6.3: Cryogenics

The field of cryogenics involves the production of very low temperatures, and the study of the behavior of matter at these temperatures. These low temperatures are needed to evaluate third-law entropies using calorimetric measurements. There are some additional interesting thermodynamic applications.

6.3.1 Joule–Thomson expansion

A gas can be cooled by expanding it adiabatically with a piston (Sec. 3.5.3), and a liquid can be cooled by pumping on its vapor to cause evaporation (vaporization). An evaporation procedure with a refrigerant fluid is what produces the cooling in an ordinary kitchen refrigerator.

For further cooling of a fluid, a common procedure is to use a continuous **throttling process** in which the fluid is forced to flow through a porous plug, valve, or other constriction that causes an abrupt drop in pressure. A slow continuous adiabatic throttling of a gas is called the **Joule–Thomson experiment**, or Joule–Kelvin experiment, after the two scientists who collaborated between 1852 and 1862 to design and analyze this procedure. (William Thomson later became Lord Kelvin.)

Figure 6.3 illustrates the principle of the technique. The solid curve shows the temperature dependence of the entropy of a paramagnetic solid in the absence of an applied magnetic field, and the dashed curve is for the solid in a constant, finite magnetic field. The temperature range shown is from $0\,\mathrm{K}$ to approximately $1\,\mathrm{K}$. At $0\,\mathrm{K}$, the magnetic dipoles are perfectly ordered. The increase of S shown by the solid curve between $0\,\mathrm{K}$ and $1\,\mathrm{K}$ is due almost entirely to increasing disorder in the orientations of the magnetic dipoles as heat enters the system.

Path A represents the process that occurs when the paramagnetic solid, surrounded by gaseous helium in thermal contact with liquid helium that has been cooled to about $1\,\mathrm{K}$, is slowly moved into a strong magnetic field. The process is *isothermal magnetization*, which partially orients the magnetic dipoles and reduces the entropy. During this process there is heat transfer to the liquid helium, which partially boils away. In path B, the thermal contact between the solid and the liquid helium has been broken by pumping away the gas surrounding the solid, and the sample is slowly moved away from the magnetic field. This step is a reversible adiabatic demagnetization. Because the process is reversible and adiabatic, the entropy change is zero, which brings the state of the solid to a lower temperature as shown.

The sign of $(\partial T/\partial B)_{S,p}$ is of interest because it tells us the sign of the temperature change during a reversible adiabatic demagnetization (path B of Fig. 6.3). To change the independent variables in Eq. 6.3.4 to S, p, and B, we define the Legendre transform

$$H' \stackrel{\text{def}}{=} U + pV - Bm_{\text{mag}} \tag{6.3.5}$$

(H' is sometimes called the *magnetic enthalpy*.) From Eqs. 6.3.4 and 6.3.5 we obtain the total differential

$$\mathrm{d}H' = T\,\mathrm{d}S + V\,\mathrm{d}p - m_{\text{mag}}\,\mathrm{d}B \tag{6.3.6}$$

From it we find the reciprocity relation

$$\left(\frac{\partial T}{\partial B}\right)_{S,p} = -\left(\frac{\partial m_{\text{mag}}}{\partial S}\right)_{p,B} \tag{6.3.7}$$

According to Curie's law of magnetization, the magnetic dipole moment m_{mag} of a paramagnetic phase at constant magnetic flux density B is proportional to $1/T$. This law applies when B is small, but even if B is not small m_{mag} decreases with increasing T. To increase the temperature of a phase at constant B, we allow heat to enter the system, and S then increases. Thus, $(\partial m_{\text{mag}}/\partial S)_{p,B}$ is negative and, according to Eq. 6.3.7, $(\partial T/\partial B)_{S,p}$ must be positive. Adiabatic demagnetization is a constant-entropy process in which B decreases, and therefore the temperature also *decreases*.

We can find the sign of the entropy change during the isothermal magnetization process shown as path A in Fig. 6.3. In order to use T, p, and B as the independent variables, we define the Legendre transform $G' \stackrel{\text{def}}{=} H' - TS$. Its total differential is

$$\mathrm{d}G' = -S\,\mathrm{d}T + V\,\mathrm{d}p - m_{\text{mag}}\,\mathrm{d}B \tag{6.3.8}$$

From this total differential, we obtain the reciprocity relation

$$\left(\frac{\partial S}{\partial B}\right)_{T,p} = \left(\frac{\partial m_{\text{mag}}}{\partial T}\right)_{p,B} \tag{6.3.9}$$

Since m_{mag} at constant B decreases with increasing T, as explained above, we see that the entropy change during isothermal magnetization is *negative*.

By repeatedly carrying out a procedure of isothermal magnetization and adiabatic demagnetization, starting each stage at the temperature produced by the previous stage, it has been possible to attain a temperature as low as $0.0015\,\text{K}$ The temperature can be reduced still further, down to 16 microkelvins, by using adiabatic nuclear demagnetization. However, as is evident from the figure, if in accordance with the third law both of the entropy curves come together at the absolute zero of the kelvin scale, then it is not possible to attain a temperature of zero kelvins in a finite number of stages of adiabatic demagnetization. This conclusion is called the *principle of the unattainability of absolute zero*.