which are very steady and reproducible, readings checking repeatedly within one or two in the third significant figure. The cell used gave about 0.2 volt, but the numerical value is significant only in showing the order of magnitude of the effect measured, since the exact value of the concentration of the Grignard solution was not known.

Summary

1. It is shown that strong magnetic fields produce no polarization in the light from the oxy-luminescence of ether solutions of Grignard compounds, but may affect the brightness.

2. The application of electric fields often causes an unpolarized luminescence at one or both electrodes, accompanying the electrolysis of the solution. The process involved appears to be quite distinct from the oxy-luminescence.

3. Preliminary study of electrode potentials in cells containing ether solutions of Grignard compounds shows that the voltage of such cells is very sensitive to light and that, following a change in illumination, the voltage may be a periodic function of the time.

4. Using a flowing-junction method, closely reproducible voltages were observed.

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A THERMODYNAMIC TREATMENT OF CERTAIN MAGNETIC EFFECTS. A PROPOSED METHOD OF PRODUCING TEMPERATURES CONSIDERABLY BELOW 1° ABSOLUTE

By W. F. Giauque

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Some years ago the author's interest in cryogenic work led to a consideration of possible substitutes for the commonly used methods of producing low temperatures.

While a method of producing very low temperatures was devised, the lack of necessary facilities has caused a temporary delay in the actual experiment and it is desired to transmit the underlying ideas at this time.

The reversible transfer of heat from one temperature to another requires a working substance which is capable of undergoing an isothermal entropy change at the temperatures concerned.

From a practical standpoint, this entropy change must be considerable in view of the unavailability of those theoretically convenient, thermally non-conducting materials.

Compared to those of pressure, the effects ordinarily produced by obtainable electric and magnetic fields on the neutral states of matter are minute. However, a critical consideration indicated that while the latter cannot compete with pressure in producing a change in entropy at ordinary temperatures, a magnetic field will produce large effects at very low temperatures.

The important point is that the magnetic effects are large when pressure is no longer practicable as a means of producing a further drop in temperature.*

Before considering the available experimental data which lead to this conclusion it will be desirable to collect or derive certain thermodynamic formulas. Where possible the nomenclature of Lewis and Randall will be adopted.[1]

The second law of thermodynamics as applied to substances in magnetic fields is $\mathfrak{H}\mathrm{d}I + T\mathrm{d}S = \mathrm{d}E + P\mathrm{d}V$.[2] Keesom omitted the $P\mathrm{d}V$ term, which actually makes but small difference. $\mathfrak{H}\mathrm{d}I$ = the magnetic work done on the substance; $T\mathrm{d}S$ = temperature times entropy change = the heat added; $\mathrm{d}E$ = the increase in internal energy; $P\mathrm{d}V$ = the work done against an external pressure; I = the intensity of magnetization in excess of that which would be in the same space if unoccupied by matter; $\chi = I/\mathfrak{H}$ = the molal susceptibility.

Since the method commonly used in the determination of magnetic properties involves the maintenance, as nearly as possible, of a constant magnetic potential, and also since we believe that the transfer of material from one maintained potential to another is somewhat easier to visualize than is an integral potential effect, we shall adopt the former viewpoint.

It will be convenient to extend the definition of heat content from $H = E + PV$ to $H = E + PV - \mathfrak{H}I$. The $\mathfrak{H}I$ term is included for a reason entirely analogous to that leading to the inclusion of the PV term. This latter is convenient, due to the maintenance of constant pressure by the earth's atmosphere under ordinary conditions.

Then as usual we may write the free energy as $F = H - TS$, $\mathrm{d}F = \mathrm{d}H - T\mathrm{d}S - S\mathrm{d}T = V\mathrm{d}P - I\mathrm{d}\mathfrak{H} - S\mathrm{d}T$. Thus, at constant T and P,

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* Since this paper was submitted for publication there has appeared in the *Annalen der Physik* **81**, 1154 (1926) a paper by P. Debye, who has independently arrived at the idea of utilizing the magnetic properties of $Gd_2(SO_4)_3.8H_2O$ for refrigeration. Although the author of the present paper has frequently discussed his proposed method with numerous colleagues since 1924, the idea was not otherwise announced until the April 9th 1926 meeting of the California Section of the American Chemical Society when Professor W. M. Latimer discussed this author's proposed use of $Gd_2(SO_4)_3.8H_2O$ for obtaining temperatures considerably below 1 °K. Since the conception of the idea, equipment for producing liquid hydrogen in the necessary amount has been constructed and placed in operation. A helium liquefaction cycle which should soon enable experimental verification is now in process of construction.

[1] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, 1923.

[2] Keesom, *Comm. Phys. Lab. Leiden*, Suppl. No. 32a; Keesom (with note by H. A. Lorentz), *ibid.*, Suppl. No. 32b.

$\mathrm{d}F = -I\mathrm{d}\mathfrak{H}$ and the work done by a mole of substance when it is reversibly drawn into a field $= -\Delta F = \int_1^{H_2} I\mathrm{d}\mathfrak{H}$.

Experimentally,[3] consider the material investigated to be in the form of a cylinder of sufficient length to extend from the uniform field between the pole pieces of a magnet, through the magnetic gradient to a position where the field is negligible. When the cylinder moves into the field the net result has been a transfer of material from $\mathfrak{H}_1 = 0$ to $\mathfrak{H}_2$. The force times the distance necessary to move one mole into the field H_2 is equal to $-\Delta F$. $(\partial \Delta F/\partial T)_{\mathfrak{H},P} = -\Delta S$, and $-T\Delta S$ is the heat given out during the isothermal magnetization.

When values of susceptibility are given, an alternative method is as follows: $T\mathrm{d}S = \mathrm{d}E + P\mathrm{d}V - \mathfrak{H}\mathrm{d}I = \mathrm{d}H + I\mathrm{d}\mathfrak{H} - V\mathrm{d}P$, from which $(\partial S/\partial \mathfrak{H})_{P,T} = (\partial I/\partial T)_{P,\mathfrak{H}} = \mathfrak{H}(\partial \chi/\partial T)_{P,\mathfrak{H}}$ and $\Delta S = \int_{\mathfrak{H}_1}^{\mathfrak{H}_2} (\partial I/\partial T)_{P,\mathfrak{H}}\mathrm{d}\mathfrak{H}$.

Diamagnetism is practically independent of temperature and thus there is nearly zero heat effect when a diamagnetic substance is introduced into a field.

The ideal paramagnetic substance follows the well-known law $\chi T = C =$ constant, proposed by Curie[4] and first explained by Langevin.[5]

For such a substance, $\Delta S = -\mathfrak{H}^2 C/2T^2$ when it is taken from zero field to field $\mathfrak{H}$. The inverse square proportionality of temperature to ΔS leads to considerable effects at very low temperatures, as will be shown later. The above expression for ΔS would lead to infinite decrease in entropy during magnetization at the absolute zero, which conflicts with the accepted view of the finiteness of entropy.[6] The explanation, as in other such cases, is furnished by quantum mechanics and the fact that Curie's law is a limiting case for $\mathfrak{H} = 0$.

The low-temperature experimental data[7] on gadolinium sulfate, $Gd_2(SO_4)_3.8H_2O$, so satisfactorily illustrate the possibilities that they alone will be considered.

Table I gives the values of the Curie constant at various temperatures for one gram atom of gadolinium as the hydrated sulfate. The various experiments have been carried out on two different tubes of material known as Gd I and Gd II.

[3] Gouy, *Compt. rend.*, **109**, 935 (1889). Onnes and Perrier, *Comm. Phys. Lab. Leiden*, Suppl. No. 139a.

[4] Curie, *J. phys.*, **4**, 197 (1895).

[5] Langevin, *Compt. rend.*, **140**, 1171 (1905).

[6] The relation of this entropy change to our viewpoint on the third law of thermodynamics will be considered in the following article [Giauque, This Journal, **49**, 1870 (1927)].

[7] (a) Onnes and Perrier, *Comm. Phys. Lab. Leiden*, No. 122a. (b) Onnes and Oosterhuis, *ibid.*, No. 129b. (c) Onnes, *ibid.*, No. 140d. (d) Woltjer, *ibid.*, No. 167b. (e) Woltjer and Onnes, *ibid.*, No. 167c.

TABLE I

CURIE CONSTANT OF $Gd_2(SO_4)_3.8H_2O$ PER GRAM ATOM OF Gd

T	χT	Tube	Observer	T	χT	Tube	Observer
290.3	7.80	Gd I	O. and P.	14.68	8.04	Gd I	W.
20.33	7.89	Gd I	O. and P.	293.1	7.54	Gd II	O. and O.
17.01	7.81	Gd I	O. and P.	20.1	7.49	Gd II	O. and O.
13.91	7.64	Gd I	O. and P.	20.42	7.59	Gd II	W.
20.31	8.01	Gd I	W.	13.98	7.57	Gd II	W.

O. and P., Onnes and Perrier; W., Woltjer; O. and O., Onnes and Oosterhuis.

The perfection of the magnetic behavior is clearly demonstrated. The constancy during a given series of measurements exceeds the agreement between the various series by a considerable amount, thus indicating constant error in a given set. For example, it is pointed out by Woltjer that the Gd I tube was out of center during his measurements.

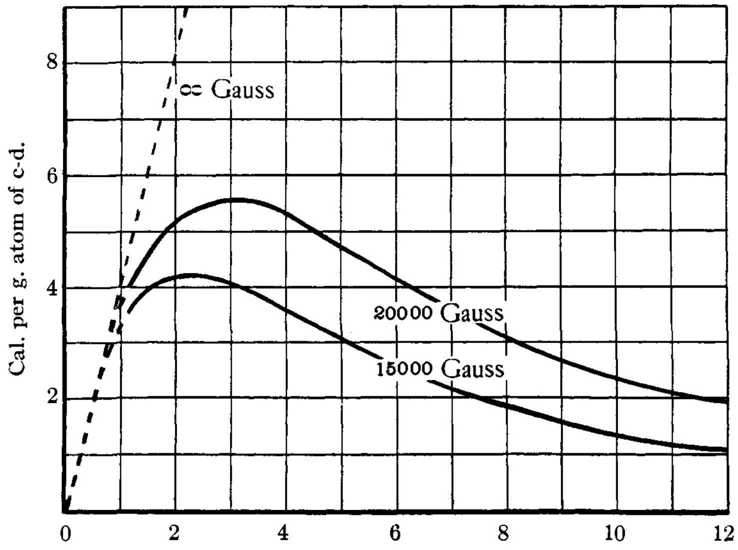

Fig. 1.

Measurements have also been carried out by Woltjer and Onnes[7e] at various temperatures from 1.3°K. to 4.2°K. with continued perfect behavior except deviations due to approaching saturation. These latter measurements have been considered in some detail in the following paper. From them we have calculated by graphical integration the values of ΔF for magnetization. The temperature coefficient of ΔF gives ΔS for the process and $-T\Delta S$ the heat given out during isothermal magnetization. At 1.3°K. a field of 20,000 gauss produces a decrease in entropy of 3.3 cal. per degree per gram atom of gadolinium. The decrease for 15,000 gauss is 2.9 cal. per degree at the same temperature. The heat evolved during magnetization by fields of 15,000 and 20,000 gauss is plotted against temperature in Fig. 1. While the amount of heat is small, the effects are actually large when the temperature at which they occur is considered. For purposes of comparison it may be noted that an entropy change of 3.3 cal. per degree at room temperature corresponds to about 1000 cal.

It is apparent that a Carnot cycle could be used to transfer heat from one temperature to another. However, we believe that the following somewhat simpler procedure would suffice to produce temperatures much lower than those produced by any present method. (1) Magnetization of the working substance while it is in thermal contact through gaseous conduction with liquid helium preferably boiling at reduced pressure. (2) Demagnetization after the space between the working substance and the liquid helium bath has been evacuated.

Dysprosium sulfate, $Dy_2(SO_4)_3.8H_2O$, or some other "diluted" dysprosium or holmium compound would apparently be the best working substance obtainable, the reason for this being that measurements indicate that dysprosium and holmium have about 10/7 the magnetic moment possessed by gadolinium. The "dilution" of the magnetic atoms by means of non-magnetic atoms appears to be necessary if perfect magnetic behavior is to be expected. This question has been discussed by Onnes and Oosterhuis.[8]

It does not appear probable that $Gd_2(SO_4)_3.8H_2O$ would have any considerable heat capacity in the region about 1°K., but no heat-capacity data are available to decide this point. We expect to investigate the heat capacity of substances of this type at very low temperatures in the near future.

The very reversible character of the process is indicated by the absence of hysteresis effects. Breit and Onnes[9] have investigated the hysteresis of chromic chloride and $Gd_2(SO_4)_3.8H_2O$ at the boiling point of hydrogen and very high frequencies, and while the susceptibility of both materials was apparently lowered they concluded that "The order of magnitude of the susceptibility is unchanged if the frequency is increased to 3.69×10^5." This indicates that the magnetons are in extremely rapid equilibrium with thermal energy.

The question as to why heat effects have not been observed by experimenters making magnetic measurements suggests itself. An amount of material containing only about 0.001 gram atom of gadolinium was used and this was in thermal contact with the bath by means of hydrogen or helium gas conduction. It would thus seem that the effect could hardly have been sufficient to be distinguished from those possible due to lack of ordinary thermal distribution in the powdered material.

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[8] Onnes and Oosterhuis, *Comm. Phys. Lab. Leiden*, No. 139e.

[9] Breit and Onnes, *ibid.*, No. 168c.

Some Applications

Bohr Magneton Number.—The very successful low temperature investigation of $Gd_2(SO_4)_3.8H_2O$ was started by Kamerlingh Onnes with the idea of obtaining the approach to saturation and thus a direct determination of the magnetic moment. This was possible only because of the high magnetic moment of the gadolinium atom. It would now seem possible to extend this method to other less magnetic substances with the assistance of cooling by relatively larger amounts of a substance with high magnetic moment. As was first pointed out by Onnes in connection with cryogenic work of this kind, the intensity of magnetization being a function of $M\mathfrak{H}/RT$, our inability to obtain very large fields combined with the fact that values of the magnetic moment are small may be overcome by lowering the temperature.

Electrical and Thermal Conductivity.—The investigation of thermal and supraconductivity at still lower temperatures may throw light on certain underlying principles and mechanisms which are as yet somewhat obscure, to say the least. The heat flow for measuring thermal conductivity could conveniently be supplied by the field and a magnetic substance if properly controlled. Further study of the lowering of the temperature at which supraconductivity begins when a magnetic field is applied should prove profitable.

Calorimetry.—Woltjer and Onnes[7e] have suggested the use of magnetic susceptibility for thermometric purposes. The following method of determining heat capacities at suitable temperatures would seem capable of development to a considerable degree of accuracy. (1) Isothermal magnetization of a working substance in thermal contact with a bath and the material to be investigated. (2) Adiabatic demagnetization of the working substance plus the material investigated to various final field strengths. (3) Measurement of the forces due to a small fraction of the paramagnetic material located in the magnetic gradient as a means of determining both initial and final temperatures.

The possibilities of this method will be more evident when the quantum treatment given to the effects concerned is considered. This will be found in the following paper. By such a method the question of zero-point entropy for supercooled liquids such as glycerol[10] could be still further investigated.

The orientation of di-poles in an electric field presents an analogous phenomenon to that which we have been discussing, but the orientation of a di-pole would probably involve the turning of a molecule in a solid. While this turning is one which might take place through some small angle, especially where the crystal consists of simple molecule units, it

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[10] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923). Simon and Lange, *Z. Physik*, **38**, 227 (1926).

seems unlikely that such an effect would be accompanied by a sufficiently large entropy change to be useful for such purposes as those considered. However, there are few data on this point.

Summary

A thermodynamic treatment of certain magnetic phenomena has been given.

The entropy change accompanying the magnetization of paramagnetic substances and its application to obtaining temperatures below 1°K. has been discussed.

Some remarks have been made concerning the analogous case of di-pole orientation in an electric field.

Some suggestions have been made concerning the application of temperatures obtainable to the direct determination of the number of magnetons in paramagnetic substances, the further investigation of thermal and supraconductivity, and a method suitable for the determination of heat capacities below 1°K.

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

PARAMAGNETISM AND THE THIRD LAW OF THERMODYNAMICS. INTERPRETATION OF THE LOW-TEMPERATURE MAGNETIC SUSCEPTIBILITY OF GADOLINIUM SULFATE

BY W. F. GIAUQUE

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It is the primary purpose of this article to show that the ordinary method of obtaining an absolute value of the entropy of a substance by means of the third law of thermodynamics is not always applicable to paramagnetic substances. It is also desired to show how the present method may be extended to correct for the paramagnetism in such cases.

Before proceeding to do this it will be desirable to interpret the measurements of Woltjer and Onnes[1] on the magnetic properties of gadolinium sulfate, $Gd_2(SO_4)_3.8H_2O$, in order that this substance may be used as an example for discussion.

Onnes and Woltjer show that their data follow the equation of Langevin[2] but express some surprise at the magnitude of the deviations. However, they did not feel able to claim that the difference was beyond the error of experiment. A decidedly systematic trend is noticeable in their observed minus calculated differences.

According to Langevin, the molal intensity of magnetization $I = M$ (coth $M\mathfrak{H}/RT - RT/M\mathfrak{H}$, where M is the molal magnetic moment, $\mathfrak{H}$

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[1] Woltjer and Onnes, *Comm. Phys. Lab. Leiden,* No. 167c.

[2] Langevin, *Compt. rend.,* **140,** 1171 (1905).