Adiabatic Demagnetization and the Temperature Scale Below 1° K

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THE QUESTION of what is a "low" temperature has been answered differently at different times. In the days when air was liquefied for the first time by Cailletet and Pictet, temperatures of 50°–90° K were considered extremely low. At present, however, since the Collins liquefier has made it possible for relatively inexperienced people to liquefy helium in reasonable quantities, few cryogenics physicists would consider the temperature of liquid hydrogen (20°–14° K) as being low. The boiling point of liquid helium is 4.2° K, and by reducing its vapor pressure the temperature can be conveniently reduced to 1° K. (This depends largely on the construction of the cryostat containing the liquid helium and on the capacity of the reducing pump. Under practical circumstances it varies between 1.5° and 0.7° K, but 1° K is a good average, and as a matter of convenience we shall call this the "lowest helium temperature".)

The region below 1° K at the present time considered "very low temperature," can now only be penetrated by the method of adiabatic demagnetization of paramagnetic salts. This method was proposed in 1926 independently by Giauque and by Debye. The first experiments were made at Berkeley, Leiden, and Oxford. The technique, now used in many of the European and American low temperature laboratories, consists of an isothermal magnetization of the salt, followed by an adiabatic demagnetization.

Consider a substance which contains magnetic ions in its crystalline lattice. When it is placed between the poles of a magnet, the ions are partly aligned by the field in such a way that equilibrium is established between the aligning force of the field and the disturbing force of the thermal vibrations of the crystalline lattice. Strictly speaking, this is true only if no other forces are working on the ions, such as magnetic or exchange interaction between the ions, or Stark effects resulting from nonmagnetic parts of the lattice. The total magnetic moment of the substance will be higher, the stronger the magnetic field and the lower the temperature. This again may not be true if strong interactions occur between the magnetic ions. Since an alignment of the magnetic ions increases the amount of order in the substance, an isothermal magnetization of a paramagnetic salt diminishes its entropy, with a consequent flow of heat from the sample. If, after the isothermal magnetization, the substance is removed from the field adiabatically, the entropy remains constant at this low value, assuming that the demagnetization is a reversible process. Thus a state is finally obtained in zero field with a lower entropy than that of the initial state. This means that the temperature is lower.

The demagnetization process can be discussed most easily with the help of some thermodynamics. From the laws of thermodynamics, applied to a paramagnetic substance in a magnetic field, we can derive (assuming again that the magnetic ions are free and independent, which proves to be equivalent to the condition that M is a function of H/T):

$$TdS = c_M dT - HdM. \qquad (1)$$

Here c_M is the specific heat at constant magnetic moment, H is the magnetic field, and M the magnetic moment. The salt is magnetized isothermally at an initial temperature T_i (essentially the lowest helium temperature) to a field H_i, then demagnetized to zero field obtaining a final temperature T_f. So we can consider three states of the salt:

The initial state $(0, T_i)$
The state in the field (H_i, T_i)
The final state $(0, T_f)$

The decrease of entropy during the isothermal magnetization according to (1) is equal to

$$S(0, T_i) - S(H_i, T_i) = \int_0^{M(H_i T_i)} \frac{H}{T}\, dM. \qquad (2)$$

The demagnetization is an isentropic process, so

$$S(H_i, T_i) - S(0, T_f) = 0. \qquad (3)$$

From (2) and (3) it follows:

$$S(0, T_i) - S(0, T_f) = \int_0^{M(H_i, T_i)} \frac{H}{T}\, dM. \qquad (4)$$

Since $(0, T_i)$ and $(0, T_f)$ are both situations in zero magnetic field we also have

$$S(0, T_i) - S(0, T_f) = \int_{T_f}^{T_i} \frac{c_0}{T}\, dT, \qquad (5)$$

c_0 being the specific heat in zero magnetic field. From (4) and (5) it follows

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$$\int_0^{M(H_i, T_i)} \frac{H}{T}\, dM = \int_{T_f}^{T_i} \frac{c_0}{T}\, dT. \qquad (6)$$

From this equation it follows that adiabatic demagnetization decreases temperature, for, if M increases with increasing H/T, the left-hand integral is positive, so, since c_0 is positive, T_f must be lower than T_i.

One of the fundamental problems is the determination of T_f, the final temperature. If at the initial temperature the relation between M, H, and T is known, the left-hand integral of (6) can be solved, and the decrease of entropy during the isothermal magnetization (2) can be calculated. If in the region below 1° K the dependence of c_0 on temperature is known, we can also solve the right-hand integral, and we can calculate T_f for given initial values H_i and T_i.

In most practical cases the functional dependence of M on H and T at T_i is actually known, either from experiment or from theoretical considerations (for instance, often a Brillouin function represents the magnetic behavior of the salt in a satisfactory way), so the decrease of entropy in the initial field can be calculated with reasonable precision. The relation between c_0 and T below 1° K is not known a priori, so that, in general, predictions of final temperatures based on Eq. (6) cannot be given. Nor can this relation be determined experimentally in the absence of a calibrated thermometer for the region below 1° K.

The basic definition of the thermodynamic temperature is Kelvin's formula for a reversible process,

$$dQ = TdS. \qquad (7)$$

At ordinary temperatures, however, secondary thermometers are never calibrated with the help of this formula but are compared with the gas thermometer, because the Kelvin scale is identical with the ideal gas scale, and the accuracy obtained in this way is much higher. At 1° K, however, the vapor pressure of helium is 0.12 mm Hg, and it falls exponentially with decreasing temperature. Since the pressure in the gas thermometer must be well below the saturation pressure of the vapor, measurements with a gas thermometer below 1° K are impracticable. For this reason the only fundamental way to determine thermodynamic temperatures below 1° K is to base the absolute measurements on Kelvin's formula (7). In order to do this, known amounts of heat must be supplied to the salt, and the variation of the entropy caused by the heat supply must be measured.

In practice the same procedure is followed as at higher temperatures: A secondary thermometer is chosen that has a high sensitivity in the region to be investigated and that can be read easily and in a short time. Its readings are calibrated against the Kelvin scale. At ordinary temperatures usually a separate thermometer is constructed and is brought into thermal contact with the substance under investigation. But, since the thermal equilibrium must be obtained through the thermal vibrations of the lattice, this method is unsuitable below 1° K. Heat transfer between the thermometer and the salt becomes more and more difficult the lower the temperature, and at the lowest temperatures a region must be expected where the thermometer does not follow the temperature of the salt at all. The simplest way of avoiding this problem is to use a property of the salt itself as a secondary thermometer. Such a property is usually called a "thermometric parameter." Any physical property of the salt that depends strongly on temperature can be used, and the quantity mostly used up to the present time is the "magnetic temperature."

The magnetic temperature is defined on the basis of Curie's law, which is obeyed in the liquid helium region by most of the paramagnetic salts used for adiabatic demagnetization experiments. This means that for low fields the magnetic moment fulfills the equation

$$M = C\frac{H}{T},$$

where C is the Curie constant of the salt. This law can be extrapolated to the region below 1° K, and temperatures can be derived from magnetic measurements:

$$T = C\frac{H}{M} = \frac{C}{\chi},$$

χ being the susceptibility at zero field. From theoretical considerations, however, it follows that Curie's law cannot hold down to absolute zero. Deviations must occur that become larger with lower temperature. Consequently the quantity C/χ is no longer the thermodynamic temperature when the temperature is sufficiently low, but it is still a function of temperature and can be used as a thermometric parameter. C/χ is called the magnetic temperature T^*:

$$T^* = \frac{C}{\chi}.$$

The purpose of many investigations below 1° K has been to discover the relation between the magnetic temperature T^* and the thermodynamic temperature T for various paramagnetic salts.

The most fundamental method for measuring absolute temperatures below 1° K, as was pointed out above, is based on Kelvin's definition (7). Unfortunately, it is a laborious process that takes much time and requires an appreciable amount of technical experience. In the region between 1° and 0.1° K, however, some interesting results have been obtained from a different method which, though less fundamental, is less tedious, and the accuracy obtained in the results is even higher. It is based on theoretical work done by Van Vleck and his colleagues.

For this method, theoretical formulas for the relations between T^* and T and between c_0 and T are used. If these formulas are available for a substance, they may be verified jointly by application in Eq. (6). Demagnetizations can be performed from various initial magnetic fields, and each time the final T^* can be determined experimentally. From the initial conditions the decrease of entropy in the magnetization process can be calculated. From the relation between

T and T^*, the T_f can be calculated and, with the help of the relation between c_0 and T, Eq. (6) can be checked. If this equation is fulfilled over a wide range of T^* values, it is plausible that both theoretical formulas are correct, and so the relation between T and T^* is corroborated by experiment. If the results are not in agreement with Eq. (6), then the method fails, and nothing is known about the absolute temperature.

I shall not give the details of the theoretical considerations mentioned above. Table 1 gives some results obtained with potassium chromic alum, a substance with which many investigations have been done, and probably the material of which the magnetic and caloric behavior is best known below 1° K. The first column gives the decrease of entropy during the isothermal magnetization (R being the gas constant), the second gives the T^* values measured in the experiment, and the last column gives the absolute temperatures as calculated with the help of the theoretical relations mentioned above. It turns out that T is always lower than T^*, but the differences are relatively small, so in this region the deviations from Curie's law are small.

TABLE 1

S/R	T^*	T
0.0102	0.946	0.944
.0154	.784	.782
.0296	.570	.566
.0687	.365	.359
.1380	.251	.242
.4180	.124	.108
0.5710	0.095	0.077

Down to $T = 0.077°$ K the theoretical formulas are in good agreement with the experimental results, and formula (6) is fulfilled within a few per cent. Below this temperature the deviations increase rapidly with falling temperature. Here the method can no longer be used, and measurements at lower temperatures are based on the Kelvin scale.

For temperature determinations based on Kelvin's definition (7), two kinds of measurements must be made: Known amounts of heat must be supplied to the salt, and the variation of entropy that is due to the heat supply must be determined. In both these investigations use is made of the thermometric parameter.

For the entropy measurements adiabatic demagnetizations are performed from a number of initial fields. For each field the decrease of entropy associated with the initial isothermal magnetization is calculated with the help of formula (2), and the thermometric parameter (usually T^*) is measured immediately after the demagnetization. In this way it is possible to set up an experimental relation between the entropy and T^*, and afterwards the variations in entropy can be derived from the measured variations in T^*.

The caloric measurements involve a problem. The thermal conductivity of the salt is very bad at the lower temperatures, so it is essential that the heat should be supplied homogeneously to the sample. An electric heater wire glued to the salt is completely inadequate below 0.2° K. At Oxford, heat was supplied by irradiation with γ-rays. Since the absorption coefficient is small, the penetration depth is great, and the absorption is sufficiently homogeneous. At Leiden use is made of relaxation and hysteresis effects occurring in the salts at the lower temperatures. In this case heat can be supplied by placing the salt in an alternating magnetic field. The advantages are obvious: The heat is supplied directly to the system of electron spins, and, if the temperature is not strictly homogeneous, most heat is developed in the coldest parts, so that the inhomogeneity is automatically decreased. A disadvantage is, however, that the method can be used only at temperatures where such hysteresis or relaxation phenomena occur—i.e., only at the very lowest temperatures.

When a salt showing hysteresis or relaxation effects is placed in an alternating magnetic field, a phase difference occurs between the field and the magnetic moment. It can be described most easily with the help of a complex susceptibility. Suppose the magnetic field is given by

$$H = Re[h_0 e^{i\omega t}] = h_0 \cos \omega t;$$

then the magnetic moment obeys

$$M = Re[(\chi' - i\chi'') h_0 e^{i\omega t}] = h_0(\chi' \cos \omega t + \chi'' \sin \omega t).$$

The energy dissipated per second in the salt, according to (1), is:

$$\mu \int_{t=0}^{t=1/\mu} H dM = \tfrac{1}{2} h_0^2 \omega \chi''$$

After the demagnetization both χ' and χ'' can be measured as functions of time with the aid of an a-c measuring bridge. From the value of χ'' at each moment one can derive the heat absorption per second. From the variation of χ' with time the variation of T^*, and so that of S, can be found. Hence both dQ/dt and dS/dt are known and, according to formula (7), absolute temperatures can be calculated from these two data. The interesting point of this method is that the same alternating current that is used as a "heating current" is also used as a "measuring current" for the T^*.

Some experimental results are collected in Table 2. Here the columns have the same meanings as in Table 1. Above $T^* = 0.060°$ both χ'' and dT^*/dt become so small that they cannot be determined with sufficient accuracy. The theoretical method discussed above gives

TABLE 2

S/R	T^*	T
0.847	0.060	0.031
.901	.054	.022
.926	.050	.015
.950	.044	.0088
.959	.040	.0065
.970	.036	.0047
0.987	0.033	0.0039

reliable results down to $T^* = 0.09°$; hence in the region between $T^* = 0.09°$ and $T^* = 0.06°$ ($T = 0.07°$ K and $T = 0.03°$ K) no experimental data are available for the relation between T and T^*.

At $T^* = 0.060°$ the thermodynamic temperature is lower than the magnetic temperature by a factor of two, and the difference increases rapidly with falling temperature. At $T^* = 0.035°$ it is down by a factor of eight. In this region, therefore, Curie's law is no longer valid, and T^* cannot be considered as even an approximation to the absolute temperature.

At $T^* = 0.033°$, $T = 0.0040°$ K, the magnetic temperature reaches a *minimum*: when demagnetizations are performed from higher fields, a higher T^* is found again. Thus at this point the susceptibility shows a maximum. Although this is an important phenomenon for the interpretation of the magnetic behavior of the salt at these very low temperatures, we shall discuss here only the consequences of its occurrence for the determination of absolute temperatures. In the neighborhood of the maximum of χ' the T^* changes only very little with the absolute temperature; in other words, T^* is no longer a good thermometric parameter, and if one wants to measure absolute temperatures in the region below the maximum of χ', a different property of the salt must be found which in this region is strongly dependent on temperature.

The most obvious thermometric parameter in this region is the imaginary part of the a-c susceptibility χ''. It happens that, in the neighborhood of the maximum of χ', the χ'' increases rapidly with falling temperature. For absolute temperature determinations with this parameter two sets of measurements have to be made. In the first place, an experimental relation must be found between the χ'' and the entropy—i.e., a number of demagnetizations must be performed from different initial fields, and each time the χ'' is measured directly after the demagnetization. In the second place, $\Delta\chi''$, the change in χ'' for a given heat supply, ΔQ, must be measured. Since this heat supply is calculated from χ'' itself, one measures χ'' for a certain period after the demagnetization. Then the entropy variation ΔS is calculated from the initial and final values of χ'', and the total heat supply ΔQ from the course of χ'' with time. From these two the average value of T during the heating period can be derived.

In the case of chromic alum only a few measurements with the χ'' thermometer have been made. The accuracy is lower than with the T^* thermometer, and the measurements could be made only in a very restricted range of temperatures, since χ'' also shows a maximum at a temperature slightly lower than χ' does. All the measurements gave thermodynamic temperatures of the order of 0.004° K, thus corroborating the measurements with the T^* thermometer without giving much new information.

For measurements in the region below $T = 0.004°$ K a new parameter had to be found. Now it happens that the maximum in χ' is something like a Curie point. Below this temperature phenomena are found that remind one of the ferromagnetic or antiferromagnetic behavior of other substances at much higher temperatures. Hysteresis effects are found in the magnetization curve. The width of the hysteresis loop is called the remanent moment and depends on the magnetic field and, for a given field, on the temperature, in such a way that the remanence is larger with lower temperature. This remanent moment, which can be easily measured with a ballistic measuring arrangement, has been used as a thermometric parameter for the very lowest temperatures.

When the remanence (usually denoted by Σ) is used as a parameter, two kinds of measurements must be made again. First, an experimental relation is needed between the entropy and the remanence, which is obtained by demagnetizing from different magnetic fields, the remanence being measured after each demagnetization by means of a small measuring field. The decrease of Σ that is due to a given heat supply is determined in such a way that, after the demagnetization, first the remanence is measured ballistically, then the alternating current is switched on, and χ'' is measured as a function of time; finally the remanence is measured again. From the two values of Σ the variation of entropy can be calculated and, from the course of χ'' with time, the total heat supply found. From these two sets of data the thermodynamic temperature is derived in the ordinary way.

Some results are collected in Table 3. The first column gives the remanence occurring after switching off a field of 1.08 oersteds. The second column gives the entropy in the same units as Tables 1 and 2. The third column gives the total heat supply derived from the χ'' measurements; the last column shows the absolute temperatures as calculated from these data. All the temperatures are below 0.004° K. The lowest temperature is 0.0029° K. It was obtained by demagnetizing from a field of 22,000 oersteds, the highest field that could be obtained with the big magnet of the Kamerlingh Onnes Laboratory at Leiden.

TABLE 3

Σ/R	S/R	$\Delta Q/R$	T
Begin: 1.09×10^{-8}	1.021	5.56×10^{-5}	0.0037
End: $0.69 \times 10\text{-}6$	1.006		
Begin: 2.07×10^{-8}	1.069	6.23×10^{-5}	.0035
End: $1.76 \times 10\text{-}6$	1.051		
Begin: 2.38×10^{-8}	1.090	6.22×10^{-5}	.0033
End: $2.11 \times 10\text{-}6$	1.071		
Begin: 2.91×10^{-8}	1.138	5.58×10^{-5}	0.0029
End: $2.73 \times 10\text{-}6$	1.119		

Thus far we have discussed only measurements with potassium chromium alum, but some other substances were also investigated. We shall mention the results briefly.

Copper potassium sulfate and manganese ammonium sulfate both show a maximum in susceptibility at very low temperatures. Above this maximum χ'' is so small that it could not be measured with any accuracy; consequently, no absolute temperature measurements could be done above the Curie point with the help of a-c heating. Below the maximum of χ' the χ'' increase rapidly, so here measurements could be made with the χ'' thermometer. But, in addition, the remanence below the Curie point is so small for both salts that it could not be used as a thermometric parameter. Thus, of three thermometric parameters used in the case of chromium alum, only the χ'' could be used, and this is the one giving the results with the lowest accuracy. With copper potassium sulfate, temperatures down to 0.0045° K were measured; in the case of manganese ammonium sulfate, the lowest temperatures were only of the order of 0.09° K.

Measurements were made with iron ammonium alum, and this salt behaved more like chromium alum. Its χ'' has reasonable values both above and below the Curie point, and also its remanence can be used as a thermometric parameter. It was found that the Curie point is at $T = 0.032°$ K, and the lowest temperature obtained with this salt was about 0.01° K.

Some measurements were made with a chromium potassium alum, which was strongly diluted with aluminum potassium alum (21.3 aluminum ions for each chromium ion). No maximum was found in susceptibility, but perhaps it occurs at a lower temperature than could be reached with the Leiden magnet. The values found for χ'' were of a suitable order of magnitude, so that caloric measurements could be made using the T^* thermometer. The lowest temperature found in these experiments was 0.0014° K, or twice as low as with ordinary chromium alum. Recently a double demagnetization was performed at Oxford with a similar salt. From the extrapolation of the Leiden measurements it could be estimated that the lowest temperature was of the order of 0.001° K.

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The Present Status of Temperature Scales

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THE THERMODYNAMIC TEMPERATURE SCALE known as the Kelvin scale, which was based upon a hundred-degree interval between the ice and steam points, was proposed in a paper by Joule and Kelvin in 1854 (*1*). This scale has been recognized as the fundamental temperature scale to which all accurate temperature measurements should ultimately be referred. In principle the Kelvin scale could be realized rather simply with a gas thermometer if the thermometer were ideal and contained an ideal gas; but since neither the thermometer nor the gas is ideal, corrections must be made for their imperfections.

A gas thermometer for accurate temperature measurements requires apparatus and skill such as are found in only a few laboratories specializing on thermometric researches. It was evident that, for uniformity and precise measurement of temperature, a practical scale was needed which could be used for expressing temperatures on the same basis in laboratories all over the world. Since reproducible temperature measurements are as basic in scientific work as are the measurements of mass, length, and time, the logical body to recommend this scale was the International Committee on Weights and Measures. In 1927, as a result of discussions and correspondence extending over nearly two decades, the national laboratories of Germany, the United States, and Great Britain agreed on a definition of an International Temperature Scale. The international committee recommended it to the 7th General Conference on Weights and Measures, then representing 33 nations, and it was adopted. The international committee also recommended in a resolution that studies be made of the official text of the International Temperature Scale in a program of special conferences on thermometry held under its auspices. This also has been done. In 1937 the international committee set up an advisory committee on thermometry and calorimetry, which met in 1939, 1948, and 1952 to discuss ways to improve the International Temperature Scale.

The International Temperature Scale was adopted in 1927 with the understanding that it should not replace the thermodynamic scale but should represent the latter in a practical manner with sufficient accuracy to serve the everyday needs of scientific and industrial laboratories. At that time the scale was the best practical realization of the thermodynamic temperature scale.

The present International Temperature Scale, revised and adopted in 1948 (*2*), is based on six fixed and reproducible equilibrium temperatures to which