[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Production of Temperatures below One Degree Absolute by Adiabatic Demagnetization of Gadolinium Sulfate

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This paper contains a description of the experimental methods and apparatus used in the initial demonstration of the feasibility of producing temperatures considerably below one degree absolute by adiabatic demagnetization of suitable paramagnetic substances. Two preliminary reports[2a,b] have been published elsewhere. More recently adiabetic demagnetization has been used to produce temperatures below one degree absolute by de Haas, Wiersma and Kramers[3,4] and by Kurti and Simon.[5] The experiments described in this paper cover only the work of the first half of the year 1933 and many later results will appear shortly.

The idea of utilizing the thermal effects associated with magnetization for producing these low temperatures was first proposed by Giauque.[6] Debye[7] has independently arrived at similar conclusions. Briefly, the method depends on the fact that any substance whose magnetic susceptibility, χ, varies with temperature exhibits a thermal effect on magnetization. The entropy change is given by the thermodynamic relation,

$$\left(\frac{\partial S}{\partial \mathbf{H}}\right)_T = \mathbf{H}\left(\frac{\partial \chi}{\partial T}\right)_{\mathbf{H}} \qquad (1)$$

where S represents entropy and $\mathbf{H}$ the magnetic field strength.

In the normal case Curie's law

$$\chi T = \text{constant} = C \qquad (2)$$

is obeyed approximately and heat is evolved during isothermal magnetization. However, quantum statistical situations are readily imaginable where the application of a field would produce cooling. In fact magnetic susceptibilities which decrease with decreasing temperature are experimentally known in several substances. While such cases are of interest and perhaps of experimental importance, it is the former type which has been utilized in the work described here.

From Equations 1 and 2

$$\Delta S = -\frac{C}{2T^2}(\mathbf{H}_2^2 - \mathbf{H}_1^2) \qquad (3)$$

One may observe that ΔS is 10^5 times larger near one degree absolute than at ordinary temperatures. It may be shown that the constant C is roughly proportional to the square of the atomic magnetic moment for larger values of this quantity. It should be emphasized that Equation 3 is very approximate since even in the ideal case the susceptibility is dependent on field strength. However, the above is useful in gaining a sense of proportion about the factors involved in the process.

$Gd_2(SO_4)_3 \cdot 8H_2O$ was used for the first measurements because this substance has been subjected to many careful and extensive magnetic investigations by Kamerlingh Onnes and his co-workers.[8] They have shown that this substance obeys Curie's law from ordinary temperatures to 1.3°K. within the limits of experimental measurement. In particular, the measurements of Woltjer and Kamerlingh Onnes[8e,f] were of great interest since they investigated the approach to saturation at liquid helium temperatures. These measurements and their thermodynamic and quantum interpretation have been discussed by Giauque,[6b,c] who also calculated the theoretical entropy of magnetization. Giauque and Clark[9] determined the heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ down to 14°K. From these measurements it may be shown that what may be called the ordinary heat capacity is negligible below one degree absolute.

From the data mentioned above it is evident that we have to deal with a system in which the effects are, to a high degree of approximation, due to the gadolinium atoms alone and their interactions on each other. That these interactions will occur sufficiently to destroy the ideal char-

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(1) Shell Research Fellow, academic years 1930–1931, 1932–1933.

(2) (a) Giauque and MacDougall, *Phys. Rev.*, **43**, 768 (1933); (b) **44**, 235 (1933).

(3) De Haas, Wiersma and Kramers, (a) *Physica*, **13**, 175 (1933); (b) *Nature*, **131**, 719 (1933); (c) *Naturwiss.*, **21**, 467 (1933); (d) *Comp. rend.*, **196**, 1975 (1933); (e) *Physica* (New Series), **1**, 1 (1933).

(4) De Haas, (a) *Nature*, **132**, 372 (1933); (b) *Naturwiss.*, **21**, 732 (1933).

(5) Kurti and Simon, (a) *Nature*, **133**, 907 (1934); (b) *ibid.*, **135**, 31 (1935).

(6) (a) Presented by Professor W. M. Latimer, California Section, American Chemical Society, April 9, 1926; (b) Giauque, THIS JOURNAL, **49**, 1864 (1927); (c) **49**, 1870 (1927).

(7) Debye, *Ann. Physik*, **81**, 1154 (1926).

(8) (a) Kamerlingh Onnes and Perrier, *Comm. Phys. Lab. Univ. Leiden* No. 122A; (b) Kamerlingh Onnes and Oosterhuis, *ibid.*, No. 129B; (c) Kamerlingh Onnes, *ibid.*, No. 140D; (d) Woltjer, *ibid.*, No. 167B; (e) Woltjer and Kamerlingh Onnes, *ibid.*, No. 167C; (f) Breit and Kamerlingh Onnes, *ibid.*, No. 168C.

(9) Giauque and Clark, THIS JOURNAL, **54**, 3135 (1932).

acteristics of the system above 0°K. is a necessary consequence of the third law of thermodynamics.[6c] Simon and Kurti[10a,b] have measured the heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ at the temperatures of liquid helium and the results indicate that the gadolinium atoms have sufficient interaction to produce a marked effect even above one degree absolute.

Experimental Apparatus.—From the first it was evident that the method rested on such a firm thermodynamic basis that all apparatus was designed, not merely with the idea of producing low temperatures, but to enable other investigations to be carried on in a considerable volume cooled to low temperatures.

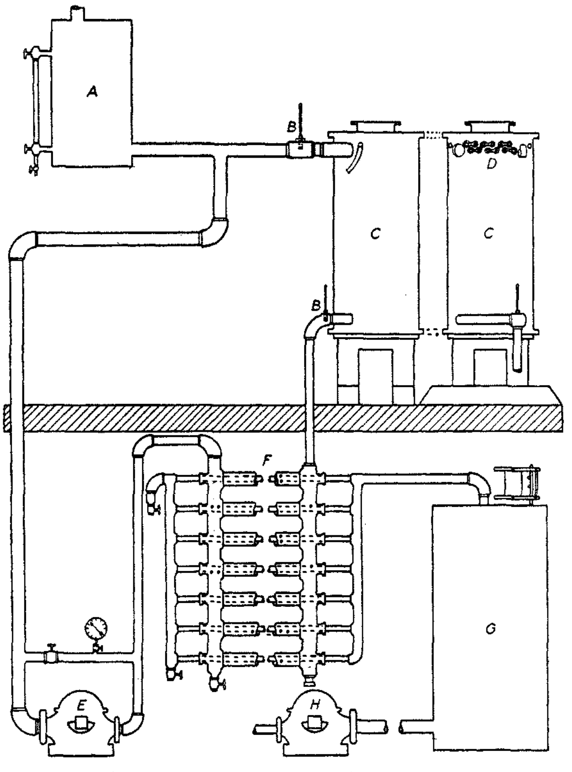

Fig. 1.—Magnet and cooling system.

It was very desirable to be able to subject a comparatively large volume to a very homogeneous and constant magnetic field for long periods of time. Despite the advantages connected with the concentrating effect of iron cores in magnets it was decided that we could best meet the above requirements by eliminating all ferromagnetic construction materials. The solenoid type magnet with an adequate cooling system meets all of the requirements in a very satisfactory manner. At low fields the power requirement is considerably larger than for the iron core type but as the field is increased to large values this disadvantage of the solenoid type magnet rapidly disappears.

The arrangement of magnet and cooling system is shown in Fig. 1. The magnet, C, is shown both in side and back view. The terminals, D, for the six independent electrical circuits are shown in the back view. They may be connected in any series or parallel combination. Each circuit is uniformly wound over the length of the solenoid. Each of the six circuits is of equal resistance. This is accomplished by having layers of smallest diameter and layers of greatest diameter in the same circuit, layers of next smallest diameter in series with the layers of next largest diameter, etc. As the magnet is ordinarily used each conductor carries equal current. The conductors are of 5.2 mm. square copper and are uninsulated except for fiber strips and impregnated cord separators such as are used in transformer construction. The copper conductors were left bare in order that heat could be transferred readily to the cooling liquid. Kerosene was selected for cooling purposes because of its low viscosity. Twenty five cubic feet of kerosene per minute is delivered to a chamber at the bottom of the solenoid. The kerosene rises vertically and at a uniform rate throughout the cross section of the magnet, leaving the top at a pressure slightly above atmospheric. It then flows to the intake of a centrifugal pump, E, located one floor below the magnet and is delivered at a pressure of seventy pounds per square inch to a typical concentric pipe cooling system, F, supplied with cooling water. The cooling water is discharged into a tank G, Fig. 1, and at intervals is automatically pumped back by centrifugal pump, H, into the main from which it came, but at a point beyond the intake. This economy is possible due to a considerable water flow in a conveniently located main which is not used for potable water. The kerosene flows in the annular space between the pipes. A low pressure kerosene reservoir, A, Fig. 1, contains reserve supply and provides for thermal expansion. As the kerosene rises from the bottom to the top of the magnet its temperature is increased by about 4° for an input of 100 kw. The kerosene temperature is measured by means of thermometers, B, B, Fig. 1. The magnet design is such that the difference in temperature produces no effect on the equality of current flow in the several electrical circuits. This point is important because the arrangement preserves magnetic homogeneity and permits accurate field strength calculations from the geometry of the circuits.

The magnet is ordinarily operated at about 50° as a measure of economy in the size of the cooling system. Financial reasons limit the supply of direct current to 100 k. w. as 500 amperes at 200 volts. However, the magnet would readily permit the introduction of between 1000 and 2000 kw. An increased flow of kerosene could be produced easily and a many-fold larger temperature rise during passage of the kerosene through the magnet would not be objectionable. The heat interchange conditions between the copper conductors and the kerosene are so favorable that the introduction of 100 kw. produces a negligible temperature head between the copper and the bath. The introduction of much larger amounts of energy would cause no difficulty in this connection.

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(10) (a) Simon and Kurti, *Naturwissenschaften*, **21B**, 178 (1933); (b) Kurti, *Z. physik. Chem.*, **20**, 305 (1933).

The windings of the magnet are in the form of a hollow cylinder 91.4 cm. in length, with an outside diameter of 43.8 cm. and an inside diameter of 15.9 cm. They are enclosed in a case 111.8 cm. in length with oil spaces at each end. The upper oil space also provides for the electrical connections, all of which are made at the top. The case wall is constructed of copper 3.18 mm. in thickness; the ends are made of brass plates. The oil lines adjacent to the magnet are of brass to avoid disturbing magnetic effects. It may be of interest to remark here that these precautions have not been overdone. In recent work we have found it necessary to evaluate the effect of the reinforcing iron, piping, etc., of the building in connection with certain observations. The copper tubing in the center has a wall 3.18 mm. in thickness and allows a free diameter of 15.2 cm. for the entire length. The introduction of 100 kw. produces a field of 8000 gauss. Although the field strength drops rapidly at the ends the center portion is very uniform. Over a cylinder 12 cm. in length and 3 cm. in diameter the field averages less than five one hundredths of one per cent. below the value at the exact center.

Figure 2 shows the sample, consisting of 61 g. of $Gd_2(SO_4)_3 \cdot 8H_2O$, mounted in the center of the solenoid. The gadolinium contained 0.5% samarium and 1.5% terbium. The material was pressed in several sections to form a cylinder 12.0 cm. in length and 1.588 cm. in diameter at ordinary temperature. The cylinder fitted very closely into a glass container of the form shown. The glass tube was suspended in a brass tube, E, in such a manner that the sample could be raised or lowered by about 0.1 cm. by means of turning rod, A. The bottoms of both sample tube and brass tube were ground to 45° cones. Since the angle of the cone should be independent of the temperature, the sample could be brought into thermal contact with the bath without breaking the surrounding vacuum. The glass container was supported by means of a thin piece of boxwood at F. The rod for raising or lowering the sample was of fiber. Radiation shields are shown in the brass tube above the sample. The whole was arranged so that various samples could be inserted without disturbing the remainder of the apparatus. Above the sample is shown a container, D, for liquid hydrogen. H is a Pyrex Dewar for liquid helium. The whole was enclosed in a brass container which in turn was within another Pyrex Dewar, I. The outer Dewar was kept filled with liquid air. A coil, G, of 7549 turns of double silk covered No. 40 B. and S. gage copper wire was wound in 12 layers outside the brass tube. The coil, which was 12.0 cm. long, 2.38 cm. i. d. and 2.97 cm. o. d., was immersed in liquid helium. The sample and the coil G were of equal length, concentric and coaxial. The system for evacuating the space between the coil and the sample was attached at tube B.

While the first experiment in the apparatus described above was satisfactory it also indicated many possible improvements. One of these is connected with the use of Pyrex glass Dewars as containers for liquid helium. We were unaware of the rapid diffusion of helium gas through Pyrex which has been well known in other connections. For example, Urry[11] has found that Pyrex glass is about 500 times more permeable to helium than is Jena glass. However, this was not long in making itself evident through the diffusion of sufficient helium to spoil the vacuum in any Pyrex Dewar after one experiment. While most of this diffusion undoubtedly occurred at ordinary temperatures and probably could be avoided to some extent by having

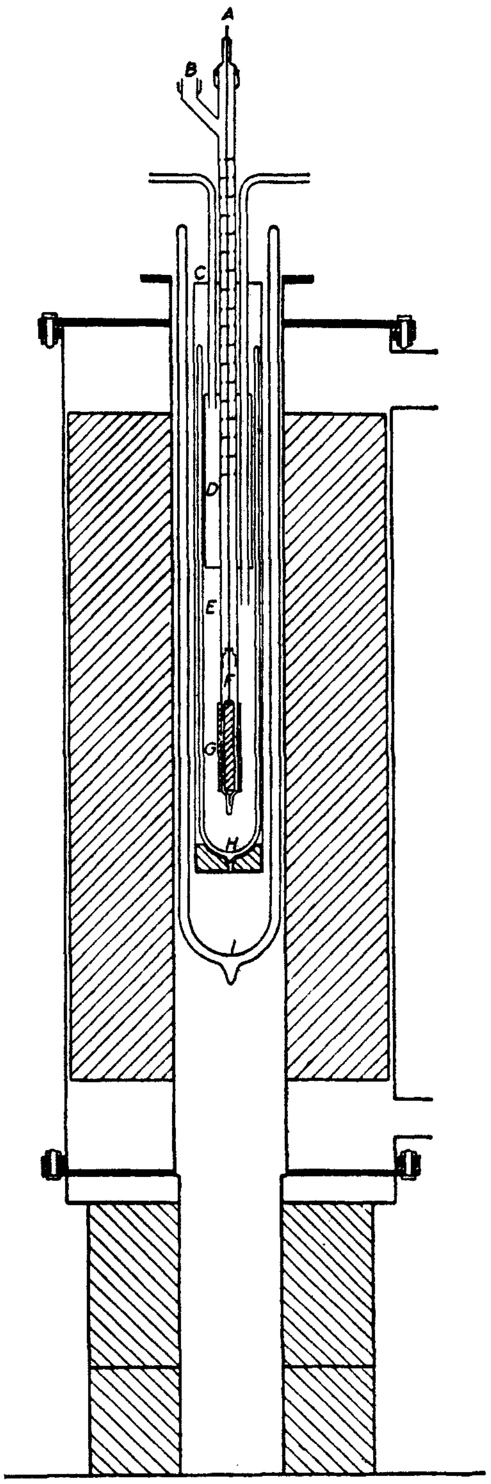

Fig. 2.—Adiabatic demagnetization apparatus.

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(11) Urry, This Journal, **54**, 5888 (1932).

helium gas in the apparatus only when it is at low temperatures, we have found it more convenient to replace the small Dewar, H, Fig. 2, with one of Jena glass, and to have evacuation lines attached to the large Pyrex Dewars, which are very useful in handling liquid helium in this Laboratory. Pumping of a Dewar vessel is unnecessary during an experiment.

The Measurement of Temperature.—When the reversible variation of any physical property can be used to produce low temperatures it will also supply a related method for measuring the temperatures produced. In the present case the measurement of magnetic susceptibility provides a simple and very sensitive thermometric scale. In this paper it will be assumed that Curie's law, $\chi T = C$, can be used to convert magnetic susceptibility into temperature. However, this assumption is unnecessary and in a following paper we will present an experimental demonstration of the determination of the true thermodynamic temperatures corresponding to various magnetic susceptibilities at temperatures below 1°K.

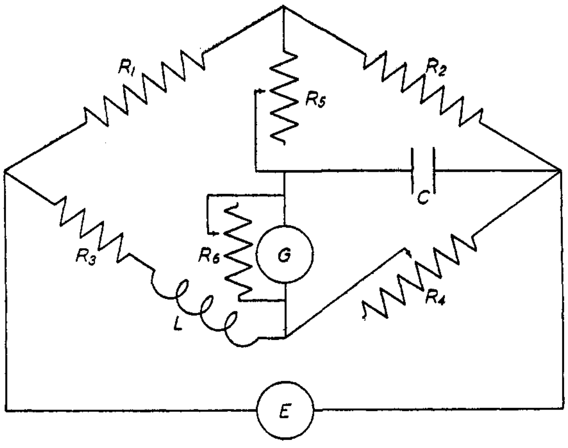

Fig. 3.—Anderson inductance bridge.

Of the several methods for measuring magnetic susceptibility one involving the measurement of the inductance of a coil surrounding the sample was selected. This method has the great advantage that glass lines, etc., can be attached to the stationary sample. When a coil of inductance L^0 is placed in a medium of magnetic permeability, μ, the inductance becomes

$$L = \mu L^0 \tag{4}$$

It is of course impossible to achieve this ideal case in practice and in the present experiments all of the space outside the coil, the coil volume, the container wall volume and a small vacuum space were of unchanging $\mu = 1$. This introduces a correction factor depending on the geometry of the arrangement and μ. This correction factor, f, is nearly constant and will be taken so for the present.

$$\mu = 1 + \frac{4\pi\chi}{V} \tag{5}$$

where $\frac{\chi}{V}$ is the volume susceptibility and

$$L = L^0\left(1 + \frac{f4\pi\chi}{V}\right) \tag{6}$$

L^0 can be obtained by measurement, at some convenient low temperature where χ is small enough to permit accurate correction. The temperature must be low enough so that the coil will not undergo further change in dimensions from thermal contraction. Time lag in contraction must be watched for in this connection. The temperature range of liquid hydrogen is suitable. In the case of Curie's law

$$L = L^0\left(1 + \frac{f4\pi\chi}{V}\right) = L^0\left(1 + \frac{f4\pi C}{TV}\right) \tag{7}$$

$$T = \frac{L^0 f4\pi C}{(L - L^0)V} = \frac{\text{const.}}{L - L^0} \tag{8}$$

The constant may be evaluated at any known temperature where $L - L^0$ is large enough to be accurately measurable. The liquid helium temperature range is convenient for this purpose. Since $L - L^0$ can be measured over the range 1–4°K. the above expression for temperature may readily be tested. In later work several gadolinium compounds have been used in comparisons against the vapor pressure of liquid helium and no appreciable deviation between the two temperature scales has been noted.

The inductance of the coil was measured by means of an Anderson bridge, using the method as described by Rosa and Grover.[12] The bridge is shown in Fig. 3, R_1, R_2 and R_3 are fixed resistances, R_4 and R_5 are variable resistances, and R_6 is to adjust the sensitivity of the alternating current vibration galvanometer or head phones, G. The fixed resistance, R_3, includes the small resistance which remains in the copper inductance coil at liquid helium temperatures. This small resistance is convenient in that little heat is developed in the liquid helium bath by passage of the measuring current. The source of alternating current is shown at E. C is a capacity. The inductance, L, of the measuring coil is given by the expression

$$L = CR_4\left[R_5\left(\frac{R_1}{R_2} + 1\right) + R_1\right] \tag{9}$$

The inductance bridge described above proved to be very satisfactory. Recently comparison with an inductance standard, calibrated to about 0.1% accuracy, showed that it measured to this absolute accuracy or better at frequencies over the range 60–1000 cycles. The precision was around two or three hundredths of one per cent.

A summarized description of three inductance coils is given in Table I. All of the wire was double silk covered copper and in each case this insulation was impregnated with bakelite lacquer. All coils were 12 cm. in length.

Table I

Inductance Coil Data

Coil	I	II	III
L^0, henries	0.2938	0.4162	0.3735
Turns	7547	....	7954
I. d., cm.	2.380	2.570	2.591
O. d., cm.	2.972	3.295	3.513
R, ohms, about 20°C.	2075	2500	1017
R, ohms, 1.5–4°K.	77	41	18
Wire size	40	40	36
Remarks	Unannealed, wound on brass tube	Annealed at 110°, wound on fiber	Annealed at 110°, wound on glass

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(12) Rosa and Grover, *U. S. Bur. Stand. Bull. Research*, **1**, 291 (1904–1905).

Experimental Procedure and Results.—The first experiment was carried out with coil I on the apparatus as described above and in Fig. 2. The 61 g. of $Gd_2(SO_4)_3 \cdot 8H_2O$ was enclosed with about 10^{-4} mole of helium gas in a sealed glass tube. Liquid hydrogen was placed in container D, Fig. 1, and finally the liquid helium was transferred until the apparatus was immersed. The liquid helium was transferred very easily through a vacuum-jacketed tube about four meters long. About half of the exterior of this tube was at or near room temperature. The liquid helium was produced in a liquefier of about seven liters per hour capacity. This liquefier will be described in a later paper.

The sample cooled very slowly as it approached the temperature of the helium bath and it soon became evident that the thermal contact through the conical bottom was not working satisfactorily. Helium gas which had been pumped from the space surrounding the sample before the addition of the liquid helium was readmitted. This greatly facilitated the cooling but there was evidence that the pressed crystalline gadolinium sulfate octahydrate had adsorbed most of the helium within the sample tube. A later experiment with a tube leading into the same sample showed that this had been the case and that cooling occurred very rapidly when a small amount of helium gas was present. Somewhat to our surprise, little difficulty was found in obtaining a vacuum better than 10^{-5} mm. in the insulating space at the temperatures of liquid helium and for this reason no further attempts were made to obtain thermal contact by means of the conical bottoms.

In the first exploratory experiment on March 19, 1933, the full field of about 8000 gauss was used in all cooling experiments. The liquid helium was boiling under a somewhat reduced pressure, the magnitude of which was not accurately known for most of the measurements. Cooling experiments were carried out at intervals between 3:00 A. M. and 9:50 A. M. In each case the field was applied, the heat developed was allowed to escape by means of a small pressure of helium gas in the insulating vacuum space, a vacuum was pumped and the current turned off. The first four trials were rather impatiently made at about ten-minute intervals and neither good equilibrium nor a good vacuum could be obtained in this total time. The temperatures produced were 0.72, 0.68, 0.67 and 0.65°K. The bath temperature, a short time after the above measurements, was read on a helium vapor pressure thermometer and found to be 3.2°K. (previously[2a] given as 3.4°K.). As mentioned above, the helium within the sample tube appeared to have been adsorbed so that equilibrium conditions were very unsatisfactory. On lengthening the time for equilibrium with the bath and for evacuation, temperatures obtained at about half-hour intervals were 0.612, 0.575, 0.554, 0.548, 0.540 and 0.530°K. At least part of the progressive lowering which occurred in successive measurements was due to a gradually lowering bath temperature. The bath temperature at the time of the first observations was probably about 4°K.

It was evident that much lower temperatures could be produced by lowering the starting temperature and that better thermal equilibrium was desirable.

The apparatus was altered by sealing a 3-mm. glass line to the sample tube. This not only permitted control of the gas pressure in the sample tube but allowed the vapor pressure of liquid helium to be accurately compared with the magnetic temperature scale. A better vacuum pump was connected to the liquid helium bath but otherwise the apparatus was left as in the first experiment. On April 8 the apparatus was again cooled and this time the sample approached the helium bath temperature with great rapidity.

Starting at a temperature of 1.8°K. (previously[2a] given as about 2°K.) and about 8000 gauss a temperature of 0.422°K. was obtained on reducing the field to zero. During this experiment a considerable amount of helium gas was in the sample tube and the connecting vacuum line. The condensation of this helium prevented a lower temperature, but of still greater interest was the fact that most of the helium did not condense. When the helium was pumped out, the same field and starting temperature produced a final temperature of 0.346°K. It became evident that in the experiment producing 0.422°K. the outer portion of the sample had condensed helium and as a result had not cooled very much while the interior, blocked off, and lacking a mechanism for rapid equilibrium cooled considerably. The temperature represented an average. That this explanation was correct was also shown by the fact that, when helium gas was admitted to the insulating space, it required sixteen minutes to warm the sample to the bath temperature 1.81°K. In later work, with small crystals, the time of warming in a similar experiment would be about a minute. The above explanation was also substantiated by other cooling experiments with various amounts of helium gas present and as a result experiments with the pressed crystalline material were discontinued after April 9. It appears that the very high pressure used in making the cylindrical sample had fractured the material into countless small pieces, thus increasing adsorption surface and also making thermal conduction very difficult. No such evidence of these conditions has been observed in later work with small crystals of several substances.

The Absence of Hysteresis.—Several other results of interest were obtained with the pressed material used in the measurements of April 8–9. The sample was cooled to 0.399°K. and allowed to warm slowly. It required about ninety minutes to reach the bath temperature of 1.8°K. During the warming a 60-cycle current was allowed to flow through the measuring coil for some time and was then turned off for a similar interval. No change in warming rate was observed. The field at the maximum of each sine wave was about 52 gauss and it is possible to state that of the energy, $\chi \mathbf{H}^2_{\text{max.}}/2$, temporarily withdrawn from the maximum field by the substance, less than 0.01% was converted to heat by possible magnetic hysteresis or eddy currents.

To obtain still lower temperatures a small amount of helium was liquefied in the sample tube. Then by evacuating the insulating space and pumping on the helium in the sample tube a starting temperature of 1.5°K. was obtained with the field at about 8000 gauss. Although liquid helium remained in the sample tube, a temperature of 0.277°K. was reached. Further pumping to remove the liquid helium permitted attainment of a temperature of 0.250°K. on each of two final trials. The sample required forty-five minutes to warm from 0.25 to 0.35°K.

In order to obtain a comparison of the magnetic and helium vapor pressure[13a,b] temperature scales, the vapor pressure of the liquid helium in the sample tube and the magnetic susceptibility were measured simultaneously near 1.5°K. Although the helium bath had nearly all evaporated by this time, thus causing a rather bad heat leak, it was possible to compare the temperatures obtained near 1.5°K. The constant had been set at the boiling point of helium. The two thermometers agreed to about 0.01°, which was well within the limit of accuracy of this measurement.

Principally as a result of difficulty in the observations on the slow warming rate of the sample, it was decided to dispense with the brass tube enclosing the insulating vacuum space. To make the reasons clear we will return to the discussion of the inductance bridge. In balancing the bridge both R_4 and R_5 must be adjusted. R_3 includes the inductance coil resistance. The inductance coil resistance consisted not only of the direct current resistance but also of an additional resistance depending on the eddy current loss in the brass tube. Since the eddy current loss in the brass tube varied with the permeability of the sample, R_3 was a function of the sample temperature. It is very desirable to have only one variable, especially when a warming rate is being taken, as it permits increased rapidity and accuracy of measurement. This was accomplished by replacing the brass tube with one of glass. Metal tubes have the advantage of space economy and accuracy of dimension but the simplification of measurement with the glass apparatus has led to its use in all of our recent work.

The coil described as II in Table I was wound on thin fiber tubing which could be slipped over the exterior of the glass apparatus. It was hoped that this coil could be used on several different pieces of apparatus. It was not very satisfactory due to warping and large contraction during cooling which eventually caused electrical breakdown. However a number of interesting measurements were made with it.

In a run of April 29–30 the first measurements to show the dependence of cooling on field intensity were carried out. The apparatus was of the same type as before but the sample tube was filled with 51.5 g. of small crystals of $Gd_2(SO_4)_3 \cdot 8H_2O$ instead of the pressed material previously used. A small glass line permitted helium to be admitted to the sample tube and also allowed vacuum evaporation of helium which could be liquefied within the sample tube. The starting temperature in each case was about 1.36°K. A small amount of liquid helium was present in the sample tube. These preliminary results are given in Table II.

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(13) (a) *Comm. Phys. Lab. Leiden*, 202b; (b) 202c.

TABLE II

TEMPERATURES OBTAINED BY ADIABATIC DEMAGNETIZATION FROM 1.36°K. AND FIELD **H**

H, gauss	4575	6200	6860	7920	7920	7920
T, °K.	0.492	0.346	0.315	0.258	0.260	0.258

Following these measurements the magnetic and helium vapor pressure thermometers were compared at 1.25°K. The magnetic thermometer which had been set at the boiling point of helium read 0.03° higher at this temperature.

As had been expected, the elimination of the brass tube permitted the inductance bridge to be balanced by adjusting the one variable R_5. The resistance of the copper coil does not change appreciably in the liquid helium temperature range.

In a run on May 3–4 an attempt was made to obtain information from measurements of the effect of applying a small field at various initial temperatures. The results are given in Table III. There was no appreciable amount of helium in the sample tube.

TABLE III

THE EFFECT OF SMALL MAGNETIC FIELDS ON $Gd_2(SO_4)_3 \cdot 8H_2O$ AT VARIOUS TEMPERATURES

Initial T, °K.	$\chi_{\mathbf{H}=0}$ $^1/_2$ mole	Applied field, gauss	$(\partial I/\partial \mathbf{H})_S$ at **H** $^1/_2$ mole
	Series I		
0.373	21.00	398	15.34
.423	18.49	405	13.75
.478	16.36	403	12.36
.554	14.12	405	10.83
.683	11.46	416	9.00
.854	9.17	418	7.36
1.115	7.02	420	5.83
1.504	5.21	433	4.46
2.069	3.78	431	3.38
2.759	2.84	436	2.59
	Series II		
0.472	16.58	270	14.51
.546	14.34	261	12.80
.662	11.82	261	10.67
.874	8.96	258	8.21
1.338	5.85	258	5.45
	Series III		
0.442	17.71	386	13.85
.520	15.06	372	12.25
.611	12.81	371	10.59
.752	10.41	359	8.78
.966	8.11	356	7.02
1.294	6.05	351	5.44
1.778	4.40	349	4.02
2.464	3.18	348	2.98

The measurements of Series III are probably more reliable as the field was obtained by using storage cells in this case. Series I and II were made while current was being supplied from the University direct current system. The fluctuations in this current caused some loss of accuracy of the bridge due to the resulting e. m. f. induced in the measuring coil.

Differential Magnetic Susceptibility.—Before using the data given in Table III we wish to make a few remarks concerning the meaning of the measurements. Magnetic susceptibility is ordinarily defined as $I/\mathbf{H}$. This is not a very useful quantity except for the limiting case where I is small and proportional to **H**. In a thermodynamic treatment the differential susceptibility $dI/d\mathbf{H}$ is of much greater importance. When $dI/d\mathbf{H}$ is measured by means of an alternating field of sufficiently high frequency, adiabatic magnetizations and demagnetizations occur and in case the system is thermally isolated the effect must be adiabatic regardless of frequency. Our measurements then are $(\partial I/\partial \mathbf{H})_S$. When entropy is held constant in such a system, any alteration in what may, rather inexactly, be called the magnetic entropy must be compensated by an equal and opposite change in entropy resulting from other degrees of freedom. At temperatures where the vibrational degrees of freedom are excited, magnetic effects are so small in comparison that $(\partial I/\partial \mathbf{H})_S$ is closely equal to $(\partial I/\partial \mathbf{H})_T$. At another extreme is the ideal magnetic system without heat capacity. Here the intensity of magnetization and the entropy each depends on the magneton distribution with reference to the external field. Thus $(\partial I/\partial \mathbf{H})_S = 0$. When magnetic atoms interact with crystal fields or with each other as well as with the external field a given intensity of magnetization does not define the entropy. This latter situation is the one that exists in gadolinium sulfate hydrate below a few degrees absolute. The resulting $(\partial I/\partial \mathbf{H})_S$ is determined by magneton interactions that are probably not of a very simple kind and in any case are unknown. It may be noted that at these temperatures the ordinary vibrational degrees of freedom are so nearly inactive that they produce no appreciable effect. As zero field is approached, thermal effects accompanying the small oscillations of the measuring field produce a negligible change in temperature and $(\partial I/\partial \mathbf{H})_S$ approaches equality with $(\partial I/\partial \mathbf{H})_T$. This fact permits adiabatic measurements of initial susceptibility to be related to Curie's law which, of course, holds only for the initial $I/\mathbf{H}$ slope. The measuring field ordinarily was about 3 or 14 gauss. We are now ready to show how such measurements as those in Table III may be related to other thermodynamic properties.

The Determination of Temperature in a Magnetic Field.—As an illustration we will calculate the change in temperature which occurs when gadolinium sulfate is magnetized adiabatically. The first two laws of thermodynamics yield the equation

$$TdS = dE + PdV - \mathbf{H}dI \qquad (10)$$

It has previously[6b] been convenient to define the heat content

$$H = E + PV - \mathbf{H}I \qquad (11)$$

Since pressure effects are negligible in the present connection, we will drop the P, V terms.

For a process at constant entropy

$$dE = \mathbf{H}dI \qquad (12)$$

and

$$\Delta E = \int \mathbf{H}\left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} \qquad (13)$$

also

$$\Delta I = \int \left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} \qquad (14)$$

$$H = E_{\mathbf{H}=0} + \int_0^{\mathbf{H}} \mathbf{H}\left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} - \mathbf{H}\int_0^{\mathbf{H}} \left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} \qquad (15)$$

and

$$T = \frac{dE - \mathbf{H}dI}{dS} = \left(\frac{\partial H}{\partial S}\right)_{\mathbf{H}} \qquad (16)$$

It is evident that measurements of energy, entropy and differential susceptibility determine the temperature on the thermodynamic scale. As stated above, we will leave a complete experimental treatment of this matter for a later paper. Here we will show how the Curie scale for initial susceptibilities may be extended, without further assumption, to apply in the presence of a magnetic field.

For the special case $\mathbf{H} = 0$

$$T_{\mathbf{H}=0} = \left(\frac{\partial E}{\partial S}\right)_{\mathbf{H}=0} \qquad (17)$$

at field $\mathbf{H}$

$$T_{\mathbf{H}} = \left(\frac{\partial E_{\mathbf{H}=0}}{\partial S}\right)_{\mathbf{H}} + \left(\frac{\partial\left[\int_0^{\mathbf{H}} \mathbf{H}\left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H} - \mathbf{H}\int_0^{\mathbf{H}}\left(\frac{\partial I}{\partial \mathbf{H}}\right)_S d\mathbf{H}\right]}{\partial S}\right)_{\mathbf{H}} \qquad (18)$$

In the present case the three terms of Equation 18 may be written

$$T_{\mathbf{H}} = T_{(\text{Curie's law}, \mathbf{H}=0)} + \Delta T_{(\text{Due to } \mathbf{H})} \qquad (19)$$

In Table IV the summarized results of the heat content calculations are given. All energies are in millicalories per one-half mole of $Gd_2(SO_4)_3 \cdot 8H_2O$. The temperatures given in the first column refer to the case where $\mathbf{H} = 0$ and mark the starting points of isentropic paths to which the several values of energy and heat content apply. One 15° calorie was taken equal to 4.185 joules.

TABLE IV

CHANGE OF ENERGY AND HEAT CONTENT DURING ADIABATIC MAGNETIZATION OF ONE-HALF MOLE OF $Gd_2(SO_4)_3 \cdot 8H_2O$

		Energy in 10^{-3} calories			H in gauss	
Initial T $\mathbf{H} = 0$	$I\mathbf{H}$ $\mathbf{H} = 100$	ΔE 0 to 100	ΔH 0 to 100	$I\mathbf{H}$ $\mathbf{H} = 200$	ΔE 0 to 200	ΔH 0 to 200
0.4	4.600	2.285	−2.315	17.98	8.90	−9.08
.5	3.692	1.836	−1.856	14.47	7.14	−7.33
.6	3.082	1.534	−1.548	12.10	5.98	−6.12
.7	2.641	1.318	−1.323	10.41	5.15	−5.26
.8	2.318	1.154	−1.164	9.13	4.52	−4.61
.9	2.064	1.028	−1.036	8.14	4.03	−4.11
1.0	1.859	0.926	−0.933	7.34	3.63	−3.71
Initial T $\mathbf{H} = 0$	$I\mathbf{H}$ $\mathbf{H} = 300$	ΔE 0 to 300	ΔH 0 to 300	$I\mathbf{H}$ $\mathbf{H} = 400$	ΔE 0 to 400	ΔH 0 to 400
0.4	39.36	19.20	−20.16	67.80	32.50	−35.30
.5	31.72	15.48	−16.24	54.75	26.83	−27.92
.6	26.59	12.99	−13.60	45.88	22.10	−23.78
.7	22.90	11.21	−11.69	39.53	19.10	−20.43
.8	20.12	9.86	−10.26	34.82	16.83	−17.99
.9	17.94	8.81	− 9.13	31.10	15.07	−16.03
1.0	16.20	7.96	− 8.24	28.11	13.65	−14.46

In order to compute the change of temperature on adiabatic magnetization, it is necessary to know the entropy which characterizes each of the isentropic paths. To obtain this a series of adiabatic cooling measurements was made. Coil III was used. In each case the starting field and the bath temperature were known. From the entropy change on magnetization which has been given previously,[3c,b] it was possible to compute the difference in entropy between the bath temperature and any obtainable low temperature. The data are summarized in Table V. In the last column the entropies are given in terms of the entropy below that possessed by the solid at 1°K. Some such convention will be necessary in work of this sort since differences of entropy can easily be measured much more accurately than the absolute entropy is likely to be known. The data have been presented graphically in the preliminary publication.[2b]

Table VI contains a summary of the changes in temperature and differential magnetic susceptibility along constant entropy lines. The entropy values referred to 1°K. are given in the second column. Although the Curie temperatures given in the first column may require later correction, this will not affect any of the other values in the table. These rest on thermodynamics without additional assumption.

TABLE V

THE CHANGE OF ENTROPY WITH TEMPERATURE FOR ONE-HALF MOLE OF $Gd_2(SO_4)_3 \cdot 8H_2O$

T_{Bath}	H_{gauss}	χ_{Final}	T_{Curie}	ΔS cal./deg.	$S_{1°K.} - S_T$
1.735	4490	14.40	0.543	0.527	0.488
1.722	2630	9.29	.843	.204	.066
1.720	5210	16.49	.475	.683	.545
1.710	8000	24.59	.319	1.265	1.128
1.700	7840	24.31	.322	1.243	1.107
1.690	6170	19.48	.402	0.902	0.767
1.700	6040	19.10	.410	.866	.730
1.715	3250	10.96	.713	.305	.168
1.715	1700	6.74	1.162	.092	− .045
1.720	1960	7.68	1.019	.118	− .020
1.722	1520	6.44	1.215	.073	− .065
1.718	7800	23.92	0.327	1.217	1.080
1.708	3050	10.61	.737	0.273	0.136
1.740	2250	7.91	.990	.151	.011
1.760	1030	5.46	1.434	.038	− .103
1.732	1650	6.82	1.148	.094	− .045
1.740	2510	8.88	0.882	.185	.046
1.745	3820	12.50	.626	.395	.255
1.495	2450	10.25	.764	.232	.118
1.497	2480	10.28	.762	.237	.123
1.499	7660	27.25	.287	1.407	1.292

TABLE VI

CHANGE OF TEMPERATURE AND DIFFERENTIAL MAGNETIC SUSCEPTIBILITY DURING ADIABATIC MAGNETIZATION BY LOW FIELDS

T Curie	$S_{1°K.} - S_T$ cal./deg. per one-half mole	H = 0 $(\partial I/\partial H)_S$	H = 100 $(\partial I/\partial H)_S$	ΔT	H = 200 $(\partial I/\partial H)_S$	ΔT	H = 300 $(\partial I/\partial H)_S$	ΔT	H = 400 $(\partial I/\partial H)_S$	ΔT
0.4	0.766	19.58	18.88	0.00149	17.86	0.0060	16.74	0.0130	14.36	0.021
.5	.477	15.66	15.19	.00163	14.44	.0063	13.54	.0138	11.96	.023
.6	.290	13.05	12.70	.00180	12.12	.0069	11.39	.0149	10.27	.024
.7	.172	11.19	10.92	.00190	10.46	.0075	9.86	.0167	8.95	.030
.8	.089	9.79	9.58	.00213	9.20	.0086	8.70	.0192	7.97	.031
.9	.036	8.70	8.53	.00270	8.22	.0104	7.83	.0238	7.18	.044
1.0	.000	7.83	7.70	.00263	7.43	.0100	7.05	.0222	6.54	.038

The values of ΔT in Table VI were calculated by means of the last term of Equations 18 and 19. As an example we may read from the table that the temperature changes from 0.5 to 0.5138°K. when the field is changed from 0 to 300 gauss at constant entropy. At the same time the differential susceptibility changes from 15.66 to 13.54.

The Heat Capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$.—The heat capacity of gadolinium sulfate octahydrate may be obtained from the data in Table V and the equation

$$\frac{dS}{d \ln T} = C \qquad (20)$$

The entropy values were plotted against the logarithm of temperature and the slopes read off. The results are given in Table VII.

The heat capacity appears to be going through a maximum at about 0.3°K. This rise in heat capacity was to be expected since magnetic interactions of the gadolinium atoms on each other give rise to energy differences which are comparable with kT at these temperatures. We have previously[2b] given a brief account of the results of a calculation based on the assumption that pairs of gadolinium atoms interact but that interaction between pairs can be neglected. Such a theory represents our entropy and heat capacity results quite well not only in form but in order of magnitude. However, we feel certain that other interaction assumptions would represent the data at least equally well.

It is quite possible that a portion of the heat capacity may be due to interaction between the electron spin and the nuclear magnetic moment in the case of one or more gadolinium isotopes. Some energy splittings obtained from nuclear fine structure observations are of the right order of magnitude to produce observable effects at the temperatures concerned. However, nothing is known about the fine structures of the gadolinium isotopes or their trivalent ions. We expect to pursue this subject further in the case of this and other atoms.

TABLE VII

HEAT CAPACITY OF ONE-HALF MOLE OF $Gd_2(SO_4)_3 \cdot 8H_2O$

T, °K.	0.3	0.35	0.4	0.5	0.6
C cal./deg.	1.60	1.59	1.48	1.14	.85
T, °K.	0.7	0.8	0.9	1.0	1.5
C cal./deg.	.64	.51	.43	0.37	0.18

The many results obtained by Kamerlingh Onnes and his co-workers at Leiden, on the increasing magnetic perfection which accompanies the dilution of magnetic atoms, leaves no reasonable doubt concerning the atomic magneton interaction explanation. This has also been confirmed by dilution experiments which we will report later.

Differential Susceptibility with a Frequency of 1000 Cycles per Second.—It is evident that if the differential susceptibility were to be measured with a sufficiently high frequency, certain orientations of the magnetons would be unable to occur within the available time. A study of the particular frequency regions where certain increments of susceptibility are lost should yield interesting information. We did not have equipment to carry out such an investigation but tried a frequency of 1000 cycles/sec. produced with a tuning fork oscillator. The inductance bridge was balanced by means of head phones which decreased the accuracy.

There was no appreciable difference in the susceptibilities as measured with 60 or 1000 cycles. Temperatures down to 0.3°K. checked within 0.01° which was within the limits of absolute accuracy obtainable with the relatively crude 1000 cycle measurement.

A few additional cooling experiments were made with a starting temperature of 1.29°K. and a field of about 8000 gauss. These conditions produced a temperature of 0.242°K.

A final check of the magnetic thermometer against the helium vapor pressure thermometer[10a,b] indicated the former to be 0.02° high at 1.58°K. The magnetic thermometer had been set at the boiling point of helium. This small difference is probably without significance. This concluded the preliminary investigation of gadolinium sulfate octahydrate.

To convey some idea of the real promise of such investigations it may be mentioned that with the most favorable conditions used in the above work, only one-third of the magnetic entropy has been removed and utilized in a single demagnetization. There are no theoretical difficulties connected with the removal of much greater amounts of magnetic entropy and the utilization of successive demagnetizations.

We wish to express our appreciation to our many associates who have in a variety of ways helped to make this work possible. We must mention the coöperation of Professor Merle Randall in connection with much of the heavy equipment necessary. We wish particularly to thank Mr. G. F. Nelson, chief mechanician, who not only contributed many useful ideas, but, through his interest in the problem, often worked day and night with us in overcoming the difficulties of our first experiments.

Summary

This paper contains a description of methods and apparatus for producing temperatures in the range below 1° absolute by adiabatic demagnetization of suitable paramagnetic substances.

A description of the first exploratory and very successful experiments demonstrating the feasibility of this method has been presented. The working substance was $Gd_2(SO_4)_3 \cdot 8H_2O$.

An inductance coil surrounding the sample but thermally insulated from it by an evacuated space has been used to measure the differential magnetic susceptibility.

The variation of magnetic susceptibility with field strength gave no indication of ferromagnetism in $Gd_2(SO_4)_3 \cdot 8H_2O$.

The reversible character of the magnetization is shown by the fact that results obtained with alternating fields of 60 and 1000 cycles per second were in agreement.

A calorimetric experiment, in which a 60-cycle field with a maximum of 52 gauss was applied, showed that of the maximum energy, $\chi \mathbf{H}^2_{\text{max.}}/2$, temporarily withdrawn from the field by the substance at each alternation, less than 0.01% was lost by magnetic hysteresis or eddy currents.

The lowest temperature produced in the above work was 0.242°K. A starting temperature of 1.29°K. and a field of about 8000 gauss gave this result. The lower temperature is based on the assumption of Curie's law.

Measurements by means of an inductance bridge have permitted a precision of about 0.0003° in temperature measurements at the lower temperatures.

Exact equations have been given to permit the determination of thermodynamic temperatures corresponding to magnetic susceptibilities. Complete experimental application of this method has been left for a later paper. Here the equations have been used to extend the Curie scale to the determination of temperature from differential susceptibility measurements in the presence of a magnetic field.

Tables have been presented showing the change of temperature, differential susceptibility, energy and heat content accompanying adiabatic magnetization from a number of temperatures below 1°K.

The interaction of gadolinium atoms gives rise to energy levels whose separation is comparable to kT at temperatures below 1°K. This effect which tends to make the magnetic system approach zero

entropy in accordance with the requirements of the third law of thermodynamics leads to a considerable heat capacity below 1 °K. This heat capacity has been determined to 0.3 °K. by means of a series of adiabatic demagnetizations from known starting temperatures and magnetic fields. The entropy corresponding to the initial conditions being known, the variation of entropy over the low temperature range is thus determined. $dS/d \ln T = C$ approaches a maximum of 1.60 cal./deg. per one-half mole of $Gd_2(SO_4)_3 \cdot 8H_2O$ at 0.3 °K.

It has been made evident that, when obviously practicable improved experimental conditions become available, the temperature range at present open for various investigations can be greatly extended. The term greatly seems very applicable since temperature range is most significant and should be thought of in logarithmic increments. On this proper basis there is still infinite room for extension.

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[CONTRIBUTION FROM THE LABORATORIES OF THE ROCKEFELLER INSTITUTE FOR MEDICAL RESEARCH]

Transference Numbers of Aqueous Solutions of Some Electrolytes at 25° by the Moving Boundary Method

BY L. G. LONGSWORTH

This paper deals with the results of a systematic research undertaken to provide transference numbers at 25° as functions of the concentration for aqueous solutions of the more common salts. MacInnes and Longsworth[1] have summarized the present knowledge of the moving boundary method for measuring transference numbers. They have also very briefly indicated the utility of these numbers in the various branches of electrochemistry. The most important uses of transference numbers are as follows. The conductances of individual ion constituents as functions of the concentration may be obtained by combining transference numbers with conductance measurements. These results may be used to obtain limiting ion mobilities.[2] Also, accurate values of activity coefficients may be evaluated from transference data and electromotive force measurements on certain cells with liquid junctions.[3] The results of both preceding combinations of transference data with other measurements are of interest in connection with the interionic attraction theory of electrolytes. The variation of transference numbers with the concentration has, however, a direct bearing on that theory, as will be shown after the experimental results have been presented.

Apparatus and Materials

The same moving boundary apparatus was used, in making the measurements which are reported in this paper, as in previous work from this Laboratory and an adequate description has already been published.[1]

The following general precautions were taken in the purification of the salts and the preparation of the solutions. The chemicals were of the best grade obtainable and all recrystallizations of these materials were made with conductivity water and centrifugal draining of the crystals. All solutions were prepared with conductivity water by direct weighing of both solvent and solute, or stock solution, and the weight formal concentrations were then converted to a volume basis. Unless otherwise indicated the density data which are necessary for this conversion were taken from the "I. C. T."[4] Moreover, all molecular weights were taken from the same source.[5] The Richards bottling apparatus[6] was used extensively in the fusion and preparation of salts for direct weighing. Platinum ware was used as containers for salts which were fused or dried at high temperatures and any solutions prepared from such salts were rejected if they were alkaline to phenolphthalein. Individual salts were purified and solutions prepared therefrom as follows.

Potassium bromide was recrystallized twice, fused in air and weighed directly.

Potassium iodide was recrystallized twice and dried in an electric oven at 120°. This product was then finely pulverized in an agate mortar and a concentrated stock solution prepared by drying the powder at 500° for two hours in the Richards bottling apparatus before weighing. This stock solution, although persistently neutral, acquired a slight brownish color on exposure to sunlight. The dilute solutions which were prepared from the stock solution were not discolored, however, and the conductance of a 0.03 *N* solution changed by less than 0.03% on standing six days, during which time it was repeatedly exposed to laboratory air and light.

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[1] MacInnes and Longsworth, *Chem. Rev.*, **11**, 171 (1932).

[2] MacInnes, Shedlovsky and Longsworth, THIS JOURNAL, **54**, 2758 (1932).

[3] MacInnes and Brown, *ibid.*, in press.

[4] "International Critical Tables," McGraw-Hill Book Co., Inc., New York, 1928, Vol. III, p. 51.

[5] *Ibid.*, 1926, Vol. 1, p. 106.

[6] Richards and Parker, *Proc. Am. Acad. Arts and Sci.*, **32**, 55 (1896).