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

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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).

the magnetic field strength, R the molal gas constant and T the absolute temperature. It may readily be shown by methods given in the preceding article that for a Langevin substance the entropy change during magnetization from zero field to field $\mathfrak{H}$ is

$$\Delta S = R\left[ln \frac{\sinh \frac{M\mathfrak{H}}{RT}}{\frac{M\mathfrak{H}}{RT}} - \frac{M\mathfrak{H}}{RT} \coth \frac{M\mathfrak{H}}{RT} \right]_{\mathfrak{H}=0}^{\mathfrak{H}=\mathfrak{H}}$$

which indicates that the entropy decreases to negative infinity as the field is increased without limit. This is obviously due to the fact that Langevin assumed the existence of a continuous series of orientations with respect to the applied field.

Pauli[3] has shown that the initial susceptibility of paramagnetic substances is best explained by the application of Langevin's method and the assumption of a small number of possible orientations. This latter can hardly be considered an assumption in view of the multiplicity observed in the Zeeman effect and the splitting of a stream of paramagnetic atoms passed through a magnetic gradient first observed by Gerlach and Stern.[4]

At the time Pauli first tested his proposal the anomalous Zeeman effect had not been sufficiently interpreted to enable the choice of the correct number of possible orientations in the various cases. However, the solution of this problem appears to be in a fairly satisfactory state at present.

Pauli's treatment of magnetic susceptibility has been for the limiting case as the field approaches zero, since at room temperature the values are independent of field strength within the limit of experimental error. However, at low temperatures this is no longer the case, and it will be necessary to derive the complete expression.

Hund[5] has shown that for the trivalent gadolinium ion the inner quantum number j is 7/2, while the ratio of magnetic over mechanical moment g is 2 in this case. When j is 7/2, eight spatial orientations with respect to the field are possible,[6] four of which have clockwise and four counterclockwise rotation. All eight of these situations are taken as equally probable in the absence of an external field.

The four angles of orientation for a gadolinium ion are given by $\cos\Theta = j/j$, $(j-1)/j$, $(j-2)/j$, $(j-3)/j$, respectively, where Θ is the angle between the plane of rotation and a plane normal to the field.

The magnetic moment is gjM, where M is now taken as the moment of a molal unit Bohr magneton.

The torque exerted by the field $= gjM\mathfrak{H} \sin \Theta$.

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[3] Pauli, *Physik. Z.*, **21**, 615 (1920).

[4] Gerlach and Stern, *Z. Physik*, **9**, 349 (1922).

[5] Hund, *ibid.*, **33**, 855 (1925).

[6] Sommerfeld, "Atombau und Spektrallinien," Vieweg, Braunschweig, **1922**, 4th ed., p. 616.

The work done by the field when the magnetic moment is turned from Position Θ to the completely lined up position in Field $\mathfrak{H}$ is $gjM\mathfrak{H}(1-\cos\Theta)$ for those with the field, $gjM\mathfrak{H}(1+\cos\Theta)$ for those against the field.

Then $N = Z\Sigma e^{\frac{-gjM\mathfrak{H}(1-\cos\Theta)}{RT}} + e^{\frac{-gjM\mathfrak{H}(1+\cos\Theta)}{RT}}$ where N is Avogadro's number and Z is the number of atoms entirely lined up; and

$$I = (Z/N)\Sigma gjM\cos\Theta\left[e^{\frac{-gjM\mathfrak{H}(1-\cos\Theta)}{RT}} - e^{\frac{-gjM\mathfrak{H}(1+\cos\Theta)}{RT}}\right]$$

$$= gjM\frac{\Sigma\cos\Theta\sinh\frac{gjM\mathfrak{H}\cos\Theta}{RT}}{\Sigma\cosh\frac{gjM\mathfrak{H}\cos\Theta}{RT}}, \qquad (1)$$

both summations being over all possible orientations. The above formula is general for all cases where $2j$ is odd, and the orientation is without restraint when $\mathfrak{H} = 0$. When $2j$ is even, a similar treatment leads to

$$I = gjM\frac{\Sigma\cos\Theta\sinh\frac{gjM\mathfrak{H}\cos\Theta}{RT}}{\frac{1}{2}+\Sigma\cosh\frac{gjM\mathfrak{H}\cos\Theta}{RT}} \qquad (2)$$

The value of the magnetic moment is given by the equation $M = (e/m)(h/4\pi)N$ where e/m is the ratio of electronic charge to mass in electromagnetic units, and h is Planck's constant. Birge,[7] after careful consideration of the available data, has adopted as the most probable values of the constants involved $e/m = 1.760 \times 10^7$ e. m. u.; $h = 6.560 \times 10^{-27}$ erg sec.; $N = 6.059 \times 10^{23}$. Thus, $M = 5567$, and for the gadolinium ion the total magnetic moment $gjM = 2 \times (7/2) \times 5567 = 38{,}970$, which is saturation value of this substance.

It has been shown by numerous experiments that the initial susceptibility of the gadolinium ion is within the limits of experimental error equal to that of $\frac{1}{2}Gd_2(SO_4)_3.8H_2O$ when corrections have been applied for the associated diamagnetic effect. The available data on this point have been summarized by Zernike and James.[8] It might be expected that the definite arrangement of the atoms in a crystal lattice would influence the magnetic properties, but this is apparently not the case with $Gd_2(SO_4)_3.8H_2O$.

TABLE I

THEORETICAL FRACTIONAL MAGNETIC SATURATION OF $Gd_2(SO_4)_3.8H_2O$

$\frac{gjM\mathfrak{H}}{RT}$	$I/I_{(\text{sat.})}$	$\frac{gjM\mathfrak{H}}{RT}$	$I/I_{(\text{satd.})}$
0.7	0.2877	4.2	0.8773
1.4	.5162	6.3	.9434
2.1	.6714	7.0	.9553
2.8	.7706		

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[7] Birge, *Science*, **64**, 180 (1926).

[8] Zernike and James, THIS JOURNAL, **48**, 2827 (1926).

Using Equation 1, values of $I/I_{(\text{sat.})}$ for various values of $gjM\mathfrak{H}/RT$ have been calculated. The results are given in Table I.

The experimental results of Woltjer and Onnes[1] on their Sample Gd II have been used to calculate values of $I_{\text{obs.}}/_{38,970}$ and the results are given in Table II. The number of the experiment is also given to facilitate reference with the original work. Their results on Gd I have not been considered, since it is stated that they are less reliable.

TABLE II

EXPERIMENTAL $I/_{38,970}$ FOR $\frac{1}{2}\text{Gd}_2(\text{SO}_4)_3.8\text{H}_2\text{O}$

Expt. no.	T°K.	$\frac{38,970\mathfrak{H}}{RT}$	$\frac{I_{\text{obs.}}}{38,970}$	Expt. no.	T°K.	$\frac{38,970\mathfrak{H}}{RT}$	$\frac{I_{\text{obs.}}}{38,970}$
4	4.20	0.2906	0.1228	12	2.30	2.701	0.7719
5	4.20	.2906	.1238	13	1.48	4.159	.8597
6	4.20	.5668	.2450	15	1.48	4.159	.8603
3	4.20	.8466	.3518	14	1.48	5.365	.9021
7	4.20	1.116	.4408	34	1.41	0.4720	.2066
2	4.20	1.510	.5516	33	1.41	0.6239	.2677
8	4.20	1.510	.5525	32	1.41	0.7707	.3348
28	4.20	1.511	.5505	31	1.41	4.343	.8778
9	4.20	1.791	.6088	30	1.41	5.185	.9046
1	4.20	1.930	.6413	29	1.41	5.804	.9320
10	4.20	1.930	.6400	36	1.31	6.047	.9343
11	3.40	1.852	.6341	35	1.31	6.266	.9403

The experimental data are compared with the theoretical curve in Fig. 1. The agreement is very satisfactory, particularly when it is considered that the theoretical curve is calculated from natural constants whose values are in no way dependent on the work of Onnes and Woltjer.

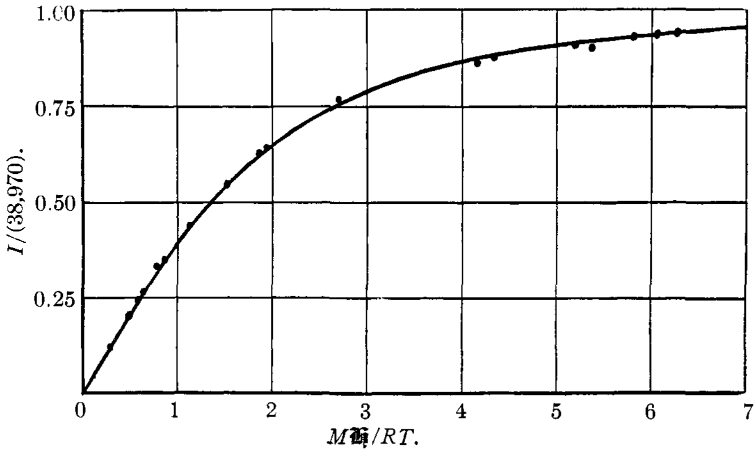

Fig. 1.

The calculation of the theoretical value of the entropy of magnetization may be carried out by a method used by Tolman and Badger[9] to obtain the rotational entropy of diatomic gases.

Let $gjM\mathfrak{H}/RT = a$ and $Q = \Sigma \cosh (a \cos \Theta)$. Then $\mathrm{d}Q/\mathrm{d}a = \Sigma \cos \Theta \sinh (a \cos \Theta)$, and $I = gjM \, \mathrm{d} \, ln \, Q/\mathrm{d}a$. From the preceding paper, $(\partial S/\partial \mathfrak{H})_T = (\partial I/\partial T)_{\mathfrak{H}}$. Therefore,

$$\left(\frac{\partial S}{\partial \mathfrak{H}}\right)_T = -\frac{a^2 R}{\mathfrak{H}} \left(\frac{\partial^2 \, ln \, Q}{\partial a^2}\right)_{\mathfrak{H}}$$

$$\Delta S = -R \int_0^{\mathfrak{H}} \frac{a^2}{\mathfrak{H}} \frac{\partial^2 \, ln \, Q}{\partial a^2} \, \mathrm{d}\mathfrak{H} = R \left[ln \, Q - a \frac{\mathrm{d} \, ln \, Q}{\mathrm{d} \, a} \right]_0^{\mathfrak{H}}$$

$$= R \left[ln \, \Sigma \cosh \frac{gjM\mathfrak{H} \cos \Theta}{RT} - ln \, 4 - \frac{gjM\mathfrak{H}}{RT} \frac{\Sigma \cos \Theta \sinh \dfrac{gjM\mathfrak{H} \cos \Theta}{RT}}{\Sigma \cosh \dfrac{gjM\mathfrak{H} \cos \Theta}{RT}} + 0 \right] \quad (3)$$

The ΔS for various values of a has been calculated by means of Formula 3 and the results are tabulated in Table III. The limiting case for large values leads to $-R \, ln \, 8$ as of course it must, since eight positions were assumed equally probable in zero field, while only one is possible for the case $a = \infty$. Thus, when 0.5 mole of $Gd_2(SO_4)_3.8H_2O$ initially in zero field is completely saturated the entropy change is -4.14 cal. per degree. It may be noted that when $a = 7$, $\mathfrak{H} = 19{,}420$ when $T = 1.3$°K.

TABLE III

THEORETICAL ENTROPY OF MAGNETIZATION OF $\frac{1}{2}Gd_2(SO_4)_3.8H_2O$

a	$-\Delta S$, cal./deg.	a	$-\Delta S$, cal./deg.
0.7	0.196	4.2	2.398
1.4	.664	6.3	3.066
2.1	1.196	7.0	3.223
2.8	1.674	∞	4.135

The use of a nearly perfect paramagnetic substance and Langevin's equation for thermometric purposes as suggested by Woltjer and Onnes[1] might be more accurately carried out if Equations 1 or 2 were substituted, depending on the character of the substance used.

Equation 3 might be used for calculation of the heat effect in the magnetic method of mixtures, proposed in the preceding article, for the measurement of heat capacities below 1°K.

A substance obeying Equation 1 would be a strong magnet if cooled to the absolute zero in any finite field. It is interesting to note that could the substance be taken to the absolute zero in the absence of any field the entropy change, if subsequent magnetization took place, would be finite. This is in some respects similar to the entropy change accompanying unmixing of the constituents of solutions, in this case the mixing (demagnetization) and unmixing (magnetization) being under the control of a field. However, if the atoms affected each other in a ferromagnetic sense the substance would become a saturated magnet even in the absence of a field.

[9] Tolman and Badger, THIS JOURNAL, 45, 2277 (1923).

The low-temperature deviations of paramagnetic substances from Curie's law are seldom of a ferromagnetic nature. The formula $\chi(T + \Delta) = C$[10] represents a large share of the initial susceptibility data surprisingly well, the values of Δ being positive in most cases. This leads at low temperatures to a susceptibility which is nearly independent of temperature, making it seem probable that such substances would approach the absolute zero without appreciable magnetization.

We may take the case of solid oxygen as an example of a substance which, while remaining strongly paramagnetic, would not become a magnet as the absolute zero is approached, since it has been shown by Perrier and Onnes[11] that the initial susceptibility of the form stable at the temperatures of liquid hydrogen is practically without temperature coefficient.

As the third law of thermodynamics has been used, entropy is calculated by the integration of specific heat with respect to the natural logarithm of temperature plus what has seemed a plausible extrapolation beyond the lowest temperature measured. When the above method is used the entropy due to the distribution of magnetic moment in the various possible states will sometimes be included, but will more often be neglected.

In view of our limited knowledge concerning atomic structure the assignation of an absolute value to the entropy of a substance would seem to be a somewhat uncertain procedure. However, for the purposes of chemistry it will be sufficient if all effects which may be produced by chemical reactions are considered.

Lewis[12] has called attention to the importance of magneto-chemical effects and one may refer to his publications for a discussion of this subject. While reactions involving a change in magnetic moment are considerably in the minority they are by no means infrequent, for example, the reactions of oxygen. Lewis has suggested that strained conditions which may be an essential part of certain types of chemical bonds may lead to only partial balancing of magnetic moment. Many chemical as well as magnetic observations support this view. In such cases the definite positions of the constituent magnetons would lead to no randomness or entropy of the type here considered. This type of paramagnetism should be practically without temperature coefficient.

Ewing[13] reconsidering his theory of ferromagnetism has discussed a very plausible explanation requiring in part random and in part fixed distribution of the magnetons in ferromagnetic substances. We presume that the fixed magnetons would be of the valence type although all electrons of the valence group may not be fixed.

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[10] Onnes and Oosterhuis, *Comm. Phys. Lab. Leiden*, No. 129b.

[11] Perrier and Onnes, *ibid.*, No. 139c.

[12] Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Co., Inc., New York, **1923**; *Chem. Rev.*, **1**, 231 (1925).

[13] Ewing, *Phil. Mag.*, **43**, 493 (1922).

Langmuir[14] mentions the possibility of interchange of electrons between the valence and kernel groups in the case of transition elements such as iron, cobalt and nickel. This seems to be consistent with both chemical and magnetic facts. This adds to the complication in these cases, especially if thermodynamic equilibrium exists between the various possibilities. This seems quite likely in some cases.

Parks and Kelley,[15] in measuring the heat capacity of magnetite, Fe_3O_4, have found a marked heat absorption in the region about 113–117°K., which they attribute to some magnetic change. It would thus be unsafe to correct for the magneton entropy on the basis of data obtained at ordinary temperatures without investigating the nature of this change. Millar, in an unpublished investigation on the same substance, has found that the heat absorption extends over a range of at least 20°.

The systems which we have been discussing are typical of those which the spectroscopist classes as degenerate, but which can be made undegenerate by the application of a magnetic, electric or gravitational field, as the case may be. It will be recalled that the adiabatic hypothesis of Ehrenfest[16] or, as it has been called by Bohr, the principle of mechanical transformability, does not necessarily hold for degenerate systems. The existence of the earth's magnetic, electric and gravitational fields will presumably keep the various degrees of freedom concerned undegenerate for ideal systems. Assuming the ideal case to hold for actual systems, thus making $S = \int_0^T C d\, ln\, T$, where C represents the heat capacity, the practical difficulty still remains that the thermal effects associated with magnetic saturation by the earth's field, for example, would occur principally below 1×10^{-5} °K. This makes a knowledge of the magnetic properties necessary in order to consider the contribution to the entropy due to unbalanced magnetic moment.

Lewis and Gibson[17] have stated that the entropy of perfect crystalline substances approaches zero at the absolute zero of temperature. A crystalline substance with random distribution of magnetic moment could not be considered perfect even though the effect on the atomic centers is practically negligible. Thus, our conclusions are in accord with those of the above authors.

We have discussed the data of $Gd_2(SO_4)_3.8H_2O$ in order to add to the reality of our statements, but in the reactions of gadolinium during which it remains trivalent it is obvious that the entropy due to magnetic moment would cancel.

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[14] Langmuir, THIS JOURNAL, **41**, 879 (1919).

[15] Parks and Kelley, *J. Phys. Chem.*, **30**, 47 (1926).

[16] Ref. 6.

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

In the general case the amount of entropy $R \ln (1 + 2j)$ should be added to the entropy due to other causes; j is the number of units of resultant angular mechanical momentum of the unit which can be oriented. It is the mechanical rather than the magnetic moment which determines the number of possible positions. At the present time we believe there are no equilibrium, heat-capacity and magnetic data of sufficient completeness and accuracy to serve as a test of the above statement. The amount is 1.38 cal. per degree for one-half and 2.18 cal. per degree for one unit of resultant angular momentum.

Summary

The low-temperature magnetic susceptibility data of gadolinium sulfate, $Gd_2(SO_4)_3.8H_2O$, have been shown to agree quantitatively with an equation, using natural constants and based on orientation without restraint within the solid.

The theoretical entropy changes accompanying the application of a magnetic field are considered.

It is suggested that the magnetic formulas proposed be used in connection with Woltjer and Onnes' suggestion of paramagnetic thermometry. It is also suggested that they be used in connection with the magnetic mixture method of low temperature calorimetry as previously suggested by this author.

Assuming that the entropy of a perfect crystalline substance is zero at the absolute zero of temperature, it is shown that it is not always feasible to obtain an absolute value of entropy from heat-capacity data alone in the case of substances with a positive susceptibility.

It is shown how to correct for the above deficiency when the number of units of unbalanced mechanical moment is known from magnetic data on the form of the substance existing at temperatures low enough to permit sufficiently accurate extrapolation of the heat-capacity curve resulting from ordinary thermal effects.

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