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Determination of Thermodynamic Temperatures near 0°K without Introducing Heat below 1°K

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Various methods of introducing heat in the region of temperature and magnetic field accessible below 1°K are compared and their experimental limitations are pointed out. The fact that all thermodynamic properties can be determined in the above region without introducing heat below 1°K is discussed. This fact also applies to the use of Kelvin's equation, $dQ=TdS$, in the determination of thermodynamic temperature.

KELVIN defined thermodynamic temperature T by the expression $TdS=dQ$, where dS and dQ refer to increments of entropy and heat, respectively. Kelvin made it obvious that this general relationship can be used to determine true thermodynamic temperatures in connection with any process if the determination can be performed in a thermodynamically reversible manner. This fact is one of the reasons why considerable ingenuity and effort have been devoted to the problem of introducing heat into substances cooled to temperatures below 1°K by adiabatic demagnetization. A brief summary of the relative advantages and disadvantages of the several existing methods of adding heat will assist in showing why it will often be of importance to avoid all of them in the temperature region below 1°K.

Six methods of heating were proposed by Giauque and MacDougall[1,2] in connection with their early experiments, which made the first use of Kelvin's equation to determine true thermodynamic temperatures in the region below 1°K.

(1) Radiation from a heated filament.
(2) Radiation from ordinary temperatures.
(3) Radiation from radioactive material.
(4) The addition of a small amount of solid of known energy content.
(5) The condensation of small amounts of helium gas.
(6) Use of an induction heater.

They also reported that heat could be introduced by means of a very small magnetic irreversibility in several salts when the cooled samples were subjected to an alternating field with a frequency of 550 cps. However, this effect was not considered for use as a calorimetric procedure for reasons which will be mentioned below.

Giauque and MacDougall selected an induction heater in order to avoid electrical leads. The heater was made in the form of a circle of No. 40 gold wire containing 0.1-percent silver. It was located at one end of a sample tube which contained gadolinium phosphomolybdate tridecahydrate. An alternating field was applied by means of the surrounding solenoid magnet, and the energy input was placed on an absolute basis by means of measurements between 1 and 4°K. It was then possible to use it for absolute measurements at temperatures below 1°K. Since the wire was close to the sample, it was necessary to consider the effect of the sample on the magnetic induction through the loop.

Giauque and Stout[3] later investigated the gold-silver alloy system and showed that induction heaters could be designed to deliver a calculable amount of energy which was practically independent of temperature. They showed that gold-silver alloys of most compositions have essentially no temperature coefficient of resistance between 1 and 12°K. The heat capacities of these alloys are so low that their temperatures will rise into the region above 1° even when the sample is at a very low temperature; thus, the resistance of such a heater is known.

Giauque and MacDougall[4] also supplied heat by the condensation of small amounts of helium gas in a chamber at one end of a sample tube. However, this was used only to obtain a controlled warming rate rather than for calorimetric purposes.

Simon[5] independently proposed, and with co-workers[6] introduced the use of radioactive heating. This can be done by irradiating the sample with γ rays.

(7) Resistance thermometer-heaters.

This type of heating below 1°K was introduced by Giauque, Stout, and Clark.[7,8] They used amorphous carbon heaters of very high resistance with electrical leads made of platinized strips on glass. These leads reduced heat conductivity to almost negligible proportions and developed nearly negligible amounts of heat. The carbon had a very large negative temperature coefficient of electrical resistance, which made it very useful in thermometry; and the carbon particles were so small that the alternating fields, useful for some

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[1] W. F. Giauque and D. P. MacDougall, presented at the Meeting of the American Chemical Society in affiliation with the American Association for the Advancement of Science, Berkeley, California, June 18–23, 1934 (unpublished).

[2] W. F. Giauque and D. P. MacDougall, Phys. Rev. **47**, 885 (1935).

[3] W. F. Giauque and J. W. Stout, J. Am. Chem. Soc. **60**, 358 (1938).

[4] W. F. Giauque and D. P. MacDougall, J. Am. Chem. Soc. **60**, 376 (1938).

[5] F. Simon, Nature **135**, 763 (1935).

[6] Kurti, Laine, and Simon, Compt. rend. **204**, 754 (1937).

[7] W. F. Giauque, Chandler Lecture, Columbia University, May 28, 1936; Ind. Eng. Chem. **28**, 743 (1936).

[8] Giauque, Stout, and Clark, J. Am. Chem. Soc. **60**, 1053 (1938).

types of magnetic measurements, produced negligible heating due to induction within the particles. This was shown[8] to be true even if the conductivity within the carbon particles should equal the largest value observed for a nonsuperconducting pure metal. The resistance was found to be relatively insensitive to magnetic fields.

De Haas, Casimir, and van den Berg[9] utilized a constantan wire coil heater which was typical except that it had long lead wires of impure lead. These minimized heat leak, and no heat was developed in the leads since they were superconducting. However, this would not be true in magnetic fields above the superconductivity threshold value for lead. Their measurements were concerned with an investigation of the resistances of gold and phosphorbronze cooled below 1°K by means of the demagnetization of iron ammonium alum.

(8) Heat introduction by means of paramagnetic relaxation and hysteresis.

Casimir, de Haas, and de Klerk[10] suggested that calorimetric heat could be introduced into samples below 1°K by means of the energy converted to heat by irreversible paramagnetic relaxation effects or hysteresis. They used this procedure to measure the heat capacity of $FeNH_4(SO_4)_2 \cdot 12H_2O$.

This method has also been used by de Klerk, Steenland, and Gorter[11,12] for heat introduction in determinations of thermodynamic temperatures down to 0.0029°K, with $KCr(SO_4)_2 \cdot 12H_2O$, and down to 0.0014°K with the same salt diluted with $KAl(SO_4)_2 \cdot 12H_2O$.

COMPARISON OF METHODS OF HEAT INTRODUCTION BELOW 1°K

In comparing various methods of heat introduction below 1°K, it is obvious that some methods may be satisfactory for limited conditions and useless in others. We suppose it is natural that authors should point out the advantages of a method as it applies to their particular experiment and place less emphasis on the experimental limitations they incur through the use of it.

In personal discussions we have had with many who are well informed concerning research at very low temperatures, it has been evident that no publication has given a critical evaluation of methods of introducing heat and making related observations at temperatures below 1°K. One of the purposes of this paper is to be thoroughly critical for the benefit of those who will acquire equipment for experimental investigations in the region made accessible by adiabatic demagnetization. We do not wish to imply that any one method of making some desired experimental observation will be the best method under all circumstances. It is necessary to consider simplicity, the accuracy required, the time and effort needed, and the expense. However, if time, effort, and expense are relatively equivalent in two methods, the experimenter should certainly adopt the method which has the greatest range of usefulness in as many respects as possible.

Only four of the above methods of introducing heat show much promise of usefulness as accurate methods even under very limited experimental conditions. These four may be classified in two groups.

A. External Heating:

(6) Induction heating in a conductor to avoid leads.
(7) Carbon resistance thermometer-heater or other resistors with leads.

B. Internal Heating:

(3) Radiation from radioactive material.
(8) Paramagnetic relaxation and hysteresis.

In our early experiments with an induction heater, difficulty in attaining equilibrium was encountered below 0.3°K, and in later experiments with carbon resistance thermometers, it could be shown that it was extremely difficult to obtain the degree of uniform energy distribution necessary for accurate calorimetry below 0.25°K. We believe that all experimenters are agreed on this point. The effect has usually been considered to be due to decreasing thermal conductivity of the substance, but the situation is more serious than that. Even if the thermal conductivity remained constant, an error equivalent to 0.001° in the absolute temperature might be tolerated at 1° where it is 0.1 percent, but not at 0.01° where it is 10 percent. Moreover, the heat capacity usually increases with decreasing temperature, and this increase can introduce an additional difficulty in the rate at which equilibrium is attained. These difficulties apply to the methods of Class A below about 0.25°K although they can be used with decreasing accuracy to at least 0.1°K. The methods of Class A have been used with the heater separated from the magnetic material by the wall of the sample tube. Giauque, Stout, Egan, and Clark[7,13] reported an experiment in which very rapid equilibrium was attained with a carbon thermometer at 0.13°K when some gadolinium phosphomolybdate tridecahydrate crystals were firmly attached to the glass wall. The gadolinium ions are separated by 10A in this cubic, magnetically dilute substance. Thus, they are surrounded by a very extensive lattice. In this experiment the amorphous carbon thermometer was painted on paper and attached to the outer wall of the glass sample tube by means of collodion. Preliminary demagnetizations were made to temperatures between 0.1 and 0.2°K so that the potentiometer could be set rather accurately on the reading to

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[9] de Haas, Casimir, and van den Berg, Comm. Phys. Lab. Leiden (1939), 251c (1938); Physica **5**, 225 (1938).

[10] Casimir, de Haas, and de Klerk, Comm. Phys. Lab. Leiden 256b (1939); Physica **6**, 255 (1939).

[11] de Klerk, Steenland, and Gorter, Comm. Phys. Lab. Leiden, 278c (1949); Physica **15**, 649 (1949).

[12] de Klerk, Steenland, and Gorter, Comm. Phys. Lab. Leiden 282a (1950); Physica **16**, 571 (1950).

[13] Giauque, Stout, Egan, and Clark, J. Am. Chem. Soc. **63**, 405 (1941).

be expected at the final low temperature. Because of the galvanometer, a time of several seconds was required to observe that this external thermometer-heater had essentially attained equilibrium, through the glass and other material, with that fraction of the salt which adhered to the inner surface of the sample tube. Subsequent temperature measurements made with both a fluxmeter and the carbon thermometer showed that heat leak eventually caused the carbon thermometer to lead the bulk temperature by several hundredths of a degree due to spaces which acted as thermal barriers between the masses of crystal in the interior of the sample tube. Thus, at the present state of our knowledge it is possible that the problem of the external heater might be greatly reduced if the heater were attached directly to a single crystal sample.

Since our present maximum magnetic fields of 8000 oersteds have seriously limited the attainment of temperatures much below 0.1°K, we have postponed this experiment until after the installation of more powerful magnetic equipment, which is now in progress. Nevertheless, we are not optimistic concerning the attainment of equilibrium with external heating at very low temperatures. Even if so-called single crystals were to be used, there might be defects which could act as thermal barriers.

The methods of Class B have the advantage that they liberate heat uniformly throughout the sample. However, if the measurements extend over an appreciable time interval, heat leak will cause non-uniform distribution of temperature. To avoid this effect experimenters can remagnetize the sample at frequent intervals to attain equilibrium at the higher temperature before recooling for a short period of observation.

At first sight it might seem that all difficulties have been removed, but this is far from the case.

We have mentioned that Giauque and MacDougall[1,2] observed that small amounts of heat could be added to samples by means of very small irreversible magnetic effects due to an alternating field. However, they did not consider using these effects for calorimetric purposes, because it was evident that losses computed from the inductance bridge measurements were primarily due to eddy currents induced in metal parts of their apparatus and magnet.

In principal the energy loss from the bridge to surrounding metal apparatus can be evaluated experimentally in the absence of the sample; however, the small relative magnitude of the heat delivered to the sample, and the difficulty in controlling temperature and other variables in the large amounts of metal in a magnet, make evaluation of the smaller amount impracticable. This means that the sample must be removed from the magnet before there is any possibility of using bridge measurements to measure the energy converted to heat within the sample. Acceptance of the magnetic relaxation method of supplying heat essentially limits the magnetic measurements to fields of minor magnitude. Since most of the phenomena which can be studied below 1°K are field-dependent, this is a rather serious limitation to incur in order to have a method of supplying heat. It should also be pointed out that there are other complications besides those related to heat measurement, when coils utilized for inductance bridge measurements are near the metal parts of magnets. The currents induced in external metal by the ac field can produce complex effects, and measurements are certainly easier to make when the sample is separated from the metal parts of magnets. However, the realities of the situation may as well be faced; the adiabatic demagnetization method opened up an area for investigation. This area is bounded by low temperatures in one dimension and magnetic fields, consistent with the minimum entropy of the sample which is available to the experimenter, in the other dimension. If an experimenter is satisfied to investigate phenomena along a boundary line of this area, corresponding to zero field, it may be desirable to separate the sample and the magnet. We have found that static arrangements have advantages with respect to reproducibility of experimental conditions and minimum time required for measurements, quite aside from the problem of the range of investigation.

The radioactive heating employed by Simon and his co-workers raises questions concerning the rate of decay of various excited states which are known to be produced. The reliability of the radioactive heating method has been questioned by de Klerk, Steenland, and Gorter[14,15] and particularly by Platzman.[16] The method has been defended by Kurti and Simon.[17] They point out that semipermanent chemical changes due to the total radiation used cannot apply to more than the order of one in 10^6 molecules. This estimate appears to be based on the assumption that the crystal defects produced involve energy disturbances of the order of an electron volt. However, one should not overlook the fact that a crystal defect of this magnitude may have a considerable effect on a large number of surrounding molecules, whereas the kinds of cooperation involved in magnetic effects are often so energetically weak that they cannot operate until the substance is cooled to tenths or hundredths of degrees absolute, corresponding to energies of the order of 10^{-6} electron volt. Quite aside from the question of crystal defects produced by radioactivity, we have long been concerned about the possible effects of other defects which are present in most crystals. It is evident that the closer the approach to the absolute zero, the more widespread will be the effect of crystal imperfections on neighboring regions. We suspect that future investigation will show that the heat capacity and magnetic properties, especially in regions involving cooperative effects at very low tem-

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[14] de Klerk, Steenland, and Gorter, Nature **161**, 678 (1948).

[15] de Klerk, Steenland, and Gorter, Physica **15**, 649 (1949).

[16] R. L. Platzman, Phil. Mag. **44**, 497 (1953).

[17] N. Kurti and F. E. Simon, Phil. Mag. **44**, 501 (1953).

peratures, will vary appreciably with crystal perfection at temperatures well below 1°K. Most of the available crystals have appreciable inclusions of impurities, electronic holes, lattice vacancies, and other assorted defects, and the consequences of producing one additional defect in 10^6 molecules (i.e., defects 100 molecules apart) must be judged by taking into consideration the perfection of the original system. It seems certain that crystal defects produced as a matter of thermodynamic equilibrium during crystal formation at ordinary temperatures would be much less serious in their long-range effects than those produced by γ rays. However, there does not appear to be any real evidence which would allow one to rule out radioactive heating on the basis of the estimated chemical changes which are produced by γ-ray heating. Nevertheless, one cannot measure the importance of possible long-range effects at extremely low temperatures by the standards appropriate to ordinary temperatures and ordinary defects, and we cannot help having reservations concerning this subject.

The evidence offered by Kurti and Simon[17] concerning the absence of delayed heat evolution from the excited states of crystals is certainly the best available but is not sufficiently detailed to be convincing. If the rate of delayed heat evolution did not change much with time, it would be included with the temperature drift due to heat leak, and the heat capacity measurements would be approximately correct. The plain facts are that no one has made very accurate measurements of heat capacity below 1°K, and we anticipate a great deal of difficulty in future measurements of this sort. Calorimetry does not become accurate until the experimenter has enough data to predict, on the basis of reproducibility, the exact amount of heat leak corresponding to the temperature difference between a calorimeter and its surroundings. At higher temperatures this makes it possible to check true equilibrium in terms of the calculable drift. The work in this laboratory has made use of the most sensitive thermometry available, but the various difficulties connected with measurements near 1°K have not enabled the use of our ordinary calorimetric procedures. One straightforward type of experiment to dispose of the question of delayed heat emission, after irradiation ceased, would be to irradiate a cooled and thermally isolated sample for a long time and arrange to stop the radiation when the sample exactly reached the temperature of a surrounding bath. Its temperature should not increase further if the excited states are stable. Platzman points out that each substance will have its own specific properties with respect to the conversion of radiation to thermal energy, and Kurti and Simon restrict their comments to the "substances employed so far." The necessity of investigating the stability of excited states in the case of each substance may not be a major handicap, but it certainly detracts somewhat from the value of the method.

Gamma-ray heating has an advantage over the magnetic relaxation method in that it can be used in strong magnetic fields. However, we believe that it has always been employed in connection with iron magnets rather than with solenoids when the sample was kept in a magnetic field. Giauque and Stout tried an unpublished experiment on γ-ray heating in their early work. The experiment was unsuccessful because they could not bring the radium source close enough to the sample which was enclosed in a solenoid magnet. Also it was not obvious how uniform irradiation could be obtained in a sample of desirable dimensions which was located within the solenoid. This latter difficulty has been minimized by experimenters using γ-ray heating by rotating samples of radium in positions which are carefully selected to improve uniformity of heating. This means that the radium must be located at an appreciable distance from the sample. This is not difficult in the case of a sample located in the pole gap of an iron magnet, but it is not obvious to us how one can afford to use the valuable volume inside a solenoid magnet in order properly to place and rotate the radioactive sources. If γ-ray heating is practicable only when the magnetized substance is in the gap of an iron magnet, the combination will seriously limit associated magnetic measurements, which are disturbed by the presence of iron.

There is another problem which can arise in the use of radioactive substances for heating. It will often, if not usually, be necessary to enclose the sample in some sort of container. Heat will be produced in the container as well as in the sample. Unless it can be arranged to make this effect of negligible proportion, the heat distribution problem will not have been avoided. If the sample and its enclosing vessel are not in equilibrium, any ordinary container material should increase considerably in temperature because of the very low heat capacity. Simon and his co-workers have so far by-passed this problem by avoiding the use of containers, but this will certainly not always be convenient or even practicable.

Many of the foregoing problems connected with γ-ray heating may be overcome, but we believe that much more work will be required before the method can be accepted as reliable.

Any conventional heater may be used to measure an increment of heat content between two low temperatures, even if the heater is not in equilibrium with a poorly conducting sample. For example, if heat is added immediately following demagnetization, and in sufficient amount to reach some temperature such as 0.5°K, then equilibrium will be attained. Similar experiments after adjacent demagnetizations will yield ΔQ at the very low temperature by difference. However, it would be experimentally inconvenient to re-establish the desired initial conditions before demagnetization after each heating to some temperature such as 0.5°K. If much time is required to add the larger increments of heat, the evaluation of heat leak may reduce the accuracy of the small increments, determined by difference.

We consider that none of the existing methods of introducing heat below 1°K is free from objections with respect to observations on a magnetic substance over the region of field and temperature accessible in adiabatic demagnetization experiments.

DETERMINATION OF THERMODYNAMIC TEMPERATURE WITHOUT INTRODUCTION OF HEAT IN THE REGION BELOW 1°K

Many of the laboratories equipped for magnetic research have typical iron yoke magnets which were acquired prior to the introduction of adiabatic demagnetization. They are indispensable for many purposes, but after they are used for adiabatic demagnetization, the sample and magnet are ordinarily separated to enable measurements of various sorts. For this reason most of the investigations below 1°K have unfortunately been restricted to the initial field condition. Perhaps as a result of the limitations of this experimental predicament, there seems to be a somewhat prevalent feeling that the utilization of Kelvin's definition of temperature requires that heat be added at the unknown low temperature T.

Kelvin's[18] own statement: "the absolute values of two temperatures are to one another in the proportion of the heat taken in to the heat rejected in a perfect thermodynamic engine working with a source and a refrigerator at the higher and lower of the temperatures respectively," has undoubtedly often conveyed the impression that the transfer of heat at both temperatures is a physical necessity in determining the temperature by this method. For example, de Klerk,[19] referring to the determination of temperatures below 1°K states, "··· the only fundamental method to measure temperatures is to make use of Kelvin's definition of the thermodynamic temperature: $dQ=TdS$. For temperature determinations based on this formula a measured amount of heat must be supplied to the salt···."

Platzman[16] states: "In research at temperatures below about 1°K, a major problem is the conversion of readily measured 'magnetic temperatures' to true thermodynamic temperatures. In one essential stage of this conversion···it is necessary to add heat at an ascertainable rate."

In view of the rather general impression that it is necessary to add heat at temperatures below 1°K and the above-mentioned difficulties of doing this accurately, it seems desirable to point out that Kelvin's equation does not imply that heat must be added. As a matter of fact, this has been pointed out previously by Giauque[7] and by Giauque and MacDougall,[4] who state with respect to the treatment of their data on $GdPO_4(MoO_3)_{12}\cdot 30\,H_2O$: "Calculations of the type given above will permit the determination of the low temperatures without the necessity of energy input in the region below 1°K. In fact the curves through the calculated temperatures···checked the initial upper temperatures within a few hundredths of a degree···. It is evident that the lower temperatures could have been based on the measured upper temperatures and heat content data determined from the magnetic observations." They also add that "the above method should prove of importance in avoiding the slow equilibrium which accompanies energy input by means of a heater." The remarks of Giauque and MacDougall are somewhat obscured by their brevity in an otherwise rather long paper, so that it seems desirable to enlarge on this subject.

The only requirement in the application of Kelvin's equation for the determination of absolute temperature is that there should be some experimental method of measuring the heat content H and the entropy S at every point in the region investigated. $H=E-\mathbf{HI}$, where E is the internal energy and $\mathbf{H}$ and $\mathbf{I}$ are the field strength and intensity of magnetization, respectively. For a process at constant magnetic field, $dH=dQ$.

Thus

$$T=(\partial H/\partial S)_{\mathbf{H}}$$

$$TdS=dH+\mathbf{I}d\mathbf{H},$$

and since the entropy can be kept constant during demagnetization,

$$\Delta H\Big|_1^2=-\int_1^2 \mathbf{I}d\mathbf{H}.$$

This means that if the relative heat content can be ascertained at temperatures above 1°K, it can be determined at any point reversibly accessible below 1°K without the introduction of heat, since the paths are all isentropies with known entropies which can be determined above 1°K. Magnetic measurements can be made in a short interval before heat leak can interfere, and if necessary the sample can be given intermediate remagnetizations to insure equilibrium before additional measurements are made. When the sample and magnet are in a static arrangement, the interval before a magnetic measurement may be made quite short, whereas the time required for the separation of magnet and sample will considerably lengthen the time of heat leak prior to a measurement. This is only one of the several reasons why iron-free solenoid magnets, rather than iron yoke magnets, should be used for most adiabatic demagnetization work. The demagnetization process must be reversible, but this is true whether heat is to be added at low temperatures or not. Fortunately most of the paramagnetic systems appear to be exceptionally reversible in the thermodynamic sense. In some cases where hysteresis effects develop at limiting low temperatures, the application of thermodynamics is of dubious value, regardless of the method.

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[18] *Mathematical and Physical Papers, Thompson (Kelvin)* (Cambridge University Press, London, 1882), Vol. 1, p. 235.

[19] D. de Klerk, Phys. Today **6**, 4 (1953).

THE PLACE OF THE CARBON THERMOMETER-HEATER IN FUTURE EXPERIMENTAL WORK

The amorphous carbon thermometer-heater has been developed in this laboratory with the above facts in mind, and it is of interest to show how it fits into the experimental situation.

Any complete investigation of the magnetic substances of interest in connection with adiabatic demagnetization should provide an accurate measurement of the initial temperature and field in the region near 1°K or above. The substance will be thermally isolated prior to demagnetization, and thus only the adiabatic differential magnetic susceptibility, $(\partial\mathbf{I}/\partial\mathbf{H})_S$, can be measured. This quantity is of practically no direct use in denoting temperature,[7,20] not only because it is usually very small in large fields, but because a given value does not correspond to a specific temperature. Carbon thermometers may be designed[21] for very high sensitivity in any low-temperature range, and they have a rather small field coefficient which can be evaluated. Moreover they can be used with high accuracy for absolute entropy determinations by means of heat input near 1°K where thermal equilibrium is excellent. The entropy change during magnetization is now ordinarily calculated from assumed ideal magnetic behavior above 1°K, but this is a temporary expedient which must be replaced by actual entropy measurements before such work proceeds much further.

The values of heat content for the same initial fields and temperature may be calculated from the isothermal equation:

$$\Delta H = T\Delta S - \int_0^{\mathbf{H}} \mathbf{I}d\mathbf{H}.$$

The values of **I** may be determined by means of the relation,

$$\mathbf{I} = \int_0^{\mathbf{H}} (\partial\mathbf{I}/\partial\mathbf{H})_S d\mathbf{H},$$

since values of the adiabatic susceptibility may be measured along the magnetization paths from low temperatures. It is, of course, necessary to show that there is no remanent magnetism at the temperature where the evaluation of **I** begins. However, this may be done readily. If the remanent magnetism is present as an equilibrium state, which will probably be rare, its evaluation will give the integration constant. If non-equilibrium remanent magnetism exists, it is unlikely that reliable values of thermodynamic temperature can be determined from such a substance by any method, since the entropy will not be known.

In measuring $(\partial\mathbf{I}/\partial\mathbf{H})_S$ it is necessary that any container used should have a negligible heat capacity to prevent irreversibility, which will occur when the field is varied if this condition is not met. Fortunately, rather substantial containers of glass and other materials can be used in the region below 1°K without contributing appreciably to the heat capacity of the system. Perhaps it should be pointed out that this is a necessary condition during any demagnetization, if it is to be assumed that the process is isentropic; and, regardless of the experimental method, this is the only way in which the entropy of the material may be evaluated at very low temperatures in terms of reference points near 1°K. It is of interest to note that the values of $(\partial\mathbf{I}/\partial\mathbf{H})_S$ become so small at high fields that most of the value of the integral used to evaluate **I** results from measurements obtained at fields ranging up to a few thousand oersteds. These are within range of storage battery operation of iron-free solenoid magnets. The resultant steady field permits relatively high accuracy when a null point fluxmeter method is used. We prefer a method of this essentially static sort in connection with the application of thermodynamics since complete equilibrium is more likely to be attained. The low accuracy obtainable with conventional ballistic galvanometers is inappropriate to the methods discussed here. Iron magnets cannot be used since the presence of large masses of ferromagnetic material prevents accurate measurements of the aforementioned type.

Giauque and MacDougall[4,7] also pointed out that the entropy and heat content changes accompanying isothermal magnetization near 1°K could be obtained from the magnetic data alone, without measured additions of heat at the upper temperatures. This can be done by means of the relation

$$\Delta S\Big|_0^{\mathbf{H}} = \int_0^{\mathbf{H}} (\partial\mathbf{I}/\partial T)_{\mathbf{H}} d\mathbf{H}.$$

They showed experimentally that this could be done with satisfactory accuracy in a specially favorable case, but it is obvious that this method, which involves taking the temperature coefficient of an integral derived from the magnetic data, will be less accurate than the one suggested here. This involves the use of **I** rather than its derivative with temperature.

This paper is not particularly concerned with the cooling of one sample by means of another for some purpose such as successive demagnetizations; however, it will be evident that the problems of thermal conduction in that case are very similar to but greater than those of the external heater. A heater may be attached directly to the sample, but the superconducting thermal switch used by Darby, Hatton, Rollin, Seymour, and Silsbee[22] involves a considerable length of wire to conduct heat from the magnetized source to the previously demagnetized sink for heat. In the present early stages of work on successive demagnetizations, one can hardly

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[20] W. F. Giauque, Proc. Intern. Congr. Refrig., 7th Congr., The Hague—Amsterdam **1**, 527 (1936).

[21] Geballe, Lyon, Whelan, and Giauque, Rev. Sci. Instr. **23**, 489 (1952).

[22] Darby, Hatton, Rollin, Seymour, and Silsbee, Proc. Phys. Soc. (London) **A64**, 861 (1951).

expect detailed experiments as a function of field as well as temperature on substances used in the lower stages. However, when improved technique permits such investigations, the general considerations given above will apply. Heat flow will always be necessary at the upper temperature of each demagnetization stage. If it is impracticable to make the heat flow in a reversible manner, the problem can still be solved if equilibrium values of the magnetic properties can be observed by taking a sufficient time.

In the case of single stage demagnetizations, an experimenter who has a solenoid magnet available has little reason for not making measurements in a field. The measuring equipment for making such observations is certainly not more complicated or expensive than that required in connection with heat introduction and associated magnetic observation in initial fields. Moreover, fluxmeter and bridge measurements can be made with great rapidity compared with those associated with heat input.

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Heat of Mixing of He^3 in He^4†

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The integral heat of mixing for an 8.6 percent solution of He^3 in He^4 at 1.0°K, measured by an adiabatic free-expansion process, is 0.17 cal/mol of solution. Combined with the free energy of mixing, obtained from vapor pressure data, this shows that at this temperature the bulk of the excess free energy of mixing is due to the heat of mixing.

We have demonstrated the existence of a large positive heat of mixing of He^3 in He^4 by adiabatically mixing the two liquids and observing the drop in temperature. A schematic diagram of the apparatus is shown in Fig. 1. Measured amounts of the two liquids were condensed in the two liquid cells at 1.02°K. The click seals on top and bottom of the He^3 cell (inner cell) were broken by lowering a fine tungsten wire, and the temperature of the mixture measured by recording the pressure on an He^3 vapor pressure thermometer inserted in the He^4 sample. From the variation of thermometer pressure with time, Fig. 2, a minimum temperature of 0.78°K[1] was deduced. Measurement of the masses in the vapor phase showed the only process which could give a net absorption of energy on breaking the click seals was the mixing of the two liquids.

A semiquantitative measurement of the value of the heat of mixing in terms of the latent heat of vaporization of the He^3 was made by conducting the adiabatic mixing in an essentially isothermal manner. During the mixing process, the vapor pressure of the He^3 above the pure liquid drops to its partial pressure over the resulting solution; if the correct mass of He^3 is in the vapor phase at the start, the heat released by the condensation will just cancel the heat absorbed by the mixing of the liquids. Figure 3 gives a plot of the vapor pressures against time for this experiment, in which the apparatus for the first run has been modified by enlarging the vapor space above the liquid He^3. The upper curve, the pressure on the He^3 thermometer against time, shows that the liquid temperature dropped from 1.060 to 1.018°K in the first minute following mixing and then rose to its final value of 1.044 in another twenty minutes. (The final temperature is lower than the initial temperature because of a decrease of film flow on mixing.) From measurements of the pressure over the sample, shown in the lower graph, we see that by two minutes mixing is essentially complete, for after that the sample has the same warm-up rate as the He^3 thermometer.

Treating the mixing as an adiabatic constant volume process, one derives the following expression for the

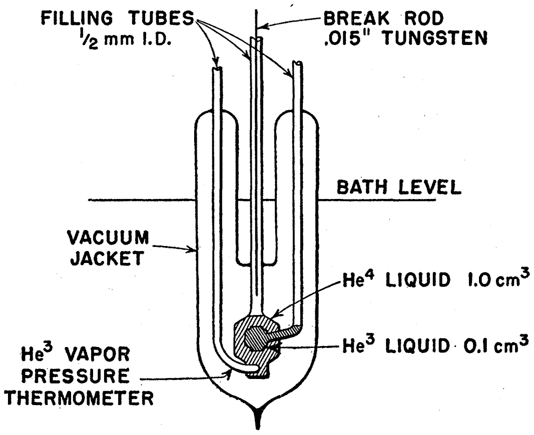

FIG. 1. He^3—He^4 sample cell.

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† This paper is based on work performed under University of California contract with the U. S. Atomic Energy Commission.

[1] Abraham, Osborne, and Weinstock, Phys. Rev. **80**, 366 (1950); extrapolation of Eq. (4).