TABLE IV

SUMMARY OF HEATS OF FORMATION, FREE ENERGIES AND ENTROPIES

Reaction	$CaCO_3 \rightarrow CaO + CO_2$	$SrCO_3 \rightarrow SrO + CO_2$	$BaCO_3 \rightarrow BaO + CO_2$
ΔH_{298} cal.	42,600[a]	53,620[b]	63,400[c]
ΔF_{298} cal.	31,258[a]	42,400[b]	51,400[d]
ΔS	38.1	37.6	40.4
S_{298} R O	9.5	13.0	16.8
S_{298} R CO_3	22.2	23.2	26.8
S_{298} CO_2 calcd.	50.8	47.8	50.4

[a] Bäckström, THIS JOURNAL, **47**, 2443 (1925). [b] John Chipman, communication to this Laboratory, preliminary calculation. [c] De Forcrand, *Compt. rend.*, **146**, 512 (1908). [d] Johnston, THIS JOURNAL, **30**, 1357 (1908).

pies are known to be the more accurate, it is better to use an entropy value for carbon dioxide, such as that determined by use of spectroscopic data, and free energies which may be obtained by several methods, such as dissociation data, and adjust the heat of formation to a value giving a system consistent with the best estimates of specific heat. An extensive series of such calculations is included in a paper entitled "Contributions to the Data on Theoretical Metallurgy. IV. Metal Carbonates. Correlations and Applications of Thermodynamic Properties," which will shortly be published as a Bureau of Mines Bulletin.

Summary

The heat capacities of strontium and barium oxides from about 55 to 300°K. have been determined and their corresponding entropies calculated as 13.0 and 16.8, respectively.

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[CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA, THE UNIVERSITY OF CHICAGO AND THE JOHNS HOPKINS UNIVERSITY]

Specific Heat and Electronic Activation in Crystals

BY J. ELSTON AHLBERG AND SIMON FREED

The rare earths offer exceptional opportunities for studying activations of a now fairly well understood kind, namely, electronic activations in crystals. In a preliminary note[1] we have pointed out how it is possible in the rare earths, at least, to determine the energy and other characteristics of these activations by means of specific heat measurements. We wish to consider the problem again here in greater detail, and also we shall report more accurate experimental data than those which formed the basis of the previous note. The energies required for such activations probably account for the "anomalies" in the specific heats of many other kinds of substances, as well, especially at higher temperatures, but these activations are usually accompanied with complications, which we shall touch upon later. Suggestive of electronic activations of the "pure type" are the deviations of the measurements from the theoretical specific heats of Debye which Simon[2] has evaluated in a number of alkali metals and other elements. The nature of these is still obscure, perhaps for lack of a detailed theory of electronic levels in metals. Moreover, the theory of Debye lacks rigor,[3] and on this account as well, these interesting deviations must await further study for their interpretation.

The electronic energy levels in the crystals we are considering may be thought of most simply as arising from single degenerate levels of the "isolated" ion when it is subject to the electrical fields of the lattice—in the first approximation, to the electrical fields of the ions and dipoles immediately surrounding the ion under consideration. In a salt such as $SmCl_3 \cdot 6H_2O$, for example, the "isolated" ion would be Sm^{+++} while the electrical fields may be thought of as originating in the H_2O dipoles and in the chloride ions surrounding the Sm^{+++}. The number and separation of the levels resulting from the degenerate level of the "isolated" ion will furnish such information as the symmetry of the electrical fields, their magnitudes, the orientations of the ions, etc. Indeed, Bethe[4] has already derived important theoretical relations of this nature. In particular ions, energy levels near the basic level may arise within the "isolated" ion itself,

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[1] J. E. Ahlberg and S. Freed, *Phys. Rev.*, **39**, 540 (1932).

[2] F. Simon, *Ber. Berl. Akad.*, **33**, 477 (1926).

[3] E. Schrödinger, "Handbuch der Physik," Vol. IX, Berlin.

[4] H. Bethe, *Ann. Physik*, [5] **3**, 133 (1929).

representing mutual electronic orientations and interactions, but such multiplets may be looked upon as accidental in the study of crystalline phenomena although the narrowness of these intervals may possibly affect the magnitude of the separations induced by the lattice fields.

The unbalanced electrons of the rare earths are shielded by closed electronic shells from outside electrical influences so that an activation to a higher member of the lattice multiplet, that is, the multiplet induced by the lattice, would not entail any marked changes in the binding with the rest of the lattice and hence would introduce only slight modifications in the elastic vibrations of the crystal. This situation is in decided contrast with the complications which accompany activation in such substances as MnO, Fe_2O_3, etc., where a change in temperature may bring about abrupt irregularities in the specific heats.[5] In the molecule MnO, the unbalanced or least stable electrons of manganese are very close to the oxygen, and their activation would violently change the strength of the bond with oxygen and hence the vibrational frequencies. Moreover, the fields of force to which such external electrons are exposed are very involved functions, and it is not surprising that the lattice appears to offer constraints to reversible electronic activation. Indeed, such activations are likely to disrupt the lattice and force a transition to another crystalline form.

In the present work, the specific heats of the homologous salts of two rare earths are compared over the temperature range from 17 to 293°K. The salts are $Sm_2(SO_4)_3 \cdot 8H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$.

Magnetic measurements of a salt of samarium in which the deviations from the Curie–Weiss law were the most significant feature[6] showed that energy levels, electronic in nature, exist in Sm^{+++} in the crystal close to the basic state and the absorption spectra[7] at various temperatures have furnished the actual energy intervals. On the other hand, magnetic measurements of the salts of gadolinium[8] have shown that practically all the gadolinium ions Gd^{+++} remain in the basic state $^8S_{7/2}$. The theory of Bethe would require that this state be left undecomposed by the electric fields of the lattice and the absorption spectra of the salts of gadolinium[9] confirm these expectations. We may say then that the heat content of the gadolinium salt distributes itself entirely among the elastic vibrations of the crystal, whereas the heat content of the samarium salts resides in electronic activations as well as in the elastic vibrations. If we can assume that the elastic vibrations of homologous salts of gadolinium and samarium possess practically the same frequencies over our temperature range, we may attribute the difference in the heat capacity of the salts directly to the thermal energy appropriated by the electronic activations in each degree rise in temperature. Any difference in the elastic frequencies of the two salts would probably manifest itself as a gradual monotonic increase or a monotonic decrease in the difference between the heat capacities as the temperature is increased. What we are seeking are differences which increase in magnitude until a particular temperature is reached and fall off at still higher temperatures.

There are many reasons for believing that the elastic vibrations of the homologous salts of samarium and gadolinium possess almost identical frequencies. The best evidence is the fact that the group of rare earths in which samarium and gadolinium are almost central and neighboring elements form isomorphous salts miscible in all proportions in the crystalline state. Such a lack of discrimination of one positive ion for another in the lattice speaks strongly for similar force-fields about the ions and the masses differing but little, for almost the same frequencies. The frequencies are functions for the most part of the mass, the size, and the charge of the ions as well as of the geometrical arrangements of the constituents of the lattice. V. Goldschmidt[10] found in his x-ray work on the sesquioxides that the relative diameters of Sm^{+++} and of Gd^{+++} could be represented in the ratios of 1.13 to 1.11. Further, the molecular volume of Sm_2O_4 was determined as 48.38 and that of Gd_2O_3 as 47.58. Von Hevesy (*loc. cit.*, p. 25) measured the molecular volumes of the octahydrated sulfates and found 247.9 for $Sm_2(SO_4)_3 \cdot 8H_2O$ and 246.4 for $Gd_2(SO_4)_3 \cdot 8H_2O$. The atomic weight of Sm^{+++} is 150.4 and that of Gd^{+++} is 157.3. That is, Sm^{+++} is lighter than Gd^{+++}, whereas its volume is larger. These differences partially compensate each other in their effect on the vibrational frequencies which, besides, are rather insensitive to variations in mass and in elastic forces, probably depending upon fractional powers of these variables. For harmonic oscillators

$$\nu = {}^1/_2\, \pi \sqrt{D/\mu}$$

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[5] R. W. Millar, THIS JOURNAL, **50**, 1875 (1928).

[6] S. Freed, *ibid.*, **52**, 2702 (1930).

[7] S. Freed and F. H. Spedding, *Nature*, **123**, 525 (1929); F. H. Spedding and R. Bear, *Phys. Rev.*, **42**, 876 (1932); S. Freed and J. G. Harwell, THIS JOURNAL, **55**, 54 (1933).

[8] H. R. Woltjer and H. Kamerlingh-Onnes, *Leiden Comm.* 167C; W. F. Giauque, THIS JOURNAL, **49**, 1870 (1927).

[9] S. Freed and F. H. Spedding, *Phys. Rev.*, **34**, 945 (1929); F. H. Spedding and G. C. Nutting, THIS JOURNAL, **55**, 496 (1933).

[10] G. von Hevesy, "Die seltenen Erden." Verlag Julius Springer, Berlin, 1927, p. 122.

where ν is the frequency, D the binding constant and μ the reduced mass; D is greater for smaller ions and for the smaller ion (*i. e.*, Gd^{+++}) μ is greater.[11] Another way of bringing out this partial compensation is to consider Einstein's[12] dimensional treatment of oscillators in the crystal which yields

$$\nu = \frac{C}{\mu^{1/3}s^{1/6}K^{1/2}}$$

C is a number depending on the geometrical arrangement of the atoms, s is the density and K the compressibility. The gadolinium salts having greater mass and density are probably less compressible than the corresponding salts of samarium.

The existence of specific heat data for the octahydrate of gadolinium sulfate persuaded us to measure the specific heat of the corresponding salt of samarium. Giauque and Clark[13] had measured the specific heat of $Gd_2(SO_4)_3\cdot 8H_2O$ from 17 to 290°K. and the data were kindly furnished us before publication by Professor W. F. Giauque, to whom we wish to express our gratitude here for aid on numerous other occasions also. In this paper we shall report the heat capacity of the octahydrate of samarium sulfate over the same temperature range as that of gadolinium sulfate. The difference between the heat capacities of the two salts would supply the electronic heat capacity of Sm^{+++} in the lattice. We have also redetermined the specific heats with greater accuracy than was obtained in our original measurements.[14]

One of us in collaboration with Chester Clark[15] has also remeasured more accurately the specific heats of the gadolinium salt. In the present paper we shall give the data obtained in both series of measurements on $Sm_2(SO_4)_3\cdot 8H_2O$ and we shall compare them with the most recent data on $Gd_2(SO_4)_3\cdot 8H_2O$.

Materials

The $Sm_2(SO_4)_3\cdot 8_2O$ was prepared from the oxalate in a manner described in a previous paper.[16] The oxalate was purchased from the Welsbach Company. Professor Wm. Fogg of the University of New Hampshire was kind enough to analyze our salt for us and he concluded that it consisted of at least 99.5% samarium oxalate. He did not test for the presence of europium. Such an impurity would have introduced a negligible error in our results. We have been advised by Dr. Richard Bear, whose work in collaboration with Dr. F. H. Spedding we have already referred to, that the absorption spectrum of the samarium salt which served for our specific heat measurements was practically the same as that of the extremely pure samarium which Professor C. James of the University of New Hampshire had presented for the magnetic investigation.[17] An analysis for the water in the sulfate employed for our first series of measurements which we shall call series A showed 19.59% H_2O instead of the stoichiometrical 19.66%. However, in our next series, series B, which was made on the same salt but redissolved and reprecipitated, the analysis for water content gave 19.44%. We have attributed this difference to the slowness with which the water vapor penetrated into the unexposed portions of the unhydrated crystalline mass. To correct for the deficiency in water we have added the heat capacity of 0.22% ice to our results.[18] Experience has shown that the heat capacity of anhydrous salts plus that of ice of crystallization gives with sufficient accuracy the heat capacity of the hydrated salt. The heat capacities of ice used are those of Simon.[19]

We shall refer to the following paper of THIS JOURNAL in regard to the purity and preparation of the octahydrate of gadolinium sulfate.

Experimental Method and Factors Affecting Accuracy

The heat capacity measurements were made with separate calorimeters of the vacuum type as developed and improved in recent years at the University of California by Giauque, Latimer and associates. The calorimeters were both 7.5 cm. long and 4.5 cm. in diameter. Calorimeters A and B weighed about 90 and 84 g., respectively.

The gold wires used as heater and thermometer on the calorimeter employed for the first set of measurements (Series A) showed temperature heads on energy input greater than those encountered in Series B. When calorimeter A was first made these temperature heads were very small but, due to repeated cooling, the bakelite loosened slightly, resulting in the higher temperature heads. Believing[20] that this difficulty could

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(11) The fractional difference between Sm^{+++} and Gd^{+++} in the binding constant and in the reduced mass is less than what one would gather at first glance from the fractional differences in their radii and in their masses. The radius of the particle with which the positive ion is vibrating is the same in both ions and must be added to the radius of the positive ion. Further, it is easy to show that if the particle with respect to which the positive ion is vibrating is infinite in mass, the fractional difference in the reduced mass is equal to that of the mass itself. When the particles are of the same size, the fractional difference in the reduced mass is one-half that of one of the particles. In fact

$$\frac{\Delta\mu}{\mu} = \frac{\Delta m}{m}\,\frac{a}{a+m}$$

where m is the mass of the particle, say Sm^{+++}, Δm is the difference between the mass of Sm^{+++} and Gd^{+++} and a is the mass of the particle with which m is in vibration.

(12) A. Einstein, *Ann. Physik*, **34**, 170 (1911).

(13) W. F. Giauque and C. W. Clark, THIS JOURNAL, **54**, 3135 (1932).

(14) J. E. Ahlberg and S. Freed, *Phys. Rev.*, **39**, 540 (1932).

(15) J. E. Ahlberg and C. W. Clark, see following paper in THIS JOURNAL.

(16) S. Freed, *ibid.*, **52**, 2702 (1930).

(17) S. Freed, *ibid.*, **52**, 2702 (1930).

(18) "International Critical Tables," Vol. V, pp. 95–101.

(19) Simon, "Handbuch der Physik," Vol. X, p. 363.

(20) J. E. Ahlberg and W. M. Latimer, THIS JOURNAL, **56**, 856 (1934).

be remedied by roughening the copper walls of the calorimeter and careful control of temperature during the baking out of the bakelite, the calorimeter used for Series B was constructed with the above improvements. Calorimeter B showed extremely small temperature heads during energy input.

Temperature heads between the radiating surfaces, wires, walls of the calorimeter and substance undergoing investigation give rise to two factors that must be taken into account in evaluating the heat capacities.[21] The first factor takes into account the heat leak during energy input with a surface hotter than one would calculate from heat leak per unit time measured before and after energy input. The second factor takes into account the apparent readings of the thermometer before and after energy input.

Readings on the thermocouple (at 100°K.) soldered to the bottom of the calorimeter A during energy input (about six calories per minute) showed the copper walls of the calorimeter to be 0.07° hotter than the average temperature of the calorimeter plus substance. The wires (of calorimeter A) at the same time were 2.3° higher than the average temperature. Under the same conditions with calorimeter B the wires were 0.15° higher than the average temperature, which we believe is as low a temperature head as can be hoped for with this type of calorimeter.

The copper exposed at the ends of the calorimeters usually has a dark film of copper oxide or sulfide. Because of this, we believe the ends are practically 100% black body. A polished gold surface is only 2% black body for heat radiation. The gold foil which covered the wires of calorimeter A and the gold leaf which covered the wires of calorimeter B had been handled during construction and assembly but we estimate that it had the properties of a body not more than 10% black. The ends comprise 25% of the total surface of the calorimeters, hence are responsible for three-fourths of the heat exchange by radiation. At temperatures below 100°K. the heat leak is primarily due to heat conduction down to the wire leads.

The corrections due to the effects just considered largely determine the accuracy of the measurements. The corrections were made with the above observations in mind. We estimate that a smooth curve drawn through the values of series A will represent the heat capacity of the sample to within a few per cent. from 15 to 30°K., to within 0.5% from 30 to 175°K., and to within

TABLE I

SERIES B

Heat capacity of 366.59 g. (1/2 mole) $Sm_2(SO_4)_3 \cdot 8H_2O$[a]

$T_{av.}$, °K.	ΔT	C_p/1/2 mole in cal./deg.	$T_{av.}$, °K.	ΔT	C_p/1/2 mole in cal./deg.
17.36	3.789	1.661	99.89	5.110	31.13
22.07	2.841	2.843	101.66	4.872	31.57
27.24	4.972	4.616	106.73	4.883	33.10
31.82	3.767	6.313	112.07	5.727	34.66
35.75	3.755	7.867	117.93	5.795	36.23
39.91	4.498	9.539	123.98	5.938	37.66
44.33	4.416	11.27	130.72	6.621	39.24
49.26	4.953	13.32	138.00	7.179	41.03
53.91	4.261	15.28	147.05	7.095	43.20
58.56	4.943	17.25	154.57	7.354	44.92
62.49	5.173	18.82	162.37	7.641	46.76
64.93	4.728	19.82	170.19	7.235	47.94
67.92	5.205	20.95	178.63	7.425	50.08
70.11	5.357	21.70	186.89	7.617	51.88
73.16	5.088	22.70	195.31	7.158	53.86
75.43	5.100	23.42	204.62	6.727	55.59
78.11	4.551	24.44	213.12	7.599	57.16
80.57	4.942	25.20	222.32	7.118	59.13
82.77	4.564	25.93	231.78	6.729	60.72
85.36	4.473	26.77	241.56	7.509	62.63
87.43	4.569	27.37	251.29	7.034	64.22
90.08	4.786	28.38	260.63	7.763	65.83
92.08	4.584	29.06	271.66	7.268	68.08
94.99	4.589	29.71	290.39	6.021	71.14
96.82	4.734	30.27	296.28	6.381	72.26

[a] Value of calorie taken equals 4.185 absolute joules.

TABLE II

DIFFERENCES IN THE HEAT CAPACITIES OF ONE-HALF MOLE OF $Sm_2(SO_4)_3 \cdot 8H_2O$ AND $Gd_2(SO_4)_3 \cdot 8H_2O$

T, °K.	Series A	Series B	T, °K.	Series A	Series B
17	0.03	0.08	125	1.64	1.76
20	.14	.13	130	1.65	1.62
25	.16	.19	135	1.55	1.58
30	.15	.32	140	1.55	1.52
35	.25	.48	145	1.53	1.60
40	.50	.63	150	1.47	1.52
45	.67	.78	160	1.40	1.48
50	.83	.91	170	1.30	1.42
55	.99	1.08	180	1.35	1.36
60	1.07	1.33	190	1.50	1.33
65	1.16	1.49	200	1.5	1.3
70	1.30	1.57	210	1.4	1.2
75	1.55	1.63	220	1.5	1.2
80	1.76	1.68	230	1.5	1.2
85	1.85	1.74	240	1.4	1.2
90	1.80	1.77	250	1.5	1.3
95	1.72	1.84	260	1.6	1.6
100	1.67	1.89	270	1.8	1.7
105	1.66	1.92	280	2.1	1.8
110	1.69	1.93	290	2.3	2.1
115	1.55	1.90	300	2.4	2.2
120	1.56	1.85			

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(21) W. F. Giauque and R. Wiebe, THIS JOURNAL, 50, 109 (1928).

1.0% from 175 to 300°K. We judge that a smooth curve drawn through the values of series B (uncorrected for water content) will represent the heat capacity of the sample to within a few per cent. from 15 to 30°K. and to within a few tenths of a per cent. from 30 to 300°K. The primary reason for the higher estimate from 15 to 30°K. is due to the small and rapidly changing temperature coefficient of gold resistance thermometers in this region.

It is to be noted that the calorimeter B was employed for the $Gd_2(SO_4)_3 \cdot 8H_2O$ measurements[15] used for determining the heat capacity of the $Sm_2(SO_4)_3 \cdot 8H_2O$ minus its electronic specific heat. As a result constant errors tend to cancel one another. It also should be noted that calorimeters A and B were identical except for the differences already recorded. Furthermore, all measurements were made using the same temperature scale.[22]

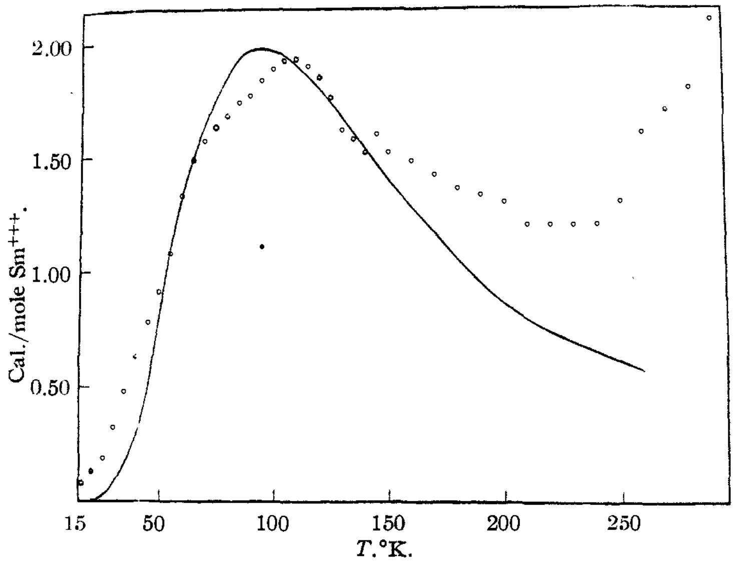

Fig. 2.—Electronic heat capacity: curve gives theoretical values; circles experimental.

The results of the measurements are given in Table I. The values for Series B represent the observed heat capacity corrected for the deficiency of water already noted.

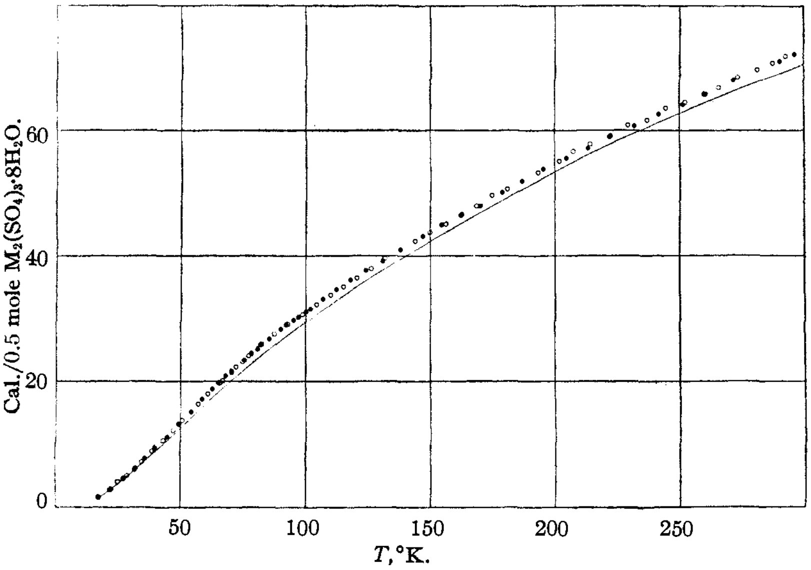

Fig. 1.—Heat capacities of $Sm_2(SO_4)_3 \cdot 8H_2O$; clear circles series A, blackened circles series B; heat capacities of $Gd_2(SO_4)_3 \cdot 8H_2O$ curve.

Treatment of Data and Discussion

The electronic heat capacity or the differences between the heat capacity of $Sm_2(SO_4)_3 \cdot 8H_2O$ and of $Gd_2(SO_4)_3 \cdot 8H_2O$ were obtained by drawing smooth curves through the experimental values of the two salts and by reading off differences at the various temperatures. The heat capacities are plotted in Fig. 1 and the differences in Fig. 2.

While it is possible to make analyses of the specific heat data to arrive at energy levels of the ion, the existence of absorption spectra of $Sm_2(SO_4)_3 \cdot 8H_2O$ seems to make the effort unnecessary provided the agreement between spectral and thermal data is satisfactory. Such an agreement is not at all necessary, however. For example, the ion may possess energy levels which are not revealed in the absorption spectra because of the operation of some selection rule and yet their presence would emerge in the heat capacity of the salt. In the event that the energy levels derived from spectra can account fully for the heat capacity of the salt, a comparison between the two types of data will

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[22] W. F. Giauque, R. M. Buffington and W. Schulze, THIS JOURNAL, **49**, 2343 (1927); W. F. Giauque, H. L. Johnston and K. K. Kelley, *ibid.*, **49**, 2367 (1927).

furnish the ratios of the statistical weights of the energy levels and aid in their interpretation.

Our analysis of the first specific heat data led to our preliminary note.[23] At that time only rather rough measurements of the absorption spectra on $SmCl_3 \cdot 6H_2O$ were known.[24]

Recently the absorption spectra of $Sm_2(SO_4)_3 \cdot 8H_2O$ itself were studied by Dr. Spedding and Dr. Bear, and they have been kind enough to furnish us with the energy intervals at the temperature of liquid nitrogen. They are 160 $cm.^{-1}$, 188 $cm.^{-1}$, and 225 $cm.^{-1}$, each as measured from the basic state. As a first attempt we assumed that all four levels have the same statistical weight (two, in all probability according to a theorem of Kramers which states that electrical fields will leave a level resulting from an odd number of electrons with an even-fold degeneracy). We have also ignored the change in the intervals with temperature, which is not great. These three intervals inserted in the sum-of-states yield the following values for the electronic heat capacity to be expected from the four energy levels.[25]

T, °K.	C_v	T, °K.	C_v
20	0.0033	110	1.90
25	.024	120	1.79
30	.08	130	1.67
50	.81	150	1.38
70	1.63	170	1.17
90	1.97	200	0.91
100	1.96	250	.62

The curve in Fig. 2 was drawn from these values; the circles give the difference between the heat capacity of samarium sulfate in series B and that of gadolinium sulfate.[26]

In all probability, the electronic activation is attended by a negligible change in volume and we shall compare the computed C_v, that is, the difference in heat capacity at constant volume, with the experimental C_p, the difference at constant pressure.

A comparison of the experimental values with the computed values shows a satisfactory agreement up to 150°K. and then a deviation points unmistakably to the existence of more energy levels, further from the basic state. Such levels are to be expected. If we identify the basic multiplet with the decomposition of $^6H_{5/2}$ term of the multiplet $^6H_{5/2, 7/2, 9/2, 11/2, 13/2, 15/2}$ of the "isolated" Sm^{+++}, the term $^6H_{7/2}$ is roughly 1000 $cm.^{-1}$ above the $^6H_{5/2}$ level and upon decomposition by the electrical fields the center of gravity of the resulting sub-levels may be perhaps at some interval 750 $cm.^{-1}$ to 1250 $cm.^{-1}$ above the basic state and hence contribute to the specific heat especially at the higher temperatures. Miss Amelia Frank[27] has computed what the electronic heat capacities would be provided no decomposition of the $^6H_{5/2}$ and $^6H_{7/2}$ states occurred. These give a rough indication of the over-all contribution to the heat capacities by the states originating in the $^6H_{7/2}$ level.

	C_v	
T, °K.	$\sigma = 34$	$\sigma = 33$
0	0.00	0.00
170	.06	.03
205	.17	.08
240	.31	.18
293	.57	.38
400	1.04	.83

σ is the assumed screening constant. The inclusion of these contributions to the specific heat would improve materially the agreement between the computed and experimental values at higher temperatures.

The existence of four levels rather than three in the basic multiplet has not been explained with any degree of certainty. The absorption spectra of other salts of Sm^{+++}. point to even more levels although the theory developed by Bethe[4] demands but three levels, each doubly degenerate. Quite independently of any theory, the specific heat definitely conforms to the energy levels revealed in the spectra and it conforms to the ideal statistical theory employed for gaseous systems. Attempts to consider only three levels rather than the four found in the spectra have led to radical disagreement with the data.

The experimental work was done at the University of California.

Summary

It is shown possible among the rare earths to determine experimentally the portion of the

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(23) J. E. Ahlberg and S. Freed, *Phys. Rev.*, **39**, 540 (1932).

(24) S. Freed and F. H. Spedding, *Nature*, **123**, 525 (1929).

(25) The average electronic energy per mole

$$E = Nhc \sum_{\nu=1}^{3} \nu_i e^{-h\nu_i c/kT} \Big/ \sum_{\nu=1}^{3} 1 + e^{-h\nu_i c/kT}$$

$$\nu_i = 160,\ 188,\ 225\ \text{cm.}^{-1}$$

and the electronic heat capacity, $C_v = \partial E/\partial T$ where the symbols have their usual meaning.

(26) Because of the greater reliability, the values in series B were employed for the plot rather than the values in series A. especially in view of the fact, previously mentioned, that the samarium sulfate in series B was measured in the same calorimeter as gadolinium sulfate. Any systematic errors would probably cancel in the difference which we are concerned with. The reader may verify that series A furnishes the same trend as series B but the results are more irregular.

(27) A. Frank, *Phys. Rev.*, **39**, 127 (1932).

specific heat associated with electronic transitions in crystals. For our particular example, we determined the heat capacities of $Sm_2(SO_4)_3 \cdot 8H_2O$ at temperatures from 17 to 295°K., and the data are reported here. These are compared with the heat capacities of $Gd_2(SO_4)_3 \cdot 8H_2O$ over the same temperature range.[15] The quantitative agreement between the observed and computed electronic specific heats is found satisfactory.[28] The statistical weights for the levels in the basic multiplet were found to be equal to each other.

[28] The computations employed the energy intervals derived from the absorption spectra of $Sm_2(SO_4)_3 \cdot 8H_2O$ by Dr. F. H. Spedding and Dr. Richard Bear. The intervals were kindly furnished us before publication.

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

The Heat Capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ from 16 to 300° Absolute

BY J. ELSTON AHLBERG AND CHESTER W. CLARK

In the treatment of the electronic specific heat of samarium ion Sm^{+++} considered in the preceding article[1] it was necessary to use the differences in the heat capacities of $Sm_2(SO_4)_3 \cdot 8H_2O$ and $Gd_2(SO_4)_3 \cdot 8H_2O$. The heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$ has been determined previously in this Laboratory by Giauque and Clark.[2] Giauque and Clark suggested that for purposes other than those with which they were immediately concerned, it would be advisable to make a redetermination of the heat capacity of this salt. For reasons which Giauque and Clark[2] have already pointed out, the particular calorimeter employed by them was unsatisfactory and was discarded after having been used only for their measurements on $Gd_2(SO_4)_3 \cdot 8H_2O$. For the purpose of comparison accuracy is gained by the measurement of the heat capacity of the two salts under as nearly identical conditions as possible.

Material.—The same sample of $Gd_2(SO_4)_3 \cdot 8H_2O$ as used by Giauque and Clark was employed for this series of measurements. Analysis furnished by Welsbach Company, Gloucester, New Jersey, showed this sample to be Gd 98.5%, Sm 0.5%, Tb 1.0%. The presence of these impurities, since they are so very similar in many respects to gadolinium, will introduce errors which are negligible compared to the inaccuracy of the measurements. Determination of the water content of the sample gave 19.25% H_2O compared to 19.29% H_2O theoretical; 180.21 g. was used in the measurements.

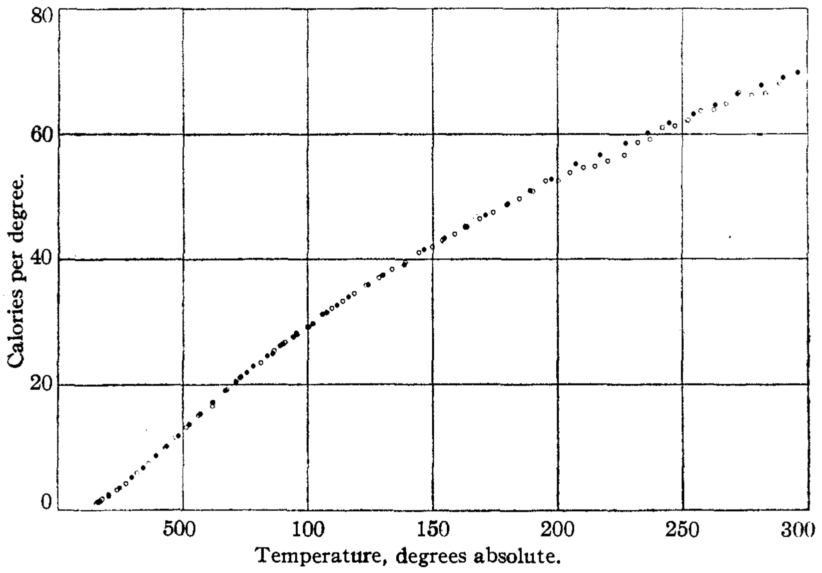

Fig. 1.—Heat capacity of 373.42 g. (1/2 mole) of $Gd_2(SO_4)_3 \cdot 8H_2O$.

Heat Capacity Measurements.—The calorimeter used also was employed for the measurements on $Sm_2(SO_4)_3 \cdot 8H_2O$, Series B, reported in the preceding article.[1] The wires on this calorimeter as already noted[1] gave rise to only very small temperature heads during energy input. The uncertainties involved in applying the heat exchange corrections for this effect largely determine the accuracy of the results obtained. We believe that a smooth curve drawn through

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[1] Ahlberg and Freed, THIS JOURNAL, **57**, 431 (1935).

[2] Giauque and Clark, *ibid.*, **54**, 3135 (1932).