Table IV shows the possible errors that may arise from coincidence, due to insufficient excess of iodine in following Schwicker's procedure. To 50-cc. portions of thiocyanate, the indicated amounts of iodine in excess for Reaction B were added and the mixture was diluted to 140 cc. Ten cc. of the ammonium borate (prepared according to Schwicker) was then added and the reaction allowed to proceed for two minutes before acidification, as Schwicker directs.

TABLE IV

Excess iodine, cc.......	0.0	0.0	0.2	0.5	2.0	4.0	4.0	5.0
Error, %.............	−1.7	−1.2	−0.9	−0.7	−0.3	−0.2	−0.2	−0.2

The possibility of this error has already been discussed in the introduction of this paper. The results were found to be quite accurate with very slight excess of iodine in the presence of 15 instead of 10 cc. of ammonium borate in a 150-cc. volume. A minimum of 4 to 5 cc. of excess iodine is, nevertheless, recommended.

Summary

It has been shown that under suitable conditions borax gives the proper alkalinity for the rapid volumetric determination of thiocyanate with iodine.

LINCOLN, NEBRASKA

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

THE EXISTENCE OF ELECTRONIC ISOMERS IN THE SOLID STATE AND IN SOLUTION. THE MAGNETIC SUSCEPTIBILITY OF $Sm_2(SO_4)_3 \cdot 8H_2O$ AND ITS VARIATION WITH THE TEMPERATURE

BY SIMON FREED

RECEIVED MARCH 26, 1930 PUBLISHED JULY 3, 1930

The quantum theory of Bohr and also the quantum mechanics[1] lead to the following relation connecting the paramagnetic susceptibility of a monatomic gas with the temperature

$$\chi = \frac{B^2g^2j(j+1)}{3RT} \qquad \text{I}^2$$

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[1] Sommerfeld, "Atombau," 4th ed., pp. 630–648; Van Vleck, *Phys. Rev.*, **31**, 604 (1928).

[2] Formula I is the quantum analog to the formula derived by Langevin on the classical theory

$$\chi = M^2/3RT = C/T$$

where M is the magnetic moment generated by the unbalanced electrons in their orbits. $C = M^2/3R$ is known as Curie's constant. This formula expresses Curie's law, which states that the paramagnetic susceptibility is inversely proportional to the absolute temperature. The magnetic field is more effective in orienting the elementary magnets when the thermal agitation is less violent.

χ is the susceptibility per mole, B is the Bohr magneton per mole, *i. e.*, $Neh/4\pi mc$ (where N is Avogadro's number, e/m is the charge divided by the mass of an electron, h is Planck's constant, and c is the velocity of light), R is the gas constant per mole, T is the absolute temperature, j is the net angular momentum of the atom (*i. e.*, the vector sum of the spin moments of the electrons and their orbital moments), g is Landé's splitting factor, which indicates that a resultant between the magnetic moment due to the spins of the electrons and that due to their orbital moment has been taken.

The magnitudes g,j are determined by the characteristics of the electronic state of the atom (or atomic ion); that is, given the quantum number designating the net spin moment of the electrons, their net orbital moment, and the resultant angular momentum of the atom or ion as a whole, the values of g and j are known and the susceptibility is determined by *I*. Ordinarily one might expect that if several electronic configurations (electronic isomers) are present, the susceptibility of the mixture would be the sum of the partial susceptibilities of the two configurations as given by *I*. Van Vleck[3] has shown on the quantum mechanics that when more than one electronic form is present, another term must be added to *I*. This term is independent of the temperature (aside from the Boltzmann factors) and corresponds to the component of the magnetic moment perpendicular to the axis of the angular momentum. *I* takes only the parallel component into account. On the model employed by Van Vleck, the precession of the perpendicular component is identified with the frequency of the light attending the transition from one state to the other.

When the writer began these experiments the results derived from the quantum mechanics were not known. It appeared highly probable then that any marked deviation from Curie's law shown by atoms implied the presence of several electronic forms whose relative amounts were a function of the temperature,[4] for each electronic form has associated with it a magnetic moment. If Curie's constant, $M^2/3R$, varies with the temperature, it means that M is varying with the temperature. However, the magnetic moment cannot vary with the temperature since electronic motions are unaffected by thermal agitation. M must then be a composite magnetic moment which includes the concentrations of several forms having different magnetic moments and these relative concentrations are varying with the temperature.

The approach to this investigation was the following. Hund[5] and others in their elucidation of the spectra of complex atoms and ions showed how to

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[3] Van Vleck, *Phys. Rev.*, **31**, 587 (1928).

[4] Laporte and Sommerfeld, *Z. physik*, **40**, 333 (1926).

[5] Hund, "Linienspectren und Periodisches System der Elemente," Julius Springer, Berlin, **1927**.

predict the value of *g* and *j* from the number of electrons in the various shells of the atoms or ions. The electronic distribution employed was the one proposed by Stoner and by Main Smith in their work on the Periodic System. Having the values of *g* and *j*, Hund was in a position to calculate the magnetic moments and the susceptibilities of the ions of the rare earths in the gaseous state. Such data, however, do not exist, so he compared his results with the experimental values obtained with the ions in the solid state and with their solutions. The agreement was extraordinarily good for all ions except Sm^{+++} and Eu^{+++}, as may be seen from the table (I). Eu^{+++} being very rare and difficult to purify was at once suspected of being contaminated with paramagnetic impurities. Sm^{+++}, however, can be obtained very pure, as is attested by the accepted atomic weight, 150.43, and the good agreement in this value obtained by various experimenters. However, the susceptibility expected by Hund was much less than that actually found.

Materials

It was decided to measure the susceptibility of Sm^{+++} as in the salt $Sm_2(SO_4)_3{\cdot}8H_2O$. This salt is of such stability as to have warranted several investigators, in particular Urbain and Lacombe,[6] to base their determination of the atomic weight of samarium upon it. Their value of 150.46 for its atomic weight was practically identical with that obtained by Stewart and James,[7] who employed the ratio $SmCl_3$:Ag.

The $Sm_2(SO_4)_3{\cdot}8H_2O$ used in the present investigation was prepared from a sample of $Sm_2(C_2O_4)_3{\cdot}10H_2O$ of exceptional purity kindly furnished the writer by the late Professor C. James of the University of New Hampshire. It contained a trace of bismuth (the salts of bismuth are diamagnetic) used in its fractionation and this was removed with hydrogen sulfide after a procedure outlined by Professor James. The oxalate was again precipitated following the method of Stewart and James[7] in their determination of the atomic weight of samarium. The oxalate was converted into the oxide by ignition, and then into the chloride with redistilled hydrochloric acid. The crystals of $SmCl_3{\cdot}6H_2O$ obtained by evaporating the water were dissolved in alcohol and pure sulfuric acid was slowly added. The $Sm_2(SO_4)_3.8H_2O$ which precipitated was twice recrystallized from conductivity water and then dried in an electric oven at 80°. The sulfate was then put in an evacuated desiccator, together with its saturated solution, until it came to a practically constant weight. The sulfate was then removed and placed in a balance case, to avoid an excess of water being taken up by the pores of the sulfate. The weight became practically constant after several days. The loss of water from the pores was slight.

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[6] Urbain and Lacombe, *Compt. rend.*, **138**, 1166 (1904).

[7] Stewart and James, THIS JOURNAL, **39**, 2605 (1917).

An analysis of the crystals showed that there were $8H_2O$ for every mole of $Sm_2(SO_4)_3$ to within 1%. As the analysis was not deemed more accurate than this uncertainty, the composition was taken as $Sm_2(SO_4)_3 \cdot 8H_2O$.

The susceptibility of the salts of trivalent samarium has been measured many times[8] and a rough attempt at determining its temperature coefficient was made by Zernike and James.[8] They gave as the fractional change in the susceptibility per degree change in temperature as $^1/_{1700}$ plus or minus 100%.

It was the aim in the present investigation to attain considerable precision and to achieve this a new sensitive method was devised for measuring susceptibilities at low temperatures.

Apparatus and Method

The best known method for measuring the susceptibilities of solids at low temperatures is that employed repeatedly at the Leiden Cryogenic Laboratory.[9] After considerable experimentation that laboratory adopted the Gouy principle. The latter is employed as follows. A glass tube G with a glass partition P is placed in a magnetic field (MM are the pole pieces of the magnet) so that P is in the center of the pole gap. The portion of the tube above P is evacuated and that below P is filled with the crystals of the substance to be investigated. The extremities of G usually extend to regions where the magnetic field is of negligible intensity. The force which a magnetic field exerts on such a tube is

$$F = \tfrac{1}{2} AK(H^2 - H_0^2)$$

where F is the force, A is the net cross section of the substance, K is the susceptibility per unit volume, H is the magnetic field at the center of the pole gap and H_0 is the intensity of the field at the end of the tube, in this case practically zero.

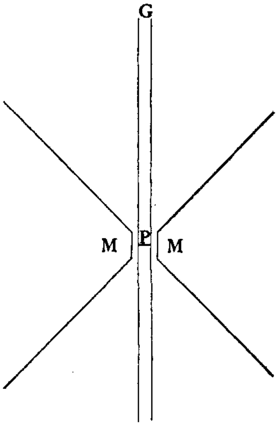

Fig. 1.

Reducing the temperature of the tube has generally been accomplished by putting it in contact with condensed gases such as boiling liquid nitrogen, liquid methane, etc. Intermediate temperatures have been obtained by reducing the pressure under which these liquids boiled. Such a reduction in pressure led to enclosing the entire apparatus in a vacuum-tight container and elaborate devices were resorted to for manipulating the enclosed system. The present method avoids these complications and permits the weighing of the tube to take place just as easily as if it were suspended in air at atmospheric pressure and at room temperature.

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

[9] Woltjer and Onnes, *Comm. Phys. Lab. Univ. Leiden*, No. 167C.

The glass tube G containing the $Sm_2(SO_4)_3 \cdot 8H_2O$ was suspended in the copper tube A (about 12 mm. in diameter and about 60 cm. long) from a stirrup of an analytical balance. The glass tube was surrounded by a gas at a known temperature with which it came in equilibrium. The gas streamed slowly through the small copper tube B of about 1 mm. bore into the bottom of A (there were actually two such tubes, B) and then out into the atmosphere at the upper end of A. The copper tubes B waved back and forth along the outside of A and not around it. C is the Dewar tube which contained the liquefied gases employed for cooling. It had a flattened constriction at D which fitted in between the pole pieces of the magnet. A rubber tube R fitted tightly around a wooden stopper F and also around the Dewar tube C. F was covered with a mixture of beeswax and rosin. TTT are double junction manganin-copper thermocouples on whose cold junctions there were fused little buttons of lead which obtruded slightly into A. The buttons were thermally and electrically insulated from the copper tube A by means of little wads of asbestos. The temperature calibration for these thermocouples was taken from the comparison of such couples with a hydrogen thermometer carried out in this Laboratory.[10]

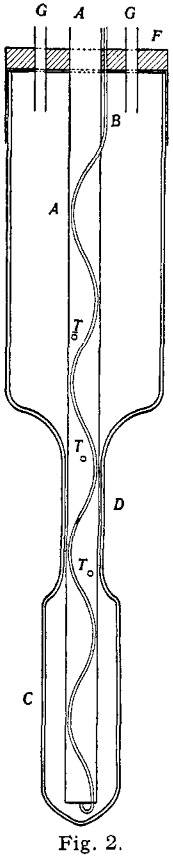

Fig. 2.

The thermocouples registered constant temperatures for hours at a time. A glass tube such as G having a thermocouple imbedded in salt was suspended in the copper tube A to see if the temperature of the thermocouples T actually read the temperature of the salt being studied. The temperature of the salt (at the temperature of liquid air) shown by the thermocouple was within less than 0.1 ° the same as that shown by the thermocouples T.

Sufficient regularity in the flow of the gas stream was achieved by means of a capillary tube about 0.001 mm. in diameter which delivered about 30 cc. of hydrogen gas per minute under normal conditions of temperature and pressure when the pressure at the hydrogen tank was about one atmosphere above the external pressure.

The upper 15 cm. of A is composed of German silver to lessen the heat leak and screwed to its upper end is a copper tube about 20 cm. long. The cold dry gas having passed through A has sufficient time to become warmed through the copper tube so that it leaves the apparatus above the dew point. Otherwise, moisture would condense upon the suspension and alter the weight. The suspension consists at its lower half of a very light brass chain. Its upper half is a silk fishing line, braided and lacquered in the usual manner. The brass chain is employed in the region of lowest temperature because the thermal contraction of brass is negligibly small and silk is used to minimize the heat leak to the chain. The same suspension was employed for all the runs including the calibration. Its length was adjusted at the beginning of the experimentation so that the glass partition P of the glass tube came in the center of the pole gap.

The *operation* is carried out as follows. Liquid air, for example, is introduced through G into C. A stream of dry hydrogen passing through B into A reaches the temperature of the liquid air and then comes in contact with the glass tube containing the $Sm_2(SO_4)_3 \cdot 8H_2O$ which is suspended in A. The gas finally passes out into the atmosphere through the top of A. To reduce the temperature of the $Sm_2(SO_4)_3 \cdot 8H_2O$,

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[10] Giauque, Buffington and Schulze, THIS JOURNAL, 49, 2343 (1927).

a large vacuum pump is connected to G and the temperature is lowered since the liquid air is now boiling under a lower pressure and in turn it further cools the hydrogen gas streaming through B. Now the $Sm_2(SO_4)_3{\cdot}8H_2O$ comes into thermal equilibrium with the colder hydrogen and the magnetic susceptibility is measured at this temperature.

The magnet was of the Weiss type employed in an earlier magnetic investigation.[11] The highest field used was about 19,000 gauss. The intensity of the field could be kept constant for considerable periods of time by a steady current from large storage batteries.

Method of Measurement

The tube A was magnetically calibrated at room temperature with a solution of nickel chloride (identical in purity with that employed in the investigation referred to).[11] The lower part of the tube A was filled with a solution of nickel chloride of known concentration. The change in weight suffered by the tube was observed as definite amperages were going through the coils of the magnet. (The diameter of the tube A had to be known and it was determined by measuring with a microscope the lengths of the tube which known weights of mercury would fill.)

The change in weight was plotted against the corresponding amperages. The solution of nickel chloride was then replaced by fine crystals of $Sm_2(SO_4)_3{\cdot}8H_2O$. The tube was now evacuated until the air between the crystals was at a pressure of about 20 mm. of mercury and it was then sealed off. Again the change in weight at fixed current strengths was observed and compared with the change experienced at the same current by the tube when it contained nickel chloride. Similar comparisons were made at the different temperatures. Equal currents imply equal field strengths. The method of calculation is as follows

$$F_s = \tfrac{1}{2}\,A_sK_sH^2$$
$$F_n = \tfrac{1}{2}\,A_nK_nH^2$$
$$\frac{F_s}{F_n} = \frac{A_sK_s}{A_nK_n}, \text{ or}$$

where F is the change in weight at the field strength H, A is the cross section of the material, K is the susceptibility per unit volume. s refers to $Sm_2(SO_4)_3{\cdot}8H_2O$; n refers to the solution of $NiCl_2$.

$$A_sK_s = A_nK_n\frac{F_s}{F_n} = \text{known magnitude} \qquad \text{(II)}$$

$$K_s = d_s\chi_s$$

where d is the density, χ is the susceptibility per gram

$$A_s = \frac{\text{grams } Sm_2(SO_4)_3{\cdot}8H_2O}{d{\cdot}l}$$

in the tube, where l is the length of the tube filled with the salt

Substituting in (II)

$$\frac{\text{grams } Sm_2(SO_4)_3{\cdot}8H_2O}{dl}\cdot d\chi_s = \text{known magnitude.} \quad \text{Hence } \chi_s \text{ is known}$$

The susceptibility per mole is equal to the susceptibility per gram χs times the molecular weight of the sulfate octahydrate. To obtain the molal susceptibility of Sm^{+++} it is necessary to subtract the contribution (diamagnetic) of SO_4 and H_2O to the

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[11] Freed, THIS JOURNAL, 49, 2456 (1927).

susceptibility of the salt. The diamagnetic susceptibility (the susceptibility due to the balanced electrons) of Sm^{+++} was neglected. It is undoubtedly very small.[12]

TABLE I

MAGNET MOMENTS OF THE RARE EARTH IONS

Element	No. of 4_4 electrons[a]	Basic Level[b]	j	g	Calcd. no. of Weiss[c] magnetons	Observed no. of Weiss magnetons Cabrera	St. Meyer	Zernike and James	Decker
La^{+++}	0	^{1}S	0	0/0	diamag.	diamag.	diamag.		diamag.
Ce^{+++}	1	^{2}F	5/2	6/7	12.5	11.4	..	11.7	10.5
Pr^{+++}	2	^{3}H	4	4/5	17.8	17.8	17.3	17.2	17.0
Nd^{+++}	3		9/2	8/11	17.8	18.0	17.5	17.4	17.1
Il^{+++}	4	^{5}J	4	3/5	13.4	..	..		..
Sm^{+++}	5	^{6}H	5/2	2/7	4.2	8.0	7.0	7.6	8.1
Eu^{+++}	6	^{7}F	0	0/0	0	17.9	15.5	..	19.7
Gd^{+++}	7	^{8}S	7/2	2	39.4	40.0	40.2	38.6	39.1
Tb^{+++}	8	^{7}F	6	3/2	48.3	47.1	44.8	46.3	48.5
Ds^{+++}	9	^{6}H	15/2	4/3	52.8	52.2	53.0	..	54.0
Ho^{+++}	10	^{5}J	8	5/4	52.8	52.0	51.9	51.2	51.6
Er^{+++}	11	^{4}J	15/2	6/5	47.7	47.0	46.7	47.6	47.4
Tu^{+++}	12	^{3}H	6	7/6	37.6	35.6	37.5	..	..
Yb^{+++}	13	^{2}F	7/2	8/7	22.5	21.9	23	21.9	22.4
Lu^{+++}	14	^{1}S	0	0/0	0	diamag.	diamag.		6.1[d]

EXPLANATORY

[a] It is assumed that the only uncompleted electronic shell is 4_4. A few electronic assignments according to the Stoner–Main Smith procedure are given.

Electronic shell		1_1	2_1	2_2	3_1	3_2	3_3	4_1	4_2	4_3	4_4	5_1	5_2
Electrons	La^{+++}	2	2	6	2	6	10	2	6	10	0	2	6
	Ce^{+++}	2	2	6	2	6	10	2	6	10	1	2	6
	Gd^{+++}	2	2	6	2	6	10	2	6	10	7	2	6
	Yb^{+++}	2	2	6	2	6	10	2	6	10	13	2	6
	Lu^{+++}	2	2	6	2	6	10	2	6	10	14	2	6

The electrons in the completed shells have neutralized each other's magnetic moments. The resultant moment of the ion is then due to the incomplete shell which is finally filled in Lu^{+++} and this ion is actually found to be diamagnetic.

[b] The character of the basic spectroscopic level is obtained from the configurations indicated above by the Hund procedure. These levels with the accompanying j values give the net orbital moment, the net spin moment and the resultant angular momentum of all the electrons in the 4_4 shell and hence of the ion as a whole (since completed shells do not contribute to the moments).

[c] The Weiss magneton is an empirical unit of magnetic moment which has been of great service in magneto-chemistry. It is based upon the formula of Langevin and is equal to

$$B_{\text{Weiss}} = \frac{\sqrt{3R\chi T}}{1126}$$

The susceptibility of a substance obeying Curie's law is sufficient to express the moment in Weiss units. However, other magnitudes such as j, g, etc., must be known to

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[12] The diamagnetic susceptibility is proportional to the sum of the areas swept out by the electrons in their orbital motion. In the case of a triple charged ion, the electrons are so strongly attracted by high positive charges that the average radii of the electronic orbits are very small.

obtain the actual magnetic of the ion which is usually expressed in terms of the fundamental Bohr unit.

[d] Decker states that his Lu^{+++} was contaminated with Yb^{+++}.[13]

TABLE II

EXPERIMENTAL RESULTS

$Sm_2(SO_4)_3 \cdot 8H_2O$ in tube, 3.570 g. Cross section of inside of tube, 0.1032 cm. Length of tube filled with the sulfate, 18.03 cm. Concentration of $NiCl_2$ solution, 1.3660 *M*. Susceptibility per cc. of solution at 17.5°, 5.332×10^{-6}. Force on $Sm_2(SO_4)_3 \cdot 8H_2O$ at 290.6°K. divided by the force on the $NiCl_2$ solution at 290.6°K., 0.9134. Average deviation in 0.9134 for fields from 15,000 to 19,000 gauss is 0.26%

Temperature, °K.	Force on $Sm_2(SO_4)_3 \cdot 8H_2O$ as compared with that found at 290.6°K. Ratio of forces	Average deviation for fields to 19,000, %
240.2	1.037	0.15
205.0	1.076	0.20
169.8	1.128	0.22
112.5	1.255	0.35
84.6	1.345	0.22
73.8	1.392	0.40
		Av., 0.26

TABLE III

SUSCEPTIBILITIES OF SM^{+++} AT VARIOUS TEMPERATURES

Temperature, °K.	χ of $\frac{1}{2}$ $Sm_2(SO_4)_3 \cdot 8H_2O$ $\times 10^6$	χ of Sm^{+++}
290.6	931	1038
240.2	965	1072
205.0	1001	1108
169.8	1050	1157
112.5	1168	1275
84.6	1252	1359
73.8	1295	1402

The figures in the third column were computed from the corresponding ones of the second by subtracting the diamagnetic susceptibility of $\frac{1}{2}(SO_4)_3 \cdot 8H_2O$, which was taken as -107. This susceptibility was based upon the value[11] -37 for the susceptibility of one mole $SO_4^{=}$ and -13 for one mole H_2O.

Perhaps it should be recalled that diamagnetic susceptibilities do not vary with the temperature.

It is obvious that Curie's law is not obeyed, for a four-fold change in temperature produces only about a 40% change in the susceptibility of Sm^{+++}.

The pull obtained within a few minutes at any particular temperature was the same as that observed after ten hours. Hence we may conclude that equilibrium is attained rapidly.

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[13] Cabrera, *J. phys.*, **6**, 252 (1925); St. Meyer, *Physik. Z.*, **26**, 51 and 479 (1925); Zernike and James, THIS JOURNAL, **48**, 2827 (1926); Decker, *Ann. physik*, **79**, 324 (1926). Decker measured the ions in solution; the others measured the solid salts.

The accuracy of the relative values is probably within 0.3%. The absolute value found for the susceptibility of Sm^{+++} at room temperature is about 4% higher than that obtained by Zernike and James and about 10% lower than that either of Cabrera or Decker.

Conclusions

It should be recalled that on the quantum theory the angular momentum j is a constant of the motion of the atomic system; that is, for a fixed energy there is a fixed angular momentum. Hence a change in j implies a change in the energy of the atom, in other words, an electronic jump. Associated with this change in j there is a change in the magnetic moment μ. In the simple case carried over from the classical theory

$$\mu = \frac{e}{2mc}j$$

The above reasoning applies also to systems of more than one electron.

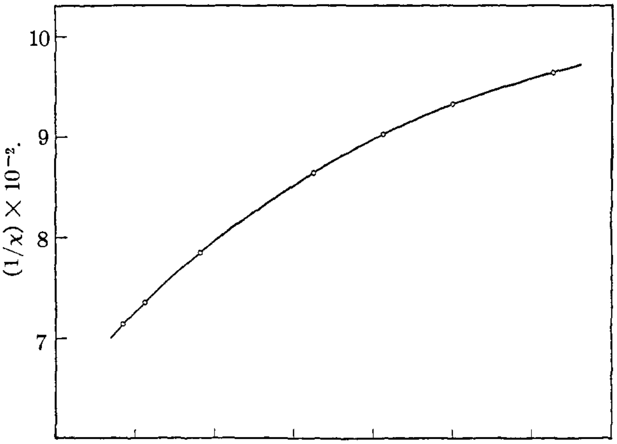

Fig. 3.

Conversely, a change in the magnetic moment is accompanied by a change in j and hence by an electronic jump or rearrangement. The experimental results show that Sm^{+++} does not have a constant Curie "Constant" (C in the relation $T = C/\chi$, is not independent of the temperature). Such a variation implies that there is a mixture of several (two in the first approximation) substances of different magnetic moments whose relative amounts are varying with the temperature. In other words, there are two electronic isomers of Sm^{+++} whose relative concentrations are varying with the temperature.

The actual amounts of the two forms cannot be calculated by assuming that each form obeys Curie's law. As has been mentioned in the introduction, the existence of more than one electronic configuration immediately carries with it, according to the quantum mechanics, a term in the susceptibility which is independent of the temperature. This term may be appreciable, as Van Vleck and Frank[14] have been led to believe, from considerations based upon screening constants from x-ray data.

The fact that the effective Curie constant of Sm^{+++} decreases with diminishing temperature suggests its approach to the low value expected by Hund for the configuration

Sm^{+++}	1_1	2_1 to 4_3	4_4	5_1	5_2
	2	full	5	2	6

The existence of this isomer at the lowest temperature would bring the electronic configuration of Sm^{+++} in line with the regular sequence of the other rare earths whose magnetic moments agree with Hund's theoretical calculations. If the presence of this form is assumed, it appears that the susceptibility contains a term independent of the temperature also. (The existence of such a term could be more readily decided by a determination of the susceptibility at the temperature of liquid hydrogen, which it is hoped to make soon.)[15]

A striking confirmation of the existence of a mixture of electronic isomers was obtained in collaboration with Dr. Frank H. Spedding,[16] from the absorption spectra of a crystal of trivalent samarium taken at different temperatures, from that of liquid hydrogen to room temperature. Certain lines in the spectrum of Sm^{+++} prominent at room temperature became faint at the temperature of liquid air and practically disappeared at that of liquid hydrogen. On the other hand, lines which were intense at the temperature of liquid hydrogen became much fainter at room temperature. This variation in relative intensity reveals the presence of different electronic isomers whose relative concentration is varying with the temperature. The isomer stable at the lowest temperature becomes more plentiful at lower temperatures and its increased concentration manifests itself in the increased intensity of the light it absorbs.

The magnetic susceptibility of Sm^{+++} in solution[17] is practically identi-

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[14] Van Vleck and Frank, *Phys. Rev.*, **34**, 1494, 1625 (1929).

[15] The experimental values do not agree with assumptions of Van Vleck and Frank that $\Delta\nu$ between the configurations of different values of j can be calculated from the Goudsmit generalization of the Sommerfeld relativity formula. The latter leads to a $\Delta\nu$ of 940 cm.$^{-1}$ between the two lowest energy levels and the corresponding Boltzmann factor shows that only 1% of Sm^{+++} is electronically activated at room temperature (with a contribution to susceptibility of about 4%) and even less, of course, at lower temperatures. Hence the difference between the measured susceptibility and the part obeying Curie's law should give values which are practically the same for all temperatures. Such is not the case.

[16] Freed and Spedding, *Nature*, **123**, 525 (1929). The magnetic results on Sm^{+++} were first referred to here.

[17] Decker, *Ann. Physik*, **79**, 324 (1926), see Table I.

cal with that in the crystal. Hence the electronic isomers are present in solution to the same concentration as in the crystal at the same temperature.

Summary

The magnetic susceptibility of $Sm_2(SO_4)_3 \cdot 8H_2O$ was measured from 73.8 to 290.6°K. by a new accurate method.

It was found that Sm^{+++} both in the solid state and in solution consists of a mixture of electronic isomers. These isomers appear to be in thermal equilibrium.

The variation of the susceptibility with the temperature suggests that the isomer stable at the lowest temperature has the electronic configuration

Sm^{+++}	1_1	2_1 to 4_3	4_4	5_1	5_2	electronic shell
	2	full	5	2	6	number of electrons

but such a configuration is not yet completely established.

The conclusion that Sm^{+++} consists of a mixture of electronic isomers varying in concentration with the temperature carried with it the prediction that its absorption spectrum would consist of lines whose relative intensities would vary with the temperature. Such a variation in the intensities of the lines was actually found (in collaboration with Dr. F. H. Spedding)[16] in the absorption spectrum of $SmCl_3 \cdot 6H_2O$ taken from room temperature to that of liquid hydrogen.

BERKELEY, CALIFORNIA

[CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF COMMERCE, IN COÖPERATION WITH THE UNIVERSITY OF CALIFORNIA]

THE HEAT CAPACITIES AT LOW TEMPERATURES OF ANTIMONY, ANTIMONY TRIOXIDE, ANTIMONY TETROXIDE AND ANTIMONY PENTOXIDE[1]

BY C. TRAVIS ANDERSON[2]

RECEIVED MARCH 26, 1930 PUBLISHED JULY 3, 1930

In a previous paper from the Pacific Experiment Station of the United States Bureau of Mines the author presented low-temperature thermal data for arsenic and its oxides. The present paper deals with the heat capacities of antimony and its oxides. The third and last of this group on bismuth and its oxides will appear later.

The method and apparatus have been described previously.[3]

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[2] Assistant Physical Chemist, Pacific Experiment Station, U. S. Bureau of Mines, Berkeley, California.

[3] Anderson, THIS JOURNAL, **52**, 2296 (1930).