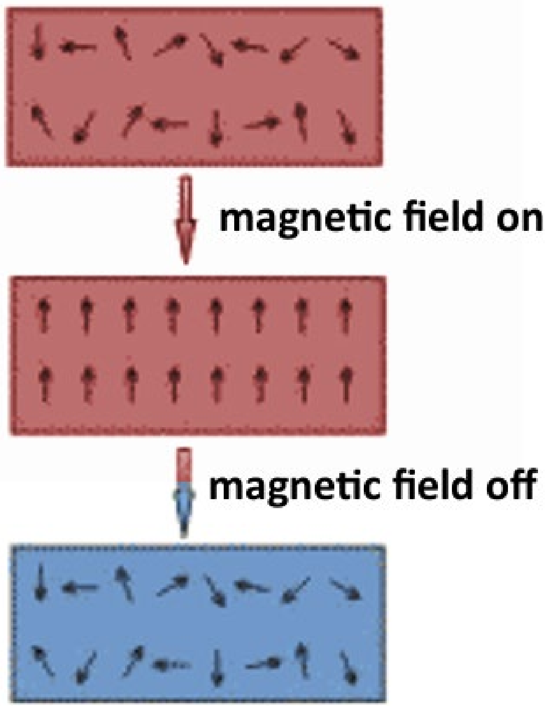
W ILLIAM F. GIAUQUE

Some consequences of low temperature research in chemical thermodynamics

Nobel Lecture, December 12, 1949



The basic purpose which underlies most of the work in the Low Temperature Laboratory, of the University of California, is the study of entropy.

It is easy for a chemist to write an equation for a desired reaction, but this does not mean that the reaction will actually take place. If one knows the heats of formation and entropies of the substances concerned in the equation, the so-called free energy or thermodynamic potential of the reaction may be calculated. A knowledge of the free energy change permits chemists to determine all reactions which are thermodynamically possible and the extent to which they are possible. When it has been found that a certain reaction should go, but experiment fails, then a catalyst can be sought or the conditions can be altered so as to secure a practicable rate of reaction. If the free energy shows that the reaction is thermodynamically impossible, a search for a catalyst is futile.

The third law of thermodynamics, which developed from the Nernst Heat Theorem, states that all perfect crystalline substances approach zero entropy as the absolute zero of temperature is approached. According to this statement a knowledge of the heat capacity, to sufficiently low temperatures, will permit the calculation of the absolute entropy of a substance. It was this possibility which interested me in low temperature research.

Similarly, the adiabatic demagnetization method of producing low temperatures, was an unexpected by-product of our interest in the third law of thermodynamics.

As we have seen, the heat capacities of substances ordinarily become very small at temperatures below 10 or 15° absolute. Thus it had been considered that essentially all of the entropy had been removed from substances at these low temperatures and, aside from a minor extrapolated amount, it was customary to assume this in calculating entropy.

During a seminar in the fall of 1924 I presented calculations showing the way in which magnetic fields affect the thermodynamic properties of various substances. Some magnetic susceptibility measurements on gadolinium sulfate octahydrate, at the temperature of liquid helium, came to my attention. These measurements had been published by Professors Woltjer and Kamerlingh Onnes, from the University of Leiden.

Fig. 23 is a photograph of the apparatus about as it was assembled and used by Dr. D. P. MacDougall and myself in the first adiabatic demagnetization experiment in 1933. The inductance bridge used to measure the magnetic susceptibility of the gadolinium sulfate octahydrate used is shown on the table in the foreground.

MacDougall sat at the table to make the first observation, I pulled the switches in the left background and watched the expression on MacDougall's face. In a short time he announced that the cooling had occurred.

The commonest question asked in the early days of this work was : "How do you know it gets cold?" This was a fair question. Obviously no one had ever made thermometers which were calibrated at temperatures that had never been produced. Since even helium gas has negligible pressure, at the low temperatures obtained, a gas thermometer is useless.

Temperature can only be measured by some property of a substance which varies with temperature. In this case the magnetic susceptibility increases as temperature decreases.

Fig. 24 illustrates the measuring coil system of an early apparatus. The coil is in several sections, two of which are around the equatorial region of the simple cylindrical sample to minimize correction for end effects. The coil system is outside the vacuum jacket and is immersed in liquid helium during use. The coils contained many thousands of turns of fine copper wire. When

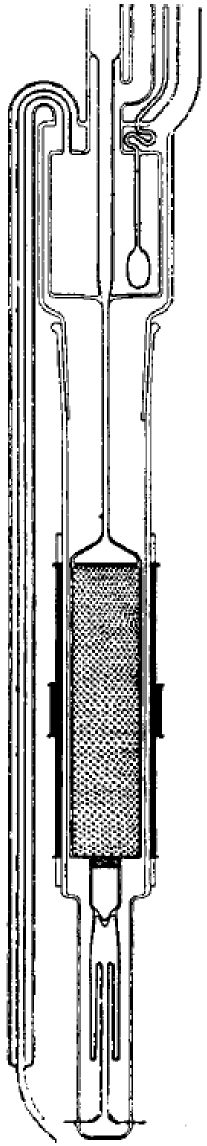


Fig.24. Measuring coil system around paramagnetic sample.

an alternating electric current is passed through a measuring coil it becomes increasingly difficult for the current to pass as the magnetic susceptibility of the substance increases. This effect permits the quantitative determination of magnetic susceptibility.

Fig. 25 shows how the magnetic susceptibility varies with temperature according to Curie's law. However, one of the consequences of the third law of thermodynamics is that Curie's law must fail as the absolute zero is approached. Curie's law has proved very useful but temperatures obtained in this way are at best approximate.

Lord Kelvin defined thermodynamic temperature in such a way that any method utilizing an entropy change to attain a lower temperature, contains within itself, a method of determining that temperature. One must, of course, be able to make the necessary measurements in a thermodynamically reversible manner. Fortunately this is a straight forward procedure in the case of many paramagnetic substances although it requires a large number of correlated experimental measurements.

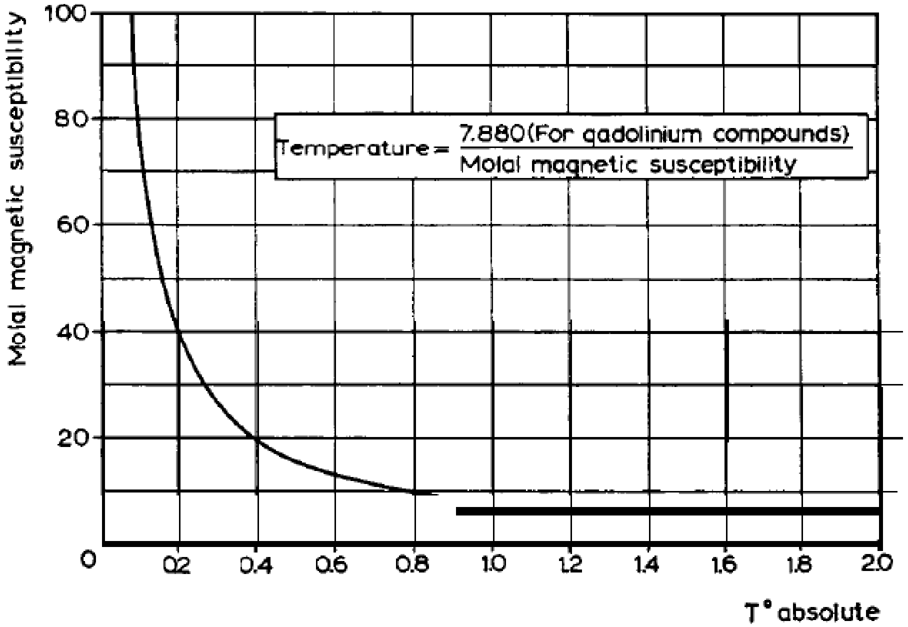


Fig. 25. Absolute temperature according to Curie's law.

Fig. 26 shows the way in which the true absolute temperature changes during the course of adiabatic demagnetization of the chemical compound, gadolinium phosphomolybdate tridecahydrate. These temperatures were calculated from the thermodynamic relationship that the absolute temperature is equal to the rate of change of heat content with entropy at constant magnetic field.

It may be seen that there is a definite lower limit of temperature which is extended downward by increasing the initial magnetic field. The field available in our present magnet is only 8,000 oersteds, however it is expected that much more powerful magnets will be available in the not too distant future.

As is well known a temperature of 0.004° K has been produced in this way with a field of 24,000 oersteds by Professors de Haas and Wiersma, at the University of Leiden.

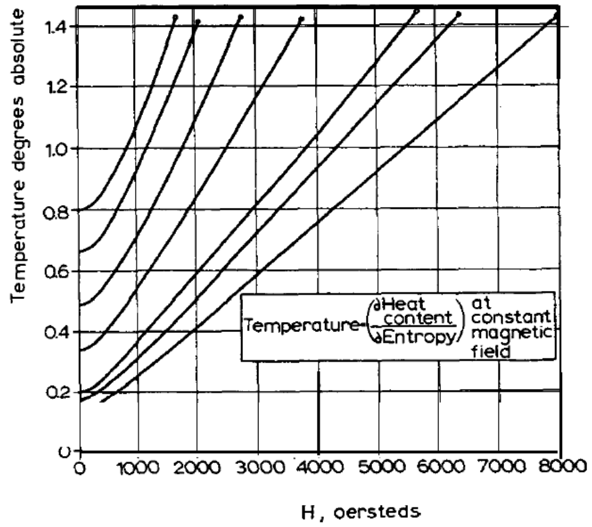


Fig. 26. Change of thermodynamic temperature with magnetic field at constant entropy for gadolinium phosphomolybdate tridecahydrate.

If a substance becomes a permanent magnet at very low temperatures, it is easy to measure the strength of the magnet. This may be done by slowly warming the magnetic material. The apparatus shown then acts as an electric generator with no moving parts except the atoms. As the paramagnetic substance is warmed, any change in the magnetic moment will generate a potential in the coil, which can be quantitatively measured by a sensitive galvanometer and used to determine the total magnetic induction.

The resistance of the wire in measuring coils drops to such low values at the temperatures of liquid helium that very large numbers of turns can be used. The sensitivity which is obtained with coils at these low temperatures is such that it is necessary to compensate for the small fluctuations in the Earth's magnetic field.

These are some examples of the type of things that are to be found by those who inquire into the subject of entropy. We consider it a rich field for further investigation.

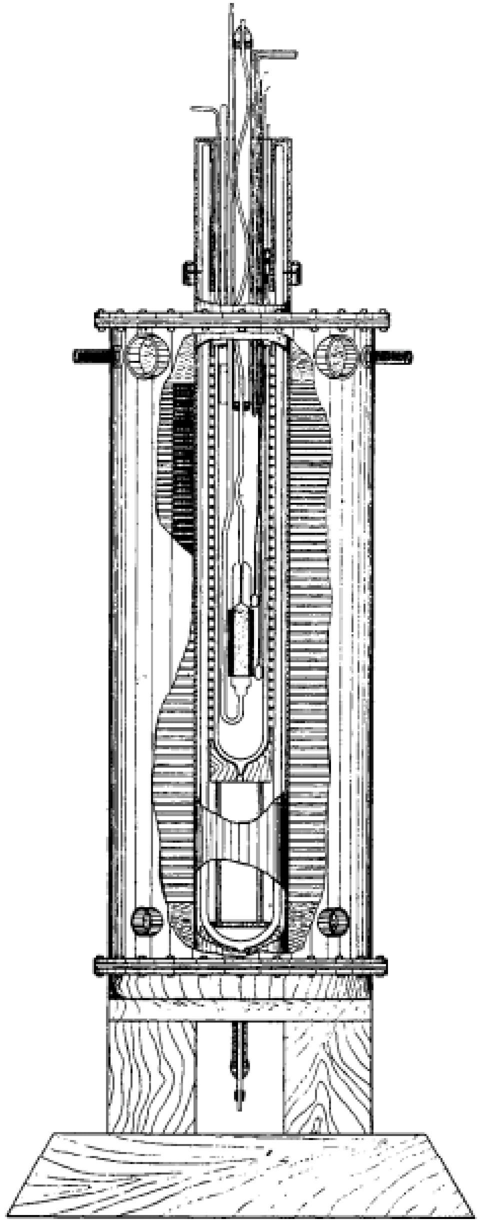


Fig. 20. Solenoid magnet with adiabatic demagnetization apparatus.

William Francis Giauque	
Born	May 12, 1895 Niagara Falls, Ontario, Canada
Died	March 28, 1982 (aged 86) Berkeley, California, US
Nationality	American
Alma mater	University of California, Berkeley
Awards	Elliott Cresson Medal (1937) Nobel Prize for Chemistry (1949) Willard Gibbs Award (1951)
Scientific career	
Fields	Physical chemistry
Institutions	University of California, Berkeley
Doctoral advisor	George Ernest Gibson
Doctoral students	Theodore H. Geballe