hoefer is 3.3×10^{-5} at 25°. The energy of activation of reaction (4) is not so easily obtained accurately. The Hirschfelder rule gives 2.7 kcal. Rollefson and Potts[6] calculated it to be 4 kcal. by a modification of Eyring's method. The latter value leads to an Arrhenius factor of 1.26×10^{-3} at 27°. The ratio of the relative rates of the reaction of a chlorine atom with a hydrogen molecule and with an iodine monochloride molecule then becomes

$$19 \times \frac{3.3 \times 10^{-5}}{1.26 \times 10^{-3}} = \frac{1}{2}$$

Since the iodine monochloride reaction with chlorine atoms is less than half as probable as the hydrogen reaction with chlorine atoms due to the steric factor, it follows that both reactions are about equally probable under the present experimental conditions. This means that the quantum yield should be one since for every two chlorine atoms formed by photodissociation one will undergo reactions (2) and (3) forming two molecules of hydrogen chloride and the other will undergo reaction (4). This is in good agreement with the experimental quantum yield of 1.5.

On the other hand, the value of the activation energy of the iodine monochloride reaction with chlorine atoms may be the lower value obtained by the Hirschfelder rule, which leads to a reaction rate nearly one hundred times as rapid. Since traces of impurities speed up the reaction very considerably, as Ashley and West[5] point out, there is a possibility that the observed reaction is due largely to impurities though great care was taken in the present work to use purified materials and to avoid stopcock grease. The value of 1.5 for the quantum yield might, therefore, appear to be an upper limit to the true yield.

However, if 1.5 is really the quantum yield, and the data of Ashley and West seem to support this view since they found the reaction seemed to approach a minimum, then the energy of activation of (4) must be large enough for (2) to compete successfully with (4) for the chlorine atom under conditions of high hydrogen pressure. On the other hand at low pressures, when the hydrogen pressure is roughly the same as that of the iodine monochloride, reaction (2) will proceed so slowly that practically all of the chlorine atoms will undergo reaction with iodine monochloride. Thus there is no essential conflict in the results of Rollefson and Lindquist, Mellor and Iredale, Ashley and West and the present authors.

Summary

The quantum yield of the photochemical reaction of hydrogen and iodine monochloride in a flow system was determined to be about 1.5 at an iodine monochloride pressure of 40 mm. and a hydrogen pressure of about 715 mm. A mechanism is advanced to account for the present data as well as for the results of previous investigators.

ROCHESTER, NEW YORK RECEIVED MAY 21, 1945

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA]

The Heat Capacity and the Entropy of Hydrated Lanthanum Magnesium Nitrate

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Heat capacity data over sizable temperature ranges and the corresponding entropies are available for only a few rare earth salts.[2] The present work was begun to obtain data for compounds of additional rare earths. A comparison of the thermodynamic properties of these elements will thus become possible.

Since previous studies have been made on sulfate octahydrates, it would have been desirable to use the same salt for additional elements. Lanthanum, however, does not form such a sulfate, and that of cerium is not isomorphous with those already studied.[3] After the properties of a hundred and fifty series of rare earth salts had been reviewed, the double magnesium nitrates $2R(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$, were selected for the present work. They form an isomorphous series for at least the first eight elements of the group and are readily prepared in the form of large crystals of reproducible composition.

Experimental

Material.—The source of lanthanum was a sample of oxide kindly loaned by Prof. L. L. Quill, then at the Ohio State University, now at the Michigan State University. It had been spectrographically studied by Mr. W. H. Thomas at the Ohio State University. The principal lines of other rare earth elements were missing. The oxide was mixed with the stoichiometric quantity of Baker and Adamson C. P. basic magnesium nitrate, and both were dissolved in C. P. nitric acid. After filtration the solution was evaporated to crystallization. The salt was recrystallized from water a number of times. Soluble impurities such as nitric acid and magnesium nitrate were further removed by several fractional crystallizations. The amount of water in the sample was adjusted by placing the sample in a desiccator with a weak desiccant for a short time.

The average residue on igniting samples was 29.35% while the theoretical is 29.25%. The ratio of lanthanum

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(2) (a) $Sa_2(SO_4)_3 \cdot 8H_2O$ from 17 to 300° A., Ahlberg and Freed, THIS JOURNAL, **57**, 431 (1935); (b) $Gd_2(SO_4)_3 \cdot 8H_2O$ from 16 to 300° A., Ahlberg and Clark, *ibid.*, **57**, 437 (1935); (c) $Eu_2(SO_4)_3 \cdot 8H_2O$ from 60 to 300° A., Long and Degraff, *ibid.*, **64**, 1346 (1942); (d) studies over limited ranges have been reported by Clark and Keesom, *Physica*, **2**, 1075 (1935); Giauque and MacDougall, *Phys. Rev.*, **44**, 235 (1933); and Giauque, Stout, Egan and Clark, THIS JOURNAL, **63**, 405 (1941).

(3) Spencer, "The Metals of the Rare Earths," Longmans, Green and Co., London, 1919, pp. 81, 101.

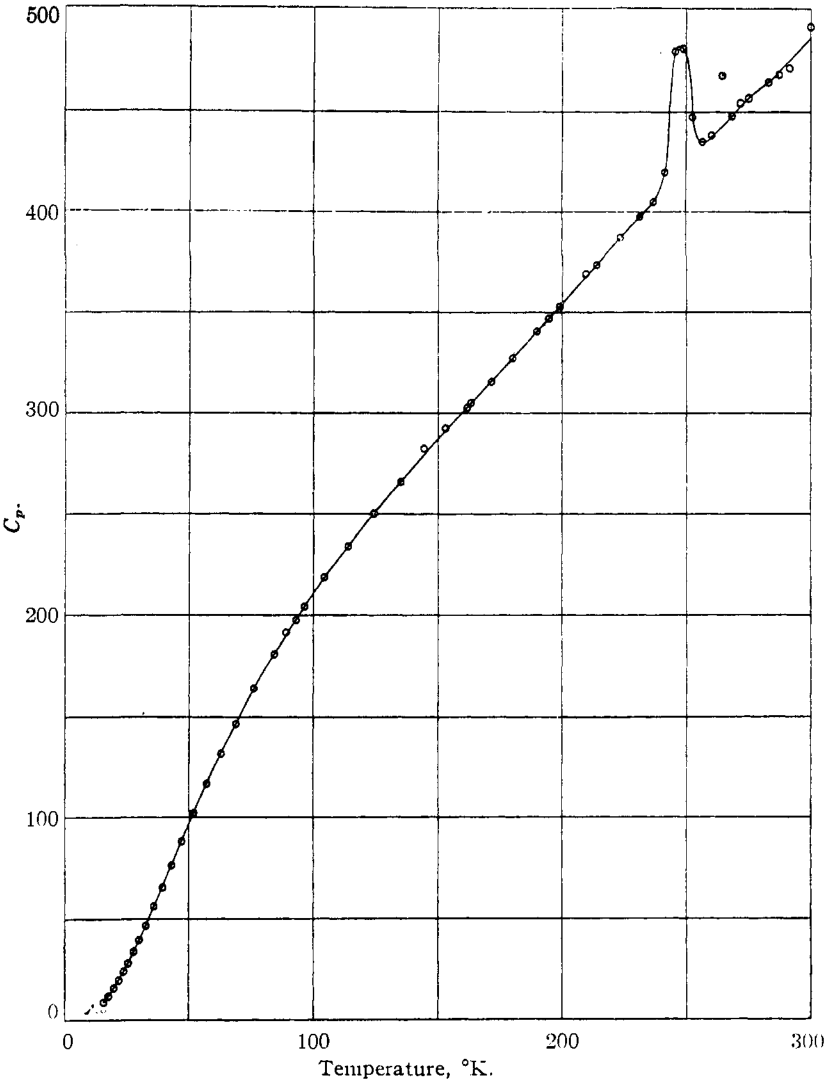

Fig. 1.—Heat capacity in cal. per degree per mole for $2La(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$.

to magnesium was determined by dissolving several samples of the oxides obtained from the ignitions, precipitating lanthanum oxalate from a dilute acid solution, and igniting the oxalate. La_2O_3 made up 72.9% of the ignition residue. The theoretical value is 72.93%.

Heat Capacity Measurements.—The calorimeter and cryostat have been previously described.[4] The highly hydrated salt made necessary one modification of the usual procedure. After the sample was placed in the calorimeter, a copper cap was loosely fitted into the open end. The cover of the calorimeter was then soldered into place while all but a small portion of it was under water. The cap prevented any local concentration of heat from the soldering so that no dehydration occurred. Correction was made for the heat capacity of the cap, which weighed 0.8021 g., by using the heat capacity data for copper reported by Dockerty.[5]

Although analyses of the sample before use showed that the salt contained too little water, the heat capacity values indicated 0.05 g. of excess water by a hump near the ice point. The salt is somewhat deliquescent in humid surroundings[6] and became moist during its handling while being sealed into the calorimeter. Correction amounting to a little more than 0.1% below the eutectic was made for the 0.05 g. of water.

The vacuum weight of the sample (water correction made) was 72.80 g. which is 0.04767 mole of the salt. The absolute temperature of the ice point was taken to be 273.16°K., and one calorie was taken as 4.1833 int. joules.

The experimental data are presented in Table I and are shown graphically in Fig. 1. Smoothed values for the heat capacities appear in Table II. Certain values are not reported due to obvious inconsistencies. These values were obtained after rapid cooling when distillation from the crystals to the calorimeter walls may have occurred or in series started in the temperature range of rapid changes of heat capacity where equilibrium is difficult to obtain.

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(4) Latimer and Greensfelder, THIS JOURNAL, **50**, 2202 (1928); Brown, Smith and Latimer, *ibid.*, **58**, 1758 (1936); Pitzer and Coulter, *ibid.*, **60**, 1310 (1938).

(5) Dockerty, *Can. J. Research*, **15A**, 59 (1937).

(6) Rough determinations of the vapor pressure of the pure salt gave a value of 1.7 cm. at 25°.

TABLE I

MOLAL HEAT CAPACITY OF $2La(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
15.552	8.708	161.12	303.0
17.404	11.71	162.98	304.6
19.646	15.81	170.84	315.6
21.499	19.53	179.57	327.4
23.400	23.98	189.22	340.4
25.32	28.00	194.20	346.6
27.52	33.46	199.00	352.0
29.75	38.96	199.12	351.0
32.58	46.28	209.17	368.8
35.73	55.80	213.71	372.4
39.13	65.94	223.37	386.6
42.70	76.28	230.71	397.6
46.62	88.08	236.55	405.2
51.76	102.2	241.47	419.6
56.93	116.5	245.29	479.4
62.65	131.4	248.77	480.4
68.70	146.0	252.61	447.6
75.78	163.4	256.67	434.2
83.98	180.3	260.58	438.2
88.73	191.4	264.59	468.2[a]
92.93	197.0	268.36	448.0
96.03	204.2	271.26	454.2
104.11	218.6	274.99	455.6
113.60	233.8	282.84	464.4
124.18	250.2	287.22	468.0
134.72	266.0	291.47	471.2
144.38	282.2	300.84	491.2
153.02	292.0		

[a] High value due to melting of excess H_2O.

Figure 1 shows a hump in the heat capacity values with the peak at 248°K. This abnormality is not explained. It falls above 231°K., the melting point of nitric acid. Some heat capacity values were determined on a different sample of this salt. Two humps, one due to the melting of free water, were observed in that case also. It was assumed that the sample required further purification. The size and location of the lower hump were little changed by remaking the salt although the shape was somewhat different. The heat capacity values of the cerium salt to be published later show a similar hump. The figure also shows the high point associated with the melting of the excess water.

TABLE II

SMOOTHED VALUES OF THE MOLAL HEAT CAPACITY OF $2La(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$

T, °K.	C_p, cal./deg.	T, °K.	C_p, cal./deg.
15	7.808	120	243.6
20	16.52	130	258.4
25	27.36	140	272.8
30	39.62	150	287.6
35	53.50	160	301.0
40	68.50	170	314.2
45	83.12	180	328.0
50	97.32	190	341.2
55	111.2	200	353.2
60	124.5	210	366.6
65	137.5	220	381.4
70	149.5	230	396.2
75	161.5	240	410.0
80	172.2	250	425.0
85	182.2	260	438.2
90	191.5	270	450.0
95	200.6	280	461.4
100	211.0	290	472.4
110	228.0	300	485.6

TABLE III

ENTROPY OF $2La(NO_3)_3 \cdot 3Mg(NO_3)_2 \cdot 24H_2O$

0–15.55°K. Debye extrapolation: $20D(159/T)$	2.8
15.55–298.16°K. Graphical integration from data	520.2
Hump[a]	2.2
S^0 298.16°K., cal./deg. mole	525.2 ± 2.6

[a] Determined graphically from the area bounded by the hump and the smooth curve through the heat capacity values below and above the hump.

Summary

The heat capacity of hydrated lanthanum magnesium nitrate has been determined from 15.5 to 300°K. The entropy value at 298.16°K. was calculated as 525.2 cal./deg. mole.

BETHLEHEM, PA. RECEIVED MAY 9, 1945