neutralization it might then be expected to be free to add to the double bond.

Franck and Rabinowitsch Hypothesis.— Franck and Rabinowitsch[7] have discussed factors which might be expected to cause lower quantum yields in solution than in the gas phase in the case of photochemical reactions in which the primary process in the gas involves the production of atoms or radicals.

The reactions of bromine atoms following neutron capture and following isomeric transition appear to offer a definite experimental example of the effect of solvent in favoring the combination of atoms and radicals which are formed in the same solvent envelope. If the mechanism which is pictured is correct, these bromine atoms split carbon tetrachloride molecules into radicals and atoms and then may react with the radicals formed. The atoms resulting from either neutron capture or isomeric transition are *tagged* with radioactivity so it is possible to determine whether the *particular* atom which forms a radical reacts with it. The fact that little or no reaction between these atoms and the carbon tetrachloride occurs in the gas phase in contrast to the liquid seems to indicate the ability of an envelope of carbon tetrachloride molecules to bring about the combination of carbon tetrachloride fragments and bromine atoms by decreasing the probability of their diffusing away from each other, and by removing their

(7) Franck and Rabinowitsch, *Trans. Faraday Soc.*, **30**, 120 (1934). See also: Rollefson and Burton, "Photochemistry," Prentice-Hall, New York, N. Y., 1939; Leighton and Noyes, "The Photochemistry of Gases," Reinhold Publishing Co., New York, N. Y., 1941; Atwood and Rollefson, *J. Chem. Phys.*, **9**, 506 (1941).

energy of combination before such diffusion occurs.

Summary

1. It has been shown that the nuclear n,γ process whereby radioactive bromine is produced is capable of causing reaction of the bromine with carbon tetrachloride in solution but that little or no reaction occurs in the gas phase.

2. An appreciable fraction of the organic bound radiobromine resulting from both the isomeric transition and neutron capture reactions of bromine with carbon tetrachloride is in compounds of higher boiling point than CCl_3Br. This indicates that the mechanism of reaction involves a disruption of the carbon tetrachloride molecule more serious than the removal of a single chlorine atom.

3. Bromine will react with liquid tetrachloroethylene following neutron capture with a probability of about 37% and following isomeric transition with a probability of about 85%. It will react in the gas phase following isomeric transition but not following neutron capture. The different probabilities of reaction following the two types of activation are discussed.

4. The difference between the probability of reaction in solution and in the gas phase, observed in this work, is evidence in support of the Franck and Rabinowitsch "cage" hypothesis.

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

Energy States of Solids: Evidence from Thermal Data for the Existence of Low Electronic Energy Levels in Europium Ion. The Heat Capacity of Europium Sulfate Octahydrate from 60 to 300°K.

BY EARL A. LONG AND RAYMOND A. DEGRAFF

The investigations of Spedding and co-workers[1] have established the existence of low-lying electronic energy levels in a number of rare-earth salts. Certain of these levels result from the splitting of a degenerate ground state of the rare-earth ion by the crystalline field; others are excited electronic levels whose energy is comparable with kT, and which may or may not be split by

(1) Spedding, Nutting and Hamlin, *J. Chem. Phys.*, **5**, 191 (1937), and previous articles.

the field. The number and spacing of the energy levels have been investigated theoretically[2] and fair agreement with the observed spectroscopic and magnetic susceptibility data has been obtained. The calculations almost invariably involve the simplifying assumption of an electrical field of cubic symmetry.

(2) *Cf.* Van Vleck, "Theory of Electric and Magnetic Susceptibilities," Oxford, 1932; Penney and Schlapp, *Phys. Rev.*, **41**, 194 (1932); Penney and Kynch, *Proc. Roy. Soc.* (London), **A170**, 112 (1939); Spedding, *J. Chem. Phys.*, **5**, 316 (1937).

Spedding, Moss and Waller[3] have recently measured the absorption spectrum of europium ion in several hydrated salts, and report levels at about 300, 390, 430, 938 and 970 cm.$^{-1}$ above the ground state. The .300, 938 and 970 cm.$^{-1}$ levels are identified as electronic in nature, while the 390 and 430 cm.$^{-1}$ states are not definitely classified, since there is some evidence in the absorption spectra that these levels are perhaps vibrational. Since the basic state of europium ion is $^7F_0$ (nondegenerate), no splitting of this state can occur. Spedding[3] has suggested that a low-temperature heat capacity investigation of europium sulfate octahydrate would establish the nature of the levels around 400 cm.$^{-1}$.

Ahlberg and Freed[4] first suggested and carried out an investigation of the contribution of low-lying electronic levels to the heat capacity of a salt, for the case of samarium sulfate, and Ahlberg, Blanchard and Lundberg[5] demonstrated by the same method the existence of a 77 cm.$^{-1}$ state in neodymium sulfate. In both cases, the excited levels arise from splitting of the basic state by a crystalline field assumed to be mainly of cubic symmetry.

The method consists essentially of comparing the heat capacity of the rare earth sulfate under investigation with that of gadolinium sulfate. Since the normal state of the gadolinium ion is an S level, it will be only very slightly affected by the crystalline field; also, it has been shown by Ahlberg and Freed[4] that the "non-electronic" heat capacities of the two salts should be practically identical. Therefore, any difference between the heat capacities of the two salts can be attributed to electronic excitation. Ahlberg and Clark[6] have determined the heat capacity curve of gadolinium sulfate with high accuracy.

In this paper we are reporting the results of heat capacity measurements on europium sulfate octahydrate.

Experimental

The measurements were made with a vacuum calorimeter similar in most respects to that described by Long and Toettcher.[7] The gold-plated copper calorimeter was fitted with an internal strain-free platinum resistance thermometer of 98 ohms ice-point resistance. This thermometer was calibrated against a copper-constantan ther-

mocouple No. M-12, which itself had been compared with our standard thermocouple No. M-10, calibrated for us by the U. S. Bureau of Standards through the courtesy of Dr. F. G. Brickwedde. The temperatures based on No. M-12 should be accurate to 0.05°, in an absolute sense.

Previous measurements in this Laboratory have been based on the use of an accurate signalling chronometer for the timing of energy input. Unfortunately, a routine check-up showed that the instrument needed minor repairs, just before the measurements on europium sulfate were started, and as a consequence, energy input was timed with a 0.1 second stop watch, which had been calibrated in terms of the chronometer, and was checked against standard time signals after the measurements were completed. The timing error should not exceed 0.03%.

The condensation ring calorimeter of Long and Toettcher was eliminated by the acquisition of a 15 cu. ft. Kinney vacuum pump, which enabled us to attain temperatures down to 57°K. by evaporation of liquid air from the larger apparatus. We used tricresyl phosphate instead of oil in the pump, in order to eliminate the hazard of serious oxygen–oil explosions in the pump reservoir.

The europium sulfate was a 77-g. sample of exceptionally high purity, which was prepared and very generously loaned to us by Dr. Herbert N. McCoy. The sample was in the form of a fine crystalline powder, prepared by Dr. McCoy in the following manner: the sulfate was precipitated by the addition of 12 N sulfuric acid to a 25% solution of europium chloride. The precipitate was washed free from hydrochloric acid and sulfuric acid with water, filtered with suction, and dried in air at room temperature. The europium chloride was made by the method of McCoy,[8] and was subsequently freed from traces of barium and calcium impurities. By analogy with a previous preparation of Dr. McCoy,[8] it may be estimated that our sample contained not more than one part in 10,000 of neodymium, and that other rare earths were absent.

In view of the value of the sample, we did not carry out a chemical analysis to check on the water content. Heat capacity measurements near the ice-point showed with high accuracy the absence of any water in excess of the water of hydration, and a consideration of the method of preparation makes it unlikely that the sample was desiccated.

Heat Capacity Measurements.—The heat capacity data are given in Table I. For the calculation of energy, one 15° calorie was taken equal to 4.1852 absolute joules. In Table II are listed values of the heat capacity at even temperatures, as read from a smooth curve through the data. These values should be accurate to 0.3% from 60 to 200°K., and to 0.5% above 200°K.

Discussion

Table III and Fig. 1 show the results of a comparison between the heat capacities per half-mole of europium and gadolinium sulfates. The values in Table III were obtained by drawing smooth curves through the experimental data for the two salts and then reading off differences at the tem-

(3) Spedding, Moss and Waller. *J. Chem. Phys.*, **8**, 908 (1940).

(4) Ahlberg and Freed, THIS JOURNAL. **57**, 431 (1935).

(5) Ahlberg, Blanchard and Lundberg, *J. Chem. Phys.*, **5**, 552 (1937).

(6) Ahlberg and Clark, THIS JOURNAL, **57**, 437 (1935).

(7) Long and Toettcher, *ibid.*, **64**, 629 (1942).

(8) McCoy, *ibid.*, **59**, 1131 (1937).

TABLE I

MOLAL HEAT CAPACITY OF EUROPIUM SULFATE OCTA-
HYDRATE

Mol. wt., 736.31.　0°C. = 273.16°K.

$T_{av.}$, °K.	C_p, cal./deg./mole	$T_{av.}$, °K.	C_p, cal./deg./mole
62.83	36.44	183.90	103.4
65.67	38.49	188.27	105.2
69.49	40.97	193.03	107.1
74.01	43.80	197.96	110.4
78.55	46.92	202.71	112.2
82.68	49.73	207.51	114.2
86.40	51.78	212.21	115.8
94.51	57.14	221.12	120.7
99.61	60.47	225.35	122.0
104.41	63.21	226.91	122.3
110.29	67.04	231.65	123.7
116.11	69.77	236.70	126.6
121.16	72.90	242.61	127.1
127.37	76.42	246.01	129.1
134.48	79.87	250.78	130.6
139.90	83.46	255.83	133.1
144.27	86.01	264.29	134.5
148.82	87.71	268.46	134.4
153.90	90.07	272.84	137.2
159.48	92.67	277.28	139.6
164.87	95.77	281.78	140.7
169.93	97.33	286.22	141.6
174.85	100.4	290.74	144.3
179.49	101.8	295.23	144.8

TABLE II

MOLAL HEAT CAPACITY OF EUROPIUM SULFATE OCTA-
HYDRATE.　VALUES TAKEN FROM SMOOTH CURVE THROUGH
THE DATA

Mol. wt., 736.31.　0°C., 273.16°K.

T, °K.	C_p, cal./deg./mole	T, °K.	C_p, cal./deg./mole
60	34.40	170	97.90
65	38.00	180	102.5
70	41.40	190	107.1
75	44.60	200	111.6
80	47.90	210	115.8
85	51.10	220	119.7
90	54.28	230	123.4
100	60.34	240	127.1
110	66.34	250	130.6
120	72.20	260	133.8
130	77.90	270	137.0
140	83.40	280	140.1
150	88.44	290	143.1
160	93.30	300	147.1

peratures listed. Within the limitations of the
method, these differences represent the electronic
heat capacities per mole of europium ion.

Amelia Frank[9] has discussed the effect of crys-
talline fields on the energy levels of Eu^{+++}.
Considering only levels up to $J = 2$, and assuming
a field of cubic symmetry, we have a non-degener-
ate ground state, a $J = 1$ state which is not af-

(9) Amelia Frank, Phys. Rev., 39, 119 (1932); 48, 765 (1935).

TABLE III

ELECTRONIC HEAT CAPACITY OF EUROPIUM ION.　DIFFER-
ENCES IN THE HEAT CAPACITIES OF ONE-HALF MOLE OF
$Eu_2(SO_4)_3 \cdot 8H_2O$ AND $Gd_2(SO_4)_3 \cdot 8H_2O$

T, °K.	C_v, cal./deg./mole of Eu^{+++}	T, °K.	C_v, cal./deg./mole of Eu^{+++}
60	0.64	170	2.16
65	.61	180	2.25
70	.62	190	2.30
75	.54	200	2.40
80	.53	210	2.47
85	.56	220	2.52
90	.69	230	2.53
100	.85	240	2.51
110	.95	250	2.52
120	1.18	260	2.51
130	1.63	270	2.51
140	1.79	280	2.51
150	1.88	290	2.53
160	2.09	300	2.54

fected by the cubic field, and a $J = 2$ state which
is split into two levels of statistical weight two and
three, the doubly degenerate level having the
higher energy.　A rhombic field of sufficient in-
tensity would completely remove the degeneracies
in the 1 and 2 states, giving three levels for the
$J = 1$ state and 5 levels for the $J = 2$ state.

If we assume that the levels determined by
Spedding, Moss and Waller at 383 and 435 cm.$^{-1}$
are vibrational states superimposed on the 302
cm.$^{-1}$ electronic state, we then identify the 302 (3)
cm.$^{-1}$ state as $J = 1$, and the 937 (3) and 983 (2)
cm.$^{-1}$ levels as resulting from splitting of the $J =
2$ state by a cubic field.　The numbers in paren-
theses represent the degeneracies.

In order to identify the 383 and 435 cm.$^{-1}$ levels
as electronic in nature, we assume a small rhombic
field which at least partially splits the $J = 1$ state
into its three components of 302 (1), 383 (1), and
435 (1) cm.$^{-1}$, but which does not contribute
enough to cause any further splitting of the $J = 2$
state.

The equation[10]

$$\frac{dE}{dT} = \frac{N}{kT^2}\left[\frac{\Sigma\epsilon^2 pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}} - \left(\frac{\Sigma\epsilon pe^{-\epsilon/kT}}{\Sigma pe^{-\epsilon/kT}}\right)^2\right]$$

was used in calculating the contribution of these
levels to the electronic heat capacities of europium
ion.　Two cases were considered, as outlined
above: first, a pure cubic field, with the states
302(3), 937(3), and 983(2) cm.$^{-1}$; and, second,
a field which includes a rhombic contribution,
with the states, 302(1), 383(1), 435(1), 937(3),
and 983(2) cm.$^{-1}$; the numbers in parentheses

(10) Cf. Giauque, THIS JOURNAL, 52, 4808 (1930).

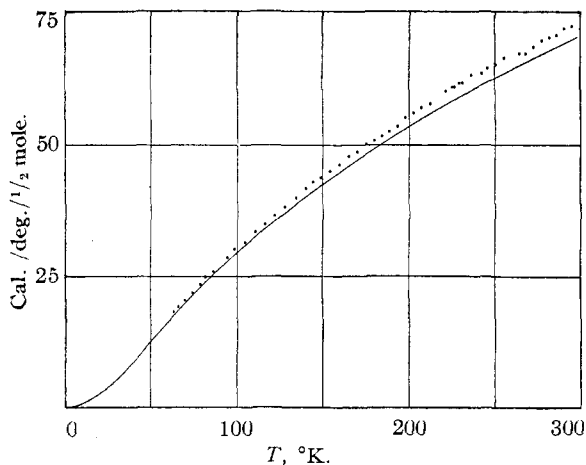Fig. 1.—Points, heat capacities of $Eu_2(SO_4)_3 \cdot 8H_2O$; smooth curve, heat capacity of $Gd_2(SO_4)_3 \cdot 8H_2O$.
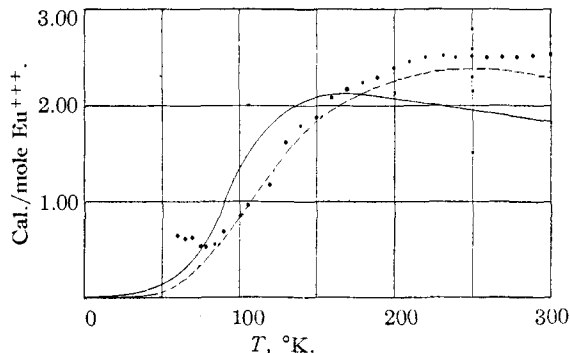

Fig. 2.—Electronic heat capacity of Eu^{+++}; solid curve, calculated for pure cubic field; broken curve, calculated for rhombic contribution; points, experimental data.

again represent the statistical weights. Figure 2 shows the results of these computations; the full curve represents the heat capacity for a cubic field, the broken curve that for a field with a rhombic contribution which affects the $J = 1$ state. The points show the experimental data taken from Table III.

It is apparent from Fig. 2 that the heat capacity data best fit the curve which includes the contribution of the 383 and 435 cm.$^{-1}$ levels, and, therefore, that the crystalline field is probably not one of pure cubic symmetry. This conclusion does not agree with the calculations of Spedding, Moss and Waller,[3] who found much better agreement with Selwood's[11] measured magnetic susceptibilities by assuming that the 383 and 435 cm.$^{-1}$ levels were vibrational. These writers point out, however, that the treatment of Frank and Van Vleck, used by them, should be re-investigated, taking into account perturbations of the assumed energy level pattern.

The points below 80°K. in Fig. 2 are definitely high, suggesting either experimental error or the existence of some lower energy excitation which could hardly be electronic in nature. We have carefully checked our temperature scale in this region, and can find no error in the experimental

heat capacity measurements. It is possible, though unlikely, that the different temperature scales used by Ahlberg and Freed, and by us, contributed to the magnitude of the deviations.

Summary

The heat capacity of europium sulfate octahydrate has been investigated in the temperature range 60 to 300°K. From these data and the corresponding heat capacities of gadolinium sulfate octahydrate, the electronic heat capacities of europium ion have been obtained.

These experimental electronic heat capacities have been compared with values calculated from the energy levels reported by Spedding, Moss and Waller in their study of the absorption spectra. The comparison indicates that the crystalline field about the europium ion in this salt is probably not one of pure cubic symmetry, but that a small rhombic contribution must be considered. Thus the energy levels observed by Spedding, et al., at 383 and 435 cm.$^{-1}$ above the ground state are probably electronic and not vibrational in character.

(11) Selwood. THIS JOURNAL. 55, 4869 (1933).

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