text{(irreversible change, isolated system)}$$

In later chapters, the inequality of Eq. 4.6.6 will turn out to be one of the most useful for deriving conditions for spontaneity and equilibrium in chemical systems: *The entropy of an isolated system continuously increases during a spontaneous, irreversible process until it reaches a maximum value at equilibrium.*

If we treat the universe as an isolated system (although cosmology provides no assurance that this is a valid concept), we can say that as spontaneous changes occur in the universe, its entropy continuously increases. Clausius summarized the first and second laws in a famous statement: *Die Energie der Welt ist constant; die Entropie der Welt strebt einem Maximum zu* (the energy of the universe is constant; the entropy of the universe strives toward a maximum).

4.6.4 Internal heat flow in an isolated system

Suppose the system is a solid body whose temperature initially is nonuniform. Provided there are no internal adiabatic partitions, the initial state is a nonequilibrium state lacking internal thermal equilibrium. If the system is surrounded by thermal insulation, and volume changes are negligible, this is an isolated system. There will be a spontaneous, irreversible internal redistribution of thermal energy that eventually brings the system to a final equilibrium state of uniform temperature.

In order to be able to specify internal temperatures at any instant, we treat the system as an assembly of phases, each having a uniform temperature that can vary with time. To describe a region that has a continuous temperature gradient, we approximate the region with a very large number of very small phases or parcels, each having a temperature infinitesimally different from its neighbors.

We use Greek letters to label the phases. The temperature of phase α at any given instant is T^α. We can treat each phase as a subsystem with a boundary across which there can be energy transfer in the form of heat. Let $đq_{\alpha\beta}$ represent an infinitesimal quantity of heat transferred during an infinitesimal interval of time to phase α from phase β. The heat transfer, if any, is to the cooler from the warmer phase. If phases α and β are in thermal contact and T^α is less than T^β, then $đq_{\alpha\beta}$ is positive; if the phases are in thermal contact and T^α is greater than T^β, $đq_{\alpha\beta}$ is negative; and if neither of these conditions is satisfied, $đq_{\alpha\beta}$ is zero.

To evaluate the entropy change, we need a reversible path from the initial to the final state. The net quantity of heat transferred to phase α during an infinitesimal time interval is $đq^\alpha = \sum_{\beta \neq \alpha} đq_{\alpha\beta}$. The entropy change of phase α is the same as it would be for the reversible transfer of this heat from a heat reservoir of temperature T^α: $\mathrm{d}S^\alpha = đq^\alpha / T^\alpha$. The entropy change of the entire system along the reversible path is found by summing over all phases:

$$\mathrm{d}S = \sum_\alpha \mathrm{d}S^\alpha = \sum_\alpha \frac{đq^\alpha}{T^\alpha} = \sum_\alpha \sum_{\beta \neq \alpha} \frac{đq_{\alpha\beta}}{T^\alpha} = \sum_\alpha \sum_{\beta > \alpha} \left(\frac{đq_{\alpha\beta}}{T^\alpha} + \frac{đq_{\beta\alpha}}{T^\beta} \right) \tag{4.6.7}$$

There is also the condition of quantitative energy transfer, $đq_{\beta\alpha} = -đq_{\alpha\beta}$, which we use to rewrite Eq. 4.6.7 in the form

$$\mathrm{d}S = \sum_\alpha \sum_{\beta > \alpha} \left(\frac{1}{T^\alpha} - \frac{1}{T^\beta} \right) đq_{\alpha\beta} \tag{4.6.8}$$

Consider an individual term of the sum on the right side of Eq. 4.6.8 that has a nonzero value of $đq_{\alpha\beta}$ due to finite heat transfer between phases α and β. If T^α is less than T^β, then both $đq_{\alpha\beta}$ and $(1/T^\alpha - 1/T^\beta)$ are positive. If, on the other hand, T^α is greater than T^β, both $đq_{\alpha\beta}$ and $(1/T^\alpha - 1/T^\beta)$ are negative. Thus each term of the sum is either zero or positive, and as long as phases of different temperature are present, $\mathrm{d}S$ is positive.

This derivation shows that during a spontaneous thermal equilibration process in an isolated system, starting with any initial distribution of the internal temperatures, the entropy continuously increases until the system reaches a state of thermal equilibrium

with a single uniform temperature throughout. The result agrees with Eq. 4.6.6. Harvey S. Leff (*Am. J. Phys.*, **45**, 252–254, 1977) obtains the same result by a more complicated derivation.

4.6.5 Free expansion of a gas

Consider the free expansion of a gas shown in Fig. 3.8. The *system* is the gas. Assume that the vessel walls are rigid and adiabatic, so that the system is isolated. When the stopcock between the two vessels is opened, the gas expands irreversibly into the vacuum without heat or work and at constant internal energy. To carry out the same change of state reversibly, we confine the gas at its initial volume and temperature in a cylinder-and-piston device and use the piston to expand the gas adiabatically with negative work. Positive heat is then needed to return the internal energy reversibly to its initial value. Because the reversible path has positive heat, the entropy change is positive.

This is an example of an irreversible process in an isolated system for which a reversible path between the initial and final states has both heat and work.

4.6.6 Adiabatic process with work

In general (Sec. 3.10), an adiabatic process with a given initial equilibrium state and a given change of a work coordinate has the least positive or most negative work in the reversible limit. Consider an irreversible adiabatic process with work w_{irr}. The same change of state can be accomplished reversibly by the following two steps: (1) a reversible adiabatic change of the work coordinate with work w_{rev}, followed by (2) reversible transfer of heat q_{rev} with no further change of the work coordinate. Since w_{rev} is algebraically less than w_{irr}, q_{rev} must be positive in order to make ΔU the same in the irreversible and reversible paths. The positive heat increases the entropy along the reversible path, and consequently the irreversible adiabatic process has a positive entropy change. This conclusion agrees with the second-law inequality of Eq. 4.6.1.