The four boxed equations will enable us to find all the desirable information about our magnetic-ion subsystem, once we have our partition function expressed as a function of $T$ and $\mathcal{H}$. Since $\epsilon_i = \delta_i - g_i \mu_B H_0 \mathcal{H} m_i$,  

$$Z = \sum g_i e^{-\delta_i + g_i \mu_B H_0 \mathcal{H} m_i / kT} = \sum g_i e^{-\delta_i/kT} \sum e^{g_i \mu_B H_0 \mathcal{H} m_i / kT},$$

or

$$Z = Z_{\text{int}} Z_{\mathcal{H}/T}. \quad (18-9)$$

We have simplified matters by assuming that the crystal field splitting gives rise to only two states: one of energy zero and degeneracy $g_0$, and the other of energy $\delta_1$ and degeneracy $g_1$. Then,

$$Z_{\text{int}} = g_0 + g_1 e^{-\delta_1/kT}, \quad (18-10)$$

which is a function of $T$ only.

In the next section, we shall evaluate $Z_{\mathcal{H}/T}$, which will be found to be a function of $\mathcal{H}/T$.

### 18.3 Magnetic Moment of a Magnetic-Ion Subsystem

The magnetic part of the partition function of a magnetic-ion subsystem is given by

$$Z_{\mathcal{H}/T} = \sum m_i e^{g_i \mu_B H_0 \mathcal{H} m_i / kT}. \quad (18-11)$$

If we let

$$a = g_i \mu_B H_0 \mathcal{H} / kT, \quad (18-12)$$

then, since $m_i$ can take on the values $-J, -J+1, \ldots, J-1, J$, we find

$$Z_{\mathcal{H}/T} = \sum_{m_i = -J}^{m_i = J} e^{am_i} = e^{-aJ} + e^{-a(J-1)} + \cdots + e^{aJ}.$$

This is a finite geometric progression with a ratio $e^a$; hence,

$$Z_{\mathcal{H}/T} = \frac{e^{-aJ} - e^{a(J+1)}}{1 - e^a}.$$

Multiplying numerator and denominator by $e^{-a/2}$, we get

$$Z_{\mathcal{H}/T} = \frac{e^{-a(J+1/2)} - e^{a(J+1/2)}}{e^{-a/2} - e^{a/2}},$$

or

$$Z_{\mathcal{H}/T} = \frac{\sinh (J + 1/2)a}{\sinh 1/2a}. \quad (18-13)$$
Therefore,
\[ \ln Z = \ln \sinh (J + \frac{1}{2})a - \ln \sinh \frac{a}{2} + \ln (g_0 + g_1 e^{-\beta_i/kT}). \] (18-14)

Since \( a = g_0 g_1 \mu_0 \mathcal{H}/kT \), \( \ln Z \) is seen to be a function of \( \mathcal{H} \) and \( T \).

We are now in a position to evaluate \( M \) with the aid of Eq. (18-6).

\[
M = \frac{NkT}{\mu_0} \left( \frac{\partial \ln Z}{\partial \mathcal{H}} \right)_T = \frac{NkT}{\mu_0} \left( \frac{\partial \ln Z}{\partial \mathcal{H}} \right)_T
= \frac{NkT}{\mu_0} \left\{ \frac{d \ln Z}{da} \right\}_T = \frac{NkT}{\mu_0} \left( \frac{g_0 g_1 \mu_0}{kT} \frac{d \ln Z}{da} \right)
= N g_0 g_1 \frac{d}{da} \left[ \ln \sinh (J + \frac{1}{2})a - \ln \sinh \frac{1}{2}a \right]
= N g_0 g_1 \left[ (J + \frac{1}{2}) \cosh (J + \frac{1}{2})a - \frac{1}{2} \cosh \frac{1}{2}a \right] \sinh (J + \frac{1}{2})a - \frac{1}{2} \sinh \frac{1}{2}a \right].
\] (18-15)

Finally,
\[
M = N g_0 g_1 \left[ \frac{1}{J} \left[ (J + \frac{1}{2}) \cosh (J + \frac{1}{2})a - \frac{1}{2} \cosh \frac{1}{2}a \right] \right].
\] (18-16)

The quantity in curved brackets is called the Brillouin function \( B_J(a) \), named after L. Brillouin, who first extended the classical theory of paramagnetism (due to Langevin) to include quantum ideas. Therefore,

\[ M = N g_0 g_1 J B_J(a), \] (18-16)

where
\[ B_J(a) = \frac{1}{J} \left[ (J + \frac{1}{2}) \cosh (J + \frac{1}{2})a - \frac{1}{2} \cosh \frac{1}{2}a \right]. \] (18-17)

Before we consider the consequences of Brillouin's equation for \( M \), let us examine the mathematical features of the Brillouin function, which is plotted in Fig. 18-2 for a number of values of \( J \). By definition,

\[ \coth x = \frac{\cosh x}{\sinh x} = \frac{e^x + e^{-x}}{e^x - e^{-x}}, \]

and for \( x \gg 1 \), \( e^x \gg e^{-x} \), so that \( \coth x = 1 \). Therefore, for large values of \( a \),

\[ B_J(a) = \frac{1}{J} \left[ (J + \frac{1}{2}) - \frac{1}{2} \right] = 1 \quad \text{(for } a \gg 1). \]
Since $a = g \mu_B H_0 / kT$, large values of $a$ are achieved when

$$\frac{g \mu_B H_0 \mathcal{K}}{kT} \gg 1,$$

or

$$\frac{\mathcal{K}}{k} \gg \frac{1.38 \times 10^{-23} \text{ J/K}}{2 \times 9.27 \times 10^{-24} \text{ J/T} \times 4\pi \times 10^{-7} \text{ H/m}},$$

or

$$\frac{\mathcal{K}}{T} \gg 6 \times 10^5 \text{ A/m}.$$

Since $M = N\mu_0 g \beta JB_s(\alpha)$, it follows that at values of $\mathcal{K}/T$ greatly in excess of $6 \times 10^5 \text{ A/m/K}$, the magnetization $M$ has its saturation value $M_{sat}$ where
$M_{\text{sat}} = N g \mu_B J$, and the magnetization per magnetic ion expressed in terms of Bohr magnetons, $M_{\text{sat}}/N \mu_B$, becomes

$$\frac{M_{\text{sat}}}{N \mu_B} = gJ \quad \text{(for } \mathcal{H}/T \gg 6 \times 10^5 \text{ A/m/K).}$$

This conclusion was tested by W. E. Henry with the first three salts listed in Table 18-1. The experimental results, plotted in Fig. 18-3, agree very well with the Brillouin equation and with the limiting value of $M/N \mu_B$.

![Figure 18-3](image-url)

Figure 18-3 The magnetization divided by the number of Bohr magnetons plotted against $\mathcal{H}/T$ for (I) chromium potassium alum ($J = \frac{3}{2}$); (II) iron ammonium alum ($J = \frac{1}{2}$); and (III) gadolinium sulfate ($J = \frac{3}{2}$). (The points are experimental results of W. E. Henry (1952), and the solid curves are graphs of the Brillouin equation.)
When \( x \ll 1 \), it is easy to show that

\[
\coth x = \frac{1}{x} + \frac{x}{3}.
\]

Therefore, for small values of \( a \),

\[
B_J(a) = \frac{1}{J} \left( \frac{1}{2} \frac{1}{(J + \frac{1}{2})} + \frac{1}{2} \frac{1}{a} + \frac{1}{2} \frac{1}{a + 6} \right)
= \frac{1}{J} \left( \frac{3}{2} \frac{a}{(J + \frac{1}{2})^2} - \frac{a}{12} \right)
= \frac{a}{3J} \left( J^2 + J + \frac{1}{4} - \frac{1}{4} \right),
\]

and finally,

\[
B_J(a) = \frac{J + 1}{3} a \quad \text{(for} \ a \ll 1 \).
\]

Small values of \( a \) are achieved when

\[
\frac{\mathcal{K}}{T} \ll 6 \times 10^5 \text{ A/m/K}.
\]

When this is the case,

\[
M = Ng \mu_0 g \frac{J + 1}{3} a = \frac{Ng^2 \mu_0 \mu_s (J + 1) \mathcal{K}}{3kT},
\]

or

\[
M = \frac{Ng^2 \mu_0 \mu_s (J + 1) \mathcal{K}}{3kT} \left( \text{for} \ \frac{\mathcal{K}}{T} \ll 6 \times 10^5 \text{ A/m/K} \right) \tag{18-18}
\]

This is Curie's equation first mentioned in Art. 2-12, and the Curie constant \( C^c \) is seen to be

\[
C^c = \frac{Ng^2 \mu_0 \mu_s (J + 1)}{3k} \tag{18-19}
\]

A mass of crystal containing exactly \( N \) (Avogadro's number) magnetic ions is known as the molar mass \( M \). The molar masses of the four crystals listed in Table 18-1 are given in Table 18-2. The Curie constant per mole is given by

\[
C^c = \frac{6.02 \times 10^{23}}{3 \times 1.38 \times 10^{-23}} \frac{1/\text{mol} \times (9.27)^2 \times 10^{-48} \text{ J}^2/\text{T}^2 \times 4\pi \times 10^{-7} \text{ H/m}}{\text{J/K} g^2 (J + 1)}.
\]

\[
C^c = 1.57 \times 10^{-6} \frac{\text{K}}{\text{mol}} \frac{g^2 (J + 1)}{\text{J}} \tag{18-20}
\]

and provides the calculated values in Table 18-2. The agreement with the measured values is very good.
Table 18-2 Curie constants and heat-capacity constants

<table>
<thead>
<tr>
<th>Paramagnetic salt</th>
<th>$\gamma / \text{kg}$</th>
<th>$J(J + 1)$</th>
<th>$C_v$ (measured) $\times 10^{-3} \text{ m}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$</th>
<th>$C_v^p$ (calculated) $\times 10^{-3} \text{ m}^3 \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$</th>
<th>$\chi / R$ $\text{K}^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cr}_2\text{SO}_4 \cdot \text{K}_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$</td>
<td>0.499</td>
<td>3.75</td>
<td>2.31</td>
<td>2.36</td>
<td>0.018</td>
</tr>
<tr>
<td>$\text{Fe}_2\text{SO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 24\text{H}_2\text{O}$</td>
<td>0.482</td>
<td>8.75</td>
<td>5.52</td>
<td>5.50</td>
<td>0.013</td>
</tr>
<tr>
<td>$\text{Cd}_2\text{SO}_4 \cdot 2\text{H}_2\text{O}$</td>
<td>0.373</td>
<td>15.75</td>
<td>9.80</td>
<td>9.89</td>
<td>0.35</td>
</tr>
<tr>
<td>$2\text{Ce(NO}_3)_3 \cdot 3\text{Mg(NO}_3)_2 \cdot 24\text{H}_2\text{O}$</td>
<td>0.765</td>
<td>~0 (l)</td>
<td>0.398 (l)</td>
<td>6.1 $\times 10^{-6}$</td>
<td></td>
</tr>
</tbody>
</table>

18-4 THERMAL PROPERTIES OF A MAGNETIC-ION SUBSYSTEM

The internal energy of a magnetic-ion subsystem is given by Eq. (18-8), namely,

$$U = NkT^2 \left( \frac{\partial \ln Z}{\partial T} \right)_\chi + \mu_0 \chi M.$$  

We have

$$\left( \frac{\partial \ln Z}{\partial T} \right)_\chi = \frac{d \ln Z}{da} \left( \frac{\partial a}{\partial T} \right)_\chi + \frac{d \ln Z_{\text{int}}}{dT}$$

$$= JB_J(a) \left( - \frac{g_{\mu_B} \mu_0 \chi}{kT^2} \right) + \frac{d}{dT} \left[ \ln \left( \frac{g_0 + g_1 e^{-\delta_1/kT}}{g_0 + g_1 e^{-\delta_1/kT}} \right) \right]$$

$$= - \frac{g_{\mu_B} \mu_0 \chi}{kT^2} JB_J(a) + \frac{(g_1 \delta_1/kT^2) e^{-\delta_1/kT}}{g_0 + g_1 e^{-\delta_1/kT}}.$$

Therefore,

$$U = -Ng_{\mu_B} \mu_0 \chi JB_J(a) + \frac{N \delta_1}{1 + (g_0/g_1)e^{\delta_1/kT}} + \mu_0 \chi M. \quad (18-21)$$

According to Eq. (18-16), the first term on the right is $-\mu_0 \chi M$, which cancels the third term, so that

$$U = \left[ \frac{N \delta_1}{1 + (g_0/g_1)e^{\delta_1/kT}} \right]. \quad (18-22)$$

Since

$$T \, dS = dU - \mu_0 \chi dM,$$

$$T \, \frac{dS}{dT} = \frac{dU}{dT} - \mu_0 \chi \frac{dM}{dT}. \quad (18-23)$$
When $\ln Z$ is introduced into the expression for $S$, the resulting equation looks rather formidable but has simple properties when the temperature range is divided into two parts:

1. $T \gg \delta_1/k$ and $S = S_1(\mathcal{K}/T)$.  
   \hspace{1cm} (18-27)

2. $T \leq \delta_1/k$ and $S = S_2(T, \mathcal{K})$.

If $S$ is plotted as a function of $T$, at various values of $\mathcal{K}$, the resulting curves resemble those of Fig. 18-6. The $ST$ curve for $\mathcal{K} = 0$ is particularly significant. Within the range indicated by vertical dashed lines, $S_{\mathcal{K} = 0}$ is constant because the temperature is too low to provide an appreciable heat capacity of the nonmagnetic particles, but too high to allow crystalline field splitting or ionic magnetic interaction to show an appreciable effect. Since the only term involving the dependence of internal energy on temperature [Eq. (18-22)] is provided by the interaction of the ions with either the crystalline field or with one another, the internal energy is also constant in this temperature region. Finally, since $C_M = T dS/dT = dU/dT$, it follows that $C_M = 0$ in this range.

18-5 PRODUCTION OF MILLIDEGREE TEMPERATURES BY ADIABATIC REDUCTION OF THE MAGNETIC FIELD

Almost every property of matter shows interesting changes or variations in the temperature range below about 20 K. Temperatures down to about 1 K are easily obtained by causing $^4$He to evaporate rapidly. With $^3$He it is possible to reach about 0.3 K. In 1926 it was suggested independently by Giauque and by Debye that much lower temperatures could be achieved with the aid of paramagnetic salts. The principle of the method is presented graphically in Fig. 18-7.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{fig18-7.png}
\caption{Figure 18-7 In the isothermal increase of the magnetic field $k \to i$, the entropy decreases. In the adiabatic decrease of the magnetic field $i \to f$ (to zero field), the temperature decreases.}
\end{figure}
where the entropy of a magnetic-ion subsystem is plotted against the temperature for two values of the external magnetic field, 0 and \( \mathcal{H}_i \). At a temperature in the neighborhood of 1 K, where the lattice heat capacity of the nonmagnetic particles is negligibly small, the salt is magnetized isothermally in the process \( k \to i \). For this process the second \( T \, dS \) equation gives

\[
T \, dS = 0 + \mu_0 T \left( \frac{\partial M}{\partial T} \right)_x \, d\mathcal{H}.
\]

The derivative \( (\partial M/\partial T)_x \) is a measure of the change of alignment of a system of magnets accompanying a rise of temperature (disordering effect) when the external field (ordering effect) is kept constant. The derivative is therefore negative for all substances of the type dealt with in this chapter. Since \( (\partial M/\partial T)_x \) is negative, heat goes out during an isothermal magnetization.

The second step, \( i \to f \), is a reversible adiabatic reduction of \( \mathcal{H} \) in which

\[
0 = C_x \, dT + \mu_0 T \left( \frac{\partial M}{\partial T} \right)_x \, d\mathcal{H}.
\]

Since \( (\partial M/\partial T)_x \) and \( d\mathcal{H} \) are both negative, it follows that \( dT \) is negative. This change in temperature is called the magnetocaloric effect. Experiments of this sort were first performed by Giauque in America and were then taken up by Kurti and Simon in England and by de Haas and Wiersma in Holland. In these experiments a paramagnetic salt is cooled to as low a temperature as possible with the aid of liquid helium. A strong magnetic field is then applied, producing a rise of temperature in the substance and a consequent flow of heat to the surrounding helium, some of which is thereby evaporated. After a while, the substance is both strongly magnetized and as cold as possible. At this moment, the space surrounding the substance is evacuated. The magnetic field is now reduced to zero, and the temperature of the paramagnetic salt drops to a low value.

The paramagnetic salt is either a single crystal, a pressed powder, or a mixture of small crystals in the form of either a sphere, a cylinder, or a spheroid. It is placed in a space that may be connected at one time to a pump or, at another time, to a gas supply. This space is surrounded by liquid helium whose pressure (and therefore temperature) may be controlled. Surrounding the liquid helium is liquid nitrogen, and the intervening space is evacuated. Helium gas is admitted into the space containing the paramagnetic salt before the magnet is switched on. The rise of temperature produced by switching on the magnet causes a flow of heat through this helium gas into the liquid helium. In other words, the helium gas is used as a conductor of heat to enable the paramagnetic salt to come to temperature equilibrium rapidly. It is therefore called the exchange gas. As soon as temperature equilibrium is attained, the exchange gas is pumped out, leaving the paramagnetic salt thermally insulated. In many past experiments, the adiabatic reduction of field was accomplished by swinging the entire cryostat out of the magnetic field produced by a huge electromagnet such
as that depicted in Fig. 18-8. In recent years, solenoids have been made of many thousands of turns of fine superconducting wire, through which from 10 to 100 A may be sent. There is no power dissipation in the coil so long as it is maintained at a temperature below which the wire is superconducting. The conventional experimental apparatus is compared roughly with the more

Figure 18-8 The famous electromagnet of the Laboratoire Aimé Cotton at Bellevue, near Paris, used by Simon and Kurti in some of their pioneer experiments. (Courtesy of N. Kurti.)
modern one in Fig. 18-9. With a superconducting magnet, (1) the sample space may be made larger; (2) the magnetic field may be made stronger; (3) the cost of the magnet may be one-quarter that of a conventional magnet; and (4) the power requirement is negligible.

The next step is to estimate the temperature. For this purpose, separate coils of wire surrounding the paramagnetic salt are used. The paramagnetic susceptibility $M/\chi$, which is a function of the temperature, is measured by means of a special bridge circuit. A new temperature scale is now defined with the aid of Curie's equation. The new temperature $T^*$, called the magnetic temperature, is defined as

$$T^* = \frac{\text{Curie constant}}{\text{susceptibility}} = \frac{C \chi}{M}.$$  

It is seen that, in the region where Curie's law holds, $T^*$ is the real Kelvin temperature, whereas in the region around absolute zero $T^*$ is expected to differ somewhat from the Kelvin temperature.
Table 18-3 Pioner results in the magnetic production of low temperatures

<table>
<thead>
<tr>
<th>Experimenters</th>
<th>Date</th>
<th>Paramagnetic Salt</th>
<th>Initial field, $10^6 \text{ A/m}$</th>
<th>Initial temp., K</th>
<th>Final magnetic temp., $T^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Giauque and MacDougall</td>
<td>1933</td>
<td>Gadolinium sulfate</td>
<td>0.64</td>
<td>1.5</td>
<td>0.25</td>
</tr>
<tr>
<td>De Haas, Wiersma, and Kramer</td>
<td>1933</td>
<td>Cerium fluoride</td>
<td>2.20</td>
<td>1.35</td>
<td>0.13</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dysprosium ethyl sulfate</td>
<td>1.55</td>
<td>1.35</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cerium ethyl sulfate</td>
<td>2.20</td>
<td>1.35</td>
<td>0.085</td>
</tr>
<tr>
<td>De Haas and Wiersma</td>
<td>1934</td>
<td>Chromium potassium alun</td>
<td>1.96</td>
<td>1.16</td>
<td>0.031</td>
</tr>
<tr>
<td></td>
<td>1935</td>
<td>Iron ammonium alun</td>
<td>1.92</td>
<td>1.20</td>
<td>0.018</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Alum mixture</td>
<td>1.92</td>
<td>1.29</td>
<td>0.0044</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cesium titanium alun</td>
<td>1.92</td>
<td>1.31</td>
<td>0.0055</td>
</tr>
<tr>
<td>Kurti and Simon</td>
<td>1935</td>
<td>Gadolinium sulfate</td>
<td>0.43</td>
<td>1.15</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Manganese ammonium sulfate</td>
<td>0.64</td>
<td>1.23</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iron ammonium alun</td>
<td>1.12</td>
<td>1.23</td>
<td>0.038</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iron ammonium alun</td>
<td>0.66</td>
<td>1.23</td>
<td>0.072</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Iron ammonium alun</td>
<td>0.39</td>
<td>1.23</td>
<td>0.114</td>
</tr>
</tbody>
</table>

The early results of the great pioneers in this field are listed in Table 18-3 (compiled by Burton, Grayson-Smith, and Wilhelm).

There is a set of conditions, easily achieved in the laboratory, under which it is possible to calculate the final temperature achieved after an adiabatic demagnetization:

1. The initial temperature is low enough to make the contributions of the non-magnetic particles negligible.
2. The temperature never gets lower than the tail of the Schottky curve where $C_M = A/T^2$.
3. Values of $\chi/T$ are always small enough that Curie's law is obeyed, $M/\chi = C_\chi/T$.
4. The external magnetic field is reduced to a low value at which the magnetization is $M_f$. Both $\chi_f$ and $M_f$ may be made equal to zero.

Under these conditions we may use the first $T dS$ equation as follows:

$$T dS = C_M dT - T \mu_0 \left( \frac{\partial \chi}{\partial T} \right)_M dM.$$  

From Curie's equation, we get

$$\left( \frac{\partial \chi}{\partial T} \right)_M = \frac{M}{C_\chi}.$$
and we also have

\[ C_M = \frac{A}{T^2}. \]

Substituting these values into the first \( T \ dS \) equation and setting \( dS = 0 \) for an adiabatic demagnetization, we get

\[ 0 = \frac{A}{T^2} \ dT - \frac{T}{C_T} \frac{M}{C_T} \ dM, \]

or

\[ A \left( \frac{T_f}{T_i} \right)^{\frac{M_f}{C_T}} \frac{M_f}{C_T} \ dM, \]

where the substance is demagnetized to magnetization \( M_f \). Upon performing the integrations,

\[ \frac{A}{2} \left( \frac{1}{T_f^2} - \frac{1}{T_i^2} \right) = \frac{\mu_0}{2C_T} (M_f^2 - M_i^2), \]

and using Curie's equation,

\[ \frac{1}{T_f^2} - \frac{1}{T_i^2} = \frac{\mu_0 C_T}{A} \left( \frac{\mathcal{K}_i^2}{T_i^2} - \frac{\mathcal{K}_f^2}{T_f^2} \right), \]

or

\[ \frac{T_f}{T_i} = \sqrt{\frac{\mu_0 C_T/A}{\mathcal{K}_i^2} \left( \frac{T_i^2}{T_f^2} \right)^{\frac{1}{\mathcal{K}_f^2}} + 1}. \quad (18-28) \]

When \( \mathcal{K}_f = 0 \),

\[ \left( \frac{T_f}{T_i} \right)^2 = 1 + \frac{\mu_0 C_T}{A} \mathcal{K}_i^2, \quad (18-29) \]

which shows that the lowest temperatures are reached by salts in which \( A \) is small and \( C_T \) is large. From the values of \( A/R \) and \( C_T \) in Table 18-2, it may be seen that cerium magnesium nitrate is the most favorable salt by a factor of over 100. The graph in Fig. 18-10 shows that the conditions under which Eq. (18-29) was derived hold well for CMN down to 0.01 K. The remainder of the graph (down to 0.002 K) is the result of experiments by Daniels and Robinson; Hudson, Kaeser, and Radford; and de Klerk, combined with experiments and theoretical calculations of Frankel, Shirley, and Stone. The entire graph enables CMN to be used as a thermometer down to 0.002 K.

Most experiments on adiabatic field reduction are performed in order to achieve the lowest possible temperature, in which case the field reduction proceeds until \( \mathcal{K}_f = 0 \). If, instead of reducing to zero field, we stay within the region of field and temperature designated by the space between the vertical dashed lines of Fig. 18-6 (e.g., \( \mathcal{K}_3 \rightarrow \mathcal{K}_2 \), or \( \mathcal{K}_3 \rightarrow \mathcal{K}_1 \)), then curious results are obtained. First of all, the entropy is expressed as a function of \( \mathcal{K}/T \) only, therefore, during an isentropic reduction of \( \mathcal{K} \) (not to zero), since \( S \) is constant, the ratio \( \mathcal{K}/T \) must remain constant. That this is true under the conditions specified is demonstrated
Upon performing

\[ \varepsilon = \frac{1}{T_0} \cdot \frac{dE}{dS} \]

(18-28)

\[ \frac{M}{T} = 10^{-6} \text{ A/m/K} \]

(18-29)

... results in which \( A \) is in the order of the graph in Fig. 18-2, it may be multiplied by a factor of over

... which Eq. (18-29) should be in the order of the graph

... and Robinson; and from experiments and

... figure graph enables

... determined in order to

... field reduction

... stay within the

... between the vertical lines, various results are

... therefore, during an

... ratio \( \varepsilon/T \) must

... is demonstrated

by the experimental results of Hill and Milner, shown in Fig. 18-11. Second, if

... is constant, since \( M \) is a function of \( \varepsilon/T \) only, \( M \) is constant! If, therefore,

... the magnetization does not change, the term adiabatic “demagnetization” is a

... misnomer. As a result, the word “degaussing” has been suggested. Because the

... gauss is a cgs unit, we shall refer to the misnamed process of adiabatic “demagnetization” as the adiabatic reduction of the magnetic field in this book. If \( M \) does
not change (and this has been experimentally verified by de Haas, Wiersma, and Casimir, 1936 and 1940), then the work $\mu_0 \int \mathcal{H} \, dM$ is zero. But in an adiabatic process, the work done is equal to the change of internal energy, so that $\Delta U$ is zero. Since the heat capacity at constant magnetization $C_M$ is equal to $(\partial U/\partial T)_M$, then $C_M$ is zero. If the first $T \, dS$ equation is applied to this process,

$$T \, dS = C_M \, dT - T \mu_0 \left( \frac{\partial \mathcal{H}}{\partial T} \right)_M \, dM,$$

we have $dS$, $C_M$, and $dM$ all equal to zero. Of course, it must be understood that these results apply only when temperatures are not too low and the field is not reduced to zero. These conditions will be found to be important in certain experiments on nuclear magnetic subsystems.

Let $\epsilon_i$ be the energy of an ion with total quantum number $m_i$ in a field $\mathcal{H}$. When the field changes a small amount $d \mathcal{H}$, the energy change $d\epsilon_i$ is

$$d\epsilon_i = -g\mu_i \mu_0 m_i \, d\mathcal{H};$$

and if $N_i$ is the population of the $m_i$th state,

$$\sum N_i \, d\epsilon_i = -\left( \sum N_i g\mu_i m_i \right) \mu_0 \, d\mathcal{H},$$

or

$$\sum N_i \, d\epsilon_i = -M \mu_0 \, d\mathcal{H}. \quad \text{(18-30)}$$
Now $\sum N_i \epsilon_i$ is the total energy of the ions, that is, the sum of the internal energy $U$ and the magnetic potential energy $-\mu_0 H M$. Thus,

$$\sum N_i \epsilon_i = U - \mu_0 H M,$$

and

$$\sum \epsilon_i dN_i + \sum N_i d\epsilon_i = dU - \mu_0 H dM - M \mu_0 dH.$$

Since $\sum N_i d\epsilon_i = -M \mu_0 dH$, this reduces to

$$\sum \epsilon_i dN_i = dU - \mu_0 H dM,$$

or

$$\sum \epsilon_i dN_i = T dS. \quad (18-31)$$

It follows that an isothermal decrease of entropy, which takes place in the first step of any experiment for producing low temperatures, must involve changes in $N_i$, that is, population changes. During the second step, however, in which an adiabatic magnetic field reduction takes place, $dS$ is zero, and therefore the $dN_i$'s are zero—that is, the populations remain unchanged.

In Fig. 18-12k, the magnetic-ion subsystem is in zero field, and therefore the magnetic energy states are extremely close together, with some of the degeneracy being removed by internal electric and magnetic effects. Since the states are so close together, they are equally populated. From $k \rightarrow i$ the populations change so that the low-energy states become highly populated, as shown in Fig. 18-12f. In the last step, $i \rightarrow f$, the populations remain constant in order to keep the entropy constant.

![Figure 18-12](image-url)

Figure 18-12 Changes in energy states and ionic populations during isothermal magnetic field production $k \rightarrow i$ and adiabatic magnetic field reduction $i \rightarrow f$. 
19-2 PRODUCTION OF NANODEGREE TEMPERATURES BY NUCLEAR MAGNETIC FIELD REDUCTION

Since nuclear magnets are only about one one-thousandth as strong as ionic magnets, their polarization requires temperatures around 0.01 K and fields from $4 \times 10^6$ to $8 \times 10^6$ A/m. We have seen how local fields of this magnitude may be provided by the uncompensated spins of the electrons circulating outside each nucleus itself. If these polarized nuclei could then be made to undergo a reversible adiabatic field reduction, they would cool off to a temperature in the neighborhood of $10^{-3}$ K. Since these nuclei occupy a thin layer on a large crystal at 0.01 K, however, any loss of polarization would be much more isothermal than adiabatic. You cannot expect a few nuclei to cool off a big crystal.

One method that has been used so far to achieve temperatures below $10^{-3}$ K involves a double process, consisting of an ionic field reduction followed by a nuclear field reduction. Two separate magnetic fields supplied by two separate magnets are used, as shown schematically in Fig. 19-3, a diagram prepared by Kurti of Oxford, in whose laboratory such experiments have been carried out. In each of the four parts of this figure, the electronic stage represents a mass of chromium potassium alum in which are embedded 1500 enameled copper wires, each with a diameter of 0.0003 in. The copper wires continue for a distance of about 8 in. and are then bent over and bound together to form the nuclear stage itself. The first part of the cooling is done with the aid of chromium

![Diagram](image)

Figure 19-3 The four steps in nuclear cooling. (N. Kurti.)
ions, and the second part by copper nuclei. The fine, insulated copper wires serve three purposes:

1. Provide a heat-conducting medium between the nuclear and the electronic stages.
2. Minimize eddy currents induced by reduction of the magnetic field.
3. Produce a low temperature by nuclear reduction of the magnetic field.

The four steps in Fig. 19-3 are as follows:

(a) Isothermal magnetization of the electronic stage.
(b) Adiabatic field reduction of the electronic stage and cooling of nuclear stage to $10^{-2}$ K.
(c) Isothermal magnetization of the nuclear stage.
(d) Adiabatic field reduction of the nuclear stage, with an accompanying temperature drop to about $10^{-5}$ K.

The experiment is not as simple as it sounds. To quote Kurti, "The stringency of the conditions to be satisfied can be illustrated by remarking that even

![Diagram of Cryostat for Nuclear Cooling](image-url)

Figure 19-4 Cryostat for nuclear cooling (symbolic).
Figure 19-5 Schematic diagram of cascade nuclear refrigerator. (O. V. Lounasmaa)

A minute amount of heating such as results from a small pin dropping through a height of one-eighth of an inch would warm a bulky specimen of several ounces from one-millionth of a degree to the starting temperature of one one-hundredth of a degree and thereby spoil the experiment.” Even the eddy currents induced in the copper wires by virtue of slight variations of current (ripples) in the magnet coils must be prevented with the aid of the metal ripple shield shown in Fig. 19-4. The magnetic fields were supplied by solenoids in which currents of thousands of amperes were maintained.

One of the biggest experimental difficulties to overcome is the heat transfer between the nuclear and electronic stages. During the isothermal increase of $H$
of the nuclear stage, this transfer must be good. During the following reduction of field, it must be poor. In the experiments of Kurti's group, the fine copper wires represent a compromise that served both purposes only moderately well. Another difficulty is to separate the electronic from the nuclear stage by a distance great enough to confine each magnetic field to its own paramagnetic particles. Both of these problems can be partially solved by a clever method conceived by Blaise. Suppose the nuclear stage constitutes a core completely surrounded by a crystal (or a group of crystals identically oriented) of cerium magnesium nitrate with its strong magnetic axis pointing toward, let us say, the $x$ axis. Suppose that we perform the following operations:

1. Magnetize isothermally at 1 K in the $x$ direction.
2. Insulate thermally.
3. Rotate the field to the $y$ direction. Since CMN is practically nonmagnetic in this direction, it therefore undergoes an adiabatic decrease of the magnetic field and its temperature drops, even though the field is still there.
4. Wait until the cold CMN has cooled the nuclear core, and then reduce the magnetic field to zero, thereby cooling the core by its own adiabatic decrease of the magnetic field.

To achieve even lower temperatures, two or more nuclear cooling stages must be operated in series. Ehnholm, Ekström, Jacquinot, Loponen, Lounasmaa, and Soini at the Helsinki University of Technology built a cryostat with two nuclear cooling stages attached to the mixing chamber of a $^3$He/$^4$He dilution refrigerator as shown in Fig. 19-5. In their study of the magnetic properties of copper nuclei, they achieved a temperature of 50 nanokelvin.

*The lowest temperature ever achieved anywhere (1979) is $5 \times 10^{-8}$ K!*

### 19-3 NEGATIVE KELVIN TEMPERATURES

Let us recall the original definition of the Kelvin scale of temperature: Two Kelvin temperatures are to each other as the heats transferred during isothermal processes at these temperatures, provided that these isothermal processes terminate on the same adiabatic surfaces. If $Q$ and $Q_s$ are the absolute values of the heats transferred at temperatures $T$ and $T_s$, respectively, the original Kelvin definition provides the relation

$$ T = T_s \frac{Q}{Q_s}. $$

If $T_s$ refers to an arbitrary standard, the choice of a number for $T_s$ is also arbitrary. If it is chosen to be negative, then all temperatures would be expressed by negative numbers. Whether $T_s$ is chosen positive or negative, as $Q$ is made smaller and smaller in any unordered way, the limiting value of $Q$ is zero (i.e.,
the least amount of heat that can be transferred is no heat at all), and therefore 
the lowest value of $T$ is zero. In other words, the lowest temperature is absolute 
zero, and if negative temperatures have any meaning at all, they cannot mean 
temperatures colder than absolute zero! But what is meant when the Kelvin scale 
is defined in the usual way with $T_0 = +273.16$ K?

A clue as to the meaning of negative Kelvin temperatures is provided by the 
expression for temperature used in statistical thermodynamics,

$$
T = \left( \frac{\partial U}{\partial S} \right)_V.
$$

The most familiar thermodynamic systems, such as a mole of ideal gas or a mole 
of crystal, have an infinite number of energy levels. As the temperature is raised, 
more and more atoms are raised to higher levels. This requires more and more 
energy, and results in greater and greater disorder as the atoms are distributed 
over more and more states. As the energy goes up (positive $dU$), the entropy also 
goes up (positive $dS$); hence the ratio $dU/dS$ is positive. For $T$ to be negative, an 
increase of energy would have to be accompanied by a decrease of entropy! This 
obviously cannot take place when a system has an infinite number of energy 
levels.

Another way of looking at the matter is with the aid of the Boltzmann 
equation,

$$
\frac{N_2}{N_1} = e^{-\frac{(e_2 - e_1)}{kT}}.
$$

If the system has an infinite number of energy levels, an increase of temperature 
produces increased populations of higher and higher energy levels, but no energy 
level ever gets populated more than the one below it, so that the ratio $N_2/N_1$ is 
always less than 1 and $T$ is positive. At $T = \infty$, $N_2$ would be equal to $N_1$, but 
this would require an infinite amount of energy because of the infinite number of 
energy levels! Evidently, for $T$ to be negative, $N_2$ would have to be larger than 
$N_1$; that is, the upper energy levels would have to be populated more than the 
lower ones. This would require even more than infinite energy—which is even 
more than nonsensical. We conclude, therefore, that in the case of an ordinary 
system which has an infinite number of energy levels, negative temperatures are an 
absurdity.

But what about a system which has only a finite number of energy levels? 
Suppose, for the sake of argument, that a system were capable of existing in only 
two energy levels. Let the system consist of $N$ particles and the levels have 
energies $0$ and $\epsilon$, where $\epsilon$ is an atomic constant, independent of any external field. 
The curve showing the relation between entropy $S$ and internal energy $U$ is 
shown in Fig. 19-6. At zero energy, all $N$ atoms are in the lower energy level, 
which is a state of minimum disorder, or zero entropy. When the two energy 
levels are equally populated, the internal energy of the system is $N\epsilon/2$ and there
is maximum disorder and, hence, maximum entropy. If and when all \( N \) atoms are in the upper energy level, \( U = N\epsilon \), and again we have minimum disorder, or zero entropy. The left half of the curve has a positive slope, and therefore \( \partial U/\partial S \) is positive. The right half, with negative slope, is the region of negative temperatures.

To achieve negative Kelvin temperatures, we must find a system with a finite number of energy levels and, somehow or other, succeed in producing a population inversion—that is, an equilibrium (or near-equilibrium) state in which there are more particles in upper states than in lower ones.

To reduce the temperature of a substance far below 1 K, the magnetic and thermal properties of a magnetic subsystem (ionic or nuclear) were used. The purpose of such experiments was to cool the entire substance, not just the subsystem. To accomplish this, it was necessary to satisfy the following conditions:

1. The magnetic ions must interact among themselves with sufficient strength and speed that (like the molecules of a gas) statistical equilibrium can be assumed and a definite temperature can be attributed to the ionic subsystem.
2. The nonmagnetic particles (called, for simplicity, the lattice) must have practically no heat capacity in the low-temperature region under consideration.
3. Equilibrium between the magnetic-ion subsystem and the lattice must be attained fairly rapidly.

To achieve negative temperatures, we must make use of the magnetic and thermal properties of a nuclear magnetic subsystem under the following condi-
the entropy change is \(-Q/50\); whereas the entropy change of the colder reservoir is \(Q/100\). The total entropy change is

\[
\frac{-Q}{-50} + \frac{Q}{-100} = \frac{Q}{100},
\]

which is positive, just as it is with positive temperatures.

In Fig. 19-10b is shown an attempt to imitate the way a heat engine behaves, but at negative temperatures. Since, by definition of the Kelvin scale,

\[
\frac{Q_H}{Q_c} = \frac{T_H}{T_c} = \frac{-50}{-100} = \frac{1}{2},
\]

when \(Q_H\) units of heat leave the hotter reservoir, twice as much heat must enter the colder one. Therefore, instead of work \(W\) being done by the engine, work would have to be done on the engine in order not to violate the principle of the conservation of energy. But the device depicted in Fig. 19-10b is an expensive gadget for doing a job that requires no device at all. If all you want is to push heat into a cold reservoir, it is sufficient merely to allow \(Q_H\) to flow naturally from the hot to the cold reservoir.

To get \(W\) units of work out of a heat engine operating between reservoirs at negative temperatures, you would have to make use of the device shown in Fig. 19-10c, where \(Q_c\) units of heat are taken from the cold reservoir (as though it were a refrigerator). Then a smaller quantity \(Q_H\) would go into the hotter reservoir, and the rest would be available for work. But the hot reservoir could be dispensed with, for the \(Q_H\) units of heat would naturally flow back to the colder reservoir. The net result would be that \(Q_c - Q_H\) units of heat were extracted from the colder reservoir and converted completely into work, in violation of the Kelvin-Planck statement of the second law. This is the only principle of classical physics that is violated by systems at negative temperatures—but it is an important and interesting one.

Up to the present time, the only real use for systems at negative temperatures has been in the rapidly expanding field of masers and lasers. Perhaps, in the future, experiments on heat engines and refrigerators will be performed at negative temperatures. Then it will truly be fun to be an engineer.

19-6 THIRD LAW OF THERMODYNAMICS

We have seen how the Joule-Kelvin effect is employed to produce liquid helium at a temperature below 5 K. The rapid adiabatic vaporization of liquid helium then results in a further lowering of the temperature to about 1 K with \(^4\)He and to about 0.3 K with \(^3\)He. The magnetocaloric effect is then used to lower the temperature of a paramagnetic compound (magnetic-ion subsystem plus lattice) to about 0.001 K. In principle, it is possible to achieve still lower temperatures of matter by repeated applications of the magnetocaloric effect. Thus, after the
original isothermal increase in magnetic field, the first adiabatic decrease in magnetic field might be used to provide a large amount of material at temperature $T_{f1}$ to serve as a heat reservoir for the next isothermal increase in magnetic field of a smaller amount of material. A second adiabatic magnetic field reduction might then give rise to a lower temperature $T_{f2}$, and so on. The question which naturally arises at this point is whether the magnetocaloric effect may be used to cool a substance to absolute zero.

Experiment shows that the fundamental feature of all cooling processes is that the lower the temperature achieved, the more difficult it is to go lower. For example, the colder a liquid is, the lower the vapor pressure, and the harder it is to produce further cooling by pumping away the vapor. The same is true for the magnetocaloric effect: if one decrease in magnetic field produces a temperature $T_{f1}$, say, one-tenth the original $T_i$, then a second decrease from the same original field will produce a temperature $T_{f2}$ which is also approximately one-tenth of $T_{f1}$. Under these circumstances, an infinite number of adiabatic field reductions would be required to attain absolute zero. Generalizing from experience, we may state the following:

By no finite series of processes is the absolute zero attainable.

This is known as either the principle of the unattainability of absolute zero or the unattainability statement of the third law of thermodynamics. Just as in the case of the second law of thermodynamics, the third law has a number of alternative or equivalent statements. Another statement of the third law is the result of experiments leading to calculations of the way the entropy change of a condensed system during a reversible, isothermal process $\Delta S_T$ behaves as $T$ approaches zero. For example, the entropy change of a solid during a reversible isothermal compression may either be measured at different $T$'s or be calculated from the second $T \, dS$ equation, leading to

$$\Delta S_T = S(T, P_{f1}) - S(T, 0) = - \int_{P_0}^{P_{f1}} \left( \frac{\partial V}{\partial T} \right)_P \, dP.$$  

Since $\beta$ decreases as $T$ decreases, this example of $\Delta S_T$ decreases as $T$ decreases. The entropy change of a paramagnetic salt during a reversible isothermal increase of magnetic field also decreases as $T$ decreases, because

$$\Delta S_T = S(T, \mathcal{N}_{f1}) - S(T, 0) = \mu_0 \int_{0}^{\mathcal{N}_{f1}} \left( \frac{\partial M}{\partial T} \right)_\mathcal{N} \, d\mathcal{N},$$

and $\mu_0 (\partial M/\partial T)_\mathcal{N}$ decreases with $T$. Experimental evidence is very strong to support the view that, as $T$ decreases, $\Delta S_T$ decreases provided that the system is a solid or a liquid—that is, a condensed system. The following principle is therefore accepted:

The entropy change associated with any isothermal reversible process of a condensed system approaches zero as the temperature approaches zero.

Let us call this theorem the Nernst-Simon statement of the third law of thermodynamics. Both this statement and the unattainability statement have had
a long and checkered career since the original paper by Nernst in 1907. It took 30 years of experimental and theoretical research, during which time there were periods of great confusion, before all differences of opinion were resolved and the statement was agreed upon. Nernst originally stated, as the third law, that the temperature derivative of the change of Helmholtz function during an isothermal process approaches zero as the temperature approaches zero. He did not think in terms of entropy and, moreover, was of the opinion that this statement and also the unattainability statement could be derived from the second law with the additional assumption that the heat capacities of all materials approached zero as the temperature approached zero. Nernst also maintained that both statements were true for all kinds of processes, both reversible and irreversible. It was mainly the experiments and arguments of Simon in the period from 1927 to 1937 that made precise the region of validity of the third law.

In order to show that the Nernst-Simon statement and the unattainability statement are equivalent, it is necessary to derive an equation for the limiting value of the entropy change accompanying an isothermal reversible process. Let us return to a paramagnetic salt and consider any isentropic increase of magnetic field, \( i \rightarrow f \) of Fig. 19-11. The entropy change between the point \( (T = 0, \mathcal{H}) \) and \( (T, 0) \) is given by

\[
\Delta S = \int_{(T = 0, \mathcal{H})}^{(T, 0)} dS = \int_{\mathcal{H} = 0}^{\mathcal{H}} dS.
\]

As the isentropic process is carried out, it is possible to obtain

1. The temperature will rise as the magnetic field is increased from zero to \( \mathcal{H} \).
2. The entropy will increase as the magnetic field is increased.

Since \( \Delta S = \int_{\mathcal{H} = 0}^{\mathcal{H}} dS \), the entropy change is

\[
\Delta S = K \ln \left( \frac{\mathcal{H}}{\mathcal{H}_0} \right),
\]

where \( K \) is a constant and \( \mathcal{H}_0 \) is a reference magnetic field.

Figure 19-11 Diagram to derive Eq. (19-4).
\( \mathcal{N} = \mathcal{N}_1 \) and the state \( i \) is
\[
S_i - S(0, \mathcal{N}_1) = \int_0^{T_f} \frac{C_{\mathcal{N} = \mathcal{N}_i}}{T} \, dT,
\]
where \( C_{\mathcal{N}} \) is the heat capacity at constant field, a positive quantity for all values of \( \mathcal{N} \). The change in entropy between the point \( (T = 0, \mathcal{N} = 0) \) and \( f \) is
\[
S_f - S(0, 0) = \int_0^{T_f} C_{\mathcal{N} = 0} \, dT.
\]
Since \( S_i = S_f \) and \( S(0, \mathcal{N}_i) - S(0, 0) = \lim_{T \to 0} [S(T, \mathcal{N}_i) - S(T, 0)] \), we have
\[
\lim_{T \to 0} [S(T, \mathcal{N}_i) - S(T, 0)] = \int_0^{T_f} \frac{C_{\mathcal{N} = 0}}{T} \, dT - \int_0^{T_f} \frac{C_{\mathcal{N} = \mathcal{N}_i}}{T} \, dT. \tag{19-4}
\]

To prove the equivalence of the unattainability and Nernst-Simon statements of the third law, we proceed in the same manner as in the case of the Kelvin-Planck and Clausius statements of the second law.

Let
\[
U = \text{truth of the unattainability statement};
- U = \text{falsity of the unattainability statement};
N = \text{truth of the Nernst-Simon statement};
- N = \text{falsity of the Nernst-Simon statement}.
\]

As before,
\[
U \equiv N
\]
when
\[
- U \geq - N \quad \text{and} \quad - N \geq - U.
\]

1. To prove that \(- U \geq - N\), suppose that it is possible to find a value of \( T_i \) which makes \( T_f = 0 \), thereby violating the unattainability statement. Then, from Eq. (19-4), the left-hand member would be negative, thereby violating the Nernst statement.

2. To prove that \(- N \geq - U\), suppose that the left-hand member of Eq. (19-4) had any negative value, thereby violating the Nernst-Simon statement. Then it would be possible to find a value of \( T_i \) in Eq. (19-4) that would make the second integral equal to this negative number. As a result, the first integral would vanish and \( T_f \) would be zero, thereby violating the unattainability statement.

The fact that \(- N \geq - U\) may also be readily seen from Fig. 19-12a. If the point \((0, \mathcal{N}_i)\) lies below the point \((0, 0)\), then the adiabatic reduction of magnetic field \( 6 \to 7 \) could be used to lower the system to absolute zero.

To complete the proof of the equivalence of the unattainability and the Nernst-Simon statements of the third law, one ought to consider a type of system that undergoes a decrease of entropy during an isothermal decrease of magnetic field and a decrease of temperature during an adiabatic increase of magnetic field, such as a superconductor in the intermediate state. Since the
proof proceeds in exactly the same way as before, however, nothing would be gained by repeating the details.

A paramagnetic substance was invoked in the proof of the equivalence of $U$ and $N$ only for convenience and concreteness. By means of a slight change in symbols, the same proof may be applied to any system whatever, since all systems are capable of undergoing an isothermal reversible decrease of entropy followed by a reversible adiabatic decrease of temperature. Furthermore, the Nernst-Simon statement also applies to materials in frozen metastable equilibrium, provided that the isothermal process in question does not disturb this frozen equilibrium.

Referring to Fig. 19-12b, we see that, in the isothermal process $1 \to 2$, there is a decrease of entropy and that in $3 \to 4$ there is another decrease, and so on. If the entropy of the system at absolute zero is called the zero-point entropy, we see that a third equivalent statement of the third law is as follows:

*By no finite series of processes can the entropy of a system be reduced to its zero-point value.*

The equivalence of all three statements of the third law is clearly displayed in Fig. 19-12b.

There are many physical and chemical facts which substantiate the third law. For example, using Clapeyron's equation,

$$\frac{dP}{dT} = \frac{s^{(f)} - s^{(i)}}{v^{(f)} - v^{(i)}}$$

in conjunction with a phase change that takes place at low temperature, the statement that

$$\lim_{T \to 0} (s^{(f)} - s^{(i)}) = 0$$
implies that

$$\lim_{T \to 0} \frac{dP}{dT} = 0,$$

since $\phi(T) - \phi(0)$ is not zero for a first-order phase transition. This is substantiated by the melting curve of solid helium shown in Figs. 13-24 and 13-26. As a matter

<table>
<thead>
<tr>
<th>Date</th>
<th>Investigator</th>
<th>Country</th>
<th>Development</th>
<th>Temp, K</th>
</tr>
</thead>
<tbody>
<tr>
<td>1860</td>
<td>Kirk</td>
<td>Scotland</td>
<td>First step toward deep refrigeration: reached temperatures below freezing point of Hg.</td>
<td>234.0</td>
</tr>
<tr>
<td>1877</td>
<td>Cailletet</td>
<td>France</td>
<td>First liquefied oxygen: used throttling process from pressure vessel, obtaining fine mist only.</td>
<td>90.2</td>
</tr>
<tr>
<td>1884</td>
<td>Wroblewski and Olzewski</td>
<td>Poland</td>
<td>First property measurements at low temperatures: used small quantities of liquid N\textsubscript{2} and O\textsubscript{2}.</td>
<td>77.3</td>
</tr>
<tr>
<td>1898</td>
<td>Dewar</td>
<td>England</td>
<td>First liquefied hydrogen: used Joule-Kelvin effect and counterflow heat exchanger.</td>
<td>20.4</td>
</tr>
<tr>
<td>1908</td>
<td>Kamerlingh-Onnes</td>
<td>The Netherlands</td>
<td>First liquefied helium: used same method as Dewar; shortly thereafter, lowered pressure over liquid to get 1 K.</td>
<td>4.2</td>
</tr>
<tr>
<td>1927</td>
<td>Simon</td>
<td>Germany and England</td>
<td>Developed helium liquefier: used adiabatic expansion from pressure vessel with liquid H\textsubscript{2} precooling.</td>
<td>4.2</td>
</tr>
<tr>
<td>1933</td>
<td>Giauque and MacDougall</td>
<td>United States</td>
<td>First adiabatic field reduction: Principle first proposed by Giauque and Debye in 1926.</td>
<td>0.25</td>
</tr>
<tr>
<td>1934</td>
<td>Kapitza</td>
<td>England and USSR</td>
<td>Developed helium liquefier using expansion engine: Made possible liquefaction of helium without liquid H\textsubscript{2} precooling.</td>
<td>4.2</td>
</tr>
<tr>
<td>1946</td>
<td>Collins</td>
<td>United States</td>
<td>Developed commercial helium liquefier: used expansion engines and counterflow heat exchangers.</td>
<td>2.0</td>
</tr>
<tr>
<td>1956</td>
<td>Simon and Kurti</td>
<td>England</td>
<td>First nuclear experiments: used adiabatic field reduction of nuclear stage of a paramagnetic salt.</td>
<td>10^{-5}</td>
</tr>
<tr>
<td>1979</td>
<td>Ehnholm and others</td>
<td>Finland</td>
<td>Reached lowest temperature so far: cascade nuclear refrigerator.</td>
<td>5 \times 10^{-8}</td>
</tr>
</tbody>
</table>
of fact, \(dP/dT\) of solid \(^4\)He approaches zero very rapidly, as shown by the experimental result of Simon and Swenson, that

\[
\frac{dP}{dT} = 0.425T^7.
\]

There are many other applications of the third law in the fields of physical chemistry and statistical mechanics. For further study, the writings of Simon and of Guggenheim are recommended.

The fact that absolute zero cannot be attained is no cause for misgiving. A temperature of \(5 \times 10^{-8} \text{ K}\) represents a fraction of room temperature (300 K) equal to

\[
\frac{5 \times 10^{-8}}{3 \times 10^3} \approx 10^{-10}.
\]

Cryogenics has therefore enabled us to get to about a ten-billionth of room temperature. The surface temperature of the sun, 6000 K, is only 20 times room temperature, and the temperature in the interior of the hottest star, about \(3 \times 10^9 \text{ K}\), is 10 million times room temperature. Cryogenics is still ahead by a factor of a thousand.

A chronological account of the progress toward lower temperatures is given in Table 19-1.

**PROBLEMS**

19-1 Sketch a Carnot engine cycle on a \(\mathcal{N}M\) diagram:

(a) At positive temperatures.

(b) At negative temperatures.

(c) Why is it impossible to operate a Carnot engine between a reservoir at a negative temperature and one at a positive temperature?

19-2 Suppose that the magnetization of a paramagnetic solid is given by

\[
M = M_{sat}f(a),
\]

where \(a = g\mu_B\mathcal{N}/kT\) and \(f(a) = 0\) when \(a = 0\), and \(f(a) \to 1\) when \(a \to \infty\). The change of entropy during an isothermal reversible increase of field from 0 to \(\mathcal{N}_f\) is given by

\[
\Delta S_T = \mu_0 \left[ \int_{\mathcal{N}_0}^{\mathcal{N}_f} \frac{\partial M}{\partial T} \right] d\mathcal{N} = \mu_0 \left[ M_{sat} \left( f(a) \frac{g\mu_B\mathcal{N}}{kT^2} \right) \frac{kT}{g\mu_B} \right] da
\]

\[
= -M_{sat}k \int_{a_0}^{a_0^*} \frac{\partial f(a)}{\partial a} da.
\]

Determine whether the Nernst-Simon statement of the third law is true in the following cases:

(a) Curie's equation: \(f(a) = a\).

(b) Langevin's equation: \(f(a) = \coth a - \frac{1}{a}\).