2. A new type of adiabatic calorimeter is described which can be used with small quantities of material in determining directly the heat of solution from large to very small concentrations, with high accuracy in all cases. In its construction a new type of thermel is used, which does not touch the calorimeter but receives its heat by radiation.

3. Heats of solution of coarsely crystalline sodium chloride are determined at 25° over a range of concentrations from 0.4 to 24.3%. A maximum value is found at 1% concentration.

4. Preparation and measurement of finely divided sodium chloride are described. The heat of solution of this material is determined and, from the results, the surface energy of solid sodium chloride is calculated.

5. The effect of saturated water vapor on the finely divided salt is described and measured.

MONTREAL, CANADA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

THE SOLUBILITIES OF SOME RARE-EARTH OXALATES[1]

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Introduction

Perhaps the most characteristic reaction of the rare-earth elements is the precipitability of their oxalates in faintly acid solution. However, a survey of the existing literature on the subject showed that it was scattered, fragmentary and somewhat contradictory, so it was decided to determine the solubilities of as many of the rare-earth oxalates as could be obtained in a sufficiently pure condition.

Early references[2] to the insolubility of the rare-earth oxalates were of a qualitative nature, the first really quantitative contribution being by Brauner,[3] who determined the solubilities of lanthanum, cerium, praseodymium, neodymium and yttrium oxalates at 20° in ammonium oxalate solution of one concentration, and in normal sulfuric acid. Schéele[4] determined the solubilities of praseodymium and lanthanum oxalates in two concentrations of nitric acid. Benedicks[5] found values for gadolinium oxalate in ammonium oxalate and in sulfuric acid of the same concentra-

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[1] From a thesis submitted to the Graduate Faculty of the University of Minnesota, by Landon A. Sarver, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Vauquelin, *Ann. chim.*, **50**, 140 (1804). Berzelius and D'Hisinger, *ibid.*, **50**, 245 (1804). Mosander, *Ann. chim. phys.*, [3] **11**, 464 (1844). Marignac, *Ann.*, **88**, 232 (1853). Clève and Hoeglund, *Bull. soc. chim.*, **18**, 289 (1872).

[3] Brauner, *J. Chem. Soc.*, **73**, 951 (1898).

[4] Schéele, *Ber.*, **32**, 409 (1899).

[5] Benedicks, *Z. anorg. Chem.*, **22**, 393 (1900).

tions as those used by Brauner; Cleve[6] gave similar data for ytterbium; Pratt and James[7] made a study of the solubility of yttrium oxalate in potassium oxalate solutions of varying concentrations. The most complete contributions to the subject have been made by Hauser, Meyer, Wirth and co-workers,[8] who gave information on the solubilities of lanthanum, cerium and samarium oxalates in several concentrations of sulfuric acid, and also in mixtures of sulfuric and oxalic acids. They also gave some transition concentrations for lanthanum oxalate (to lanthanum sulfate) in sulfuric acid solutions at 25°. Rimbach and Schubert,[8b,9] and Hauser and Herzfeld determined the solubilities of lanthanum, cerium, praseodymium, neodymium, samarium, yttrium and ytterbium oxalates in water at 25°, using the electrical conductivity as well as gravimetric and volumetric methods, but good agreement between the different methods was not obtained. Finally in 1917, Grant and James[10] determined the solubilities of lanthanum, neodymium, gadolinium, dysprosium, yttrium, thulium and ytterbium oxalates in 20% methylamine oxalate, ethylamine oxalate and triethylamine oxalate.

Although existing information for the whole series is meager, it has been possible to obtain only the elements of the cerium group and one element, gadolinium, of the intermediate terbium group in a sufficient state of purity for this investigation. It is hoped that the study which has been made with these materials, and the improvement in experimental methods of procedure, will greatly facilitate subsequent work which is now in progress in this Laboratory.

Materials and Apparatus

Lanthanum Oxalate.—The purest lanthanum ammonium nitrate was procured through the courtesy of Dr. H. S. Miner of the Welsbach Company, Gloucester, New Jersey. Examination of a 10cm. layer of a saturated solution showed no trace of absorption lines, and the arc spectrum, photographed with a quartz spectrograph, also showed the material to be free from other rare earths. To be entirely certain of the absence of cerium, the whole batch was treated with ammonia and hydrogen peroxide in such a manner that a small amount of lanthanum was precipitated together wih any cerium present. The lanthanum was then precipitated thrice as oxalate from a very dilute sulfuric acid solution, thoroughly washed, and dried at 105°.

Cerous Oxalate.—A sample of cerous sulfate, supplied by Professor Charles James of the University of New Hampshire, was said to be free from other rare earths but to contain small amounts of iron and calcium. It was dehydrated to render it soluble,

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[6] Cleve, *Z. anorg. Chem.*, **32**, 129 (1902).

[7] Pratt and James, This Journal, **33**, 488 (1911).

[8] (a) Hauser and Wirth, *Z. anal. Chem.*, **47**, 389 (1908); *Z. prakt. Chem.*, **79**, 358 (1909). Wirth, *Z. anorg. Chem.*, **58**, 213 (1908); **76**, 174 (1912). (b) Results of unpublished work are given in Meyer and Hauser's "Die Analyse der seltenen Erden und Erdsäuren," Ferdinand Enke, Stuttgart, **1912**.

[9] Rimbach and Schubert, *Z. physik. Chem.*, **67**, 183 (1909).

[10] Grant and James, This Journal, **39**, 933 (1917).

dissolved in ice water, acidified with hydrochloric acid, and precipitated in the cold with an excess of oxalic acid. The oxalate was fumed with sulfuric acid, redissolved in ice water, and precipitated as sulfate by mixing with an equal volume of 95% alcohol. The product was again dehydrated, redissolved and precipitated again as sulfate by concentrating the solution; this was dehydrated, dissolved and precipitated as oxalate, converted to sulfate by fuming with sulfuric acid, dissolved and precipitated as sulfate by mixing with alcohol, dehydrated and dissolved again, and finally precipitated thrice as oxalate, thoroughly washed, and dried at 105°. The arc and absorption spectra then showed no impurities present.

Praseodymium Oxalate.—The praseodymium material was obtained in the form of fractions which had come originally from Travancore monazite by double manganese nitrate fractionation and had then been fractionally crystallized many hundred times as the double ammonium nitrate. The fractionation was continued 50 times more, and then the two purest fractions precipitated twice, separately, as oxalates. The arc and absorption spectra showed no impurities in either fraction, so the two were combined. The material was well washed, and dried at 105°.

Neodymium Oxalate.—A large sample of partially purified neodymium ammonium nitrate was obtained through the courtesy of the Welsbach Company. No samarium absorption lines were visible, but those of praseodymium showed plainly. The material was converted to the double manganese nitrate and fractionated in nitric acid; d., 1.30. After a few crystallizations, the head fractions were removed from the system. After 50 crystallizations as neodymium manganese nitrate, the two purest fractions were combined, converted to the simple neodymium nitrate, and fractionally crystallized 30 times more, the order of solubility being thus reversed. At the end of this fractionation the arc and absorption spectra showed no impurities in the three purest fractions, so these were combined, precipitated thrice as oxalate, washed thoroughly and dried at 105°.

Samarium Oxalate.—The samarium sample was kindly supplied by Professor Charles James from material used in the determination of the atomic weight of samarium.[11] It was converted from the sulfate to the oxalate in the conventional way, washed, and dried at 105°. The arc and absorption spectra were then examined and no impurities found.

Gadolinium Oxalate.—The gadolinium material was also pure, having been used by Brinton and James[12] in the study of the hydrolysis of the carbonate. It was entirely free from absorption lines in the visible region, and the arc spectrum also showed it to be very pure. It was already in the form of oxalate, and was merely dried at 105°.

Thermostat.—There was not to be found on the market a thermostat of sufficient size and suitable construction for the purpose of this research, so it was necessary to design and build one to meet our particular needs. It was made of alberene stone 2.5 cm. thick, with outside dimensions of 135 × 84 × 91 cm. A heavy steel shaft with worm gear, carrying specially constructed bronze frames to hold the bottles, was hung horizontally on wood block bearings supported by well-painted iron cradles at each end, inside the tank. A vertical driving shaft, in mesh with the worm gear and reaching several inches above the top at one end, was driven by a quarter horsepower split-phase electric motor mounted on brackets at the side of the tank.

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[11] Stewart and James, This Journal, **39**, 2605 (1917).

[12] Brinton and James, *ibid.*, **43**, 1446 (1921).

Each of the bronze frames (Fig. 1) on the long horizontal shaft carries four of the 2400cc. acid bottles of commerce, the bottom of each resting in a triangular base next to the shaft and the necks passing through forks which can be screwed down to hold the bottles in position. The bolts holding these forks and retaining nuts were set in holes in the frame, filled with molten solder, and then secured by a bronze brad passing through bolt and frame. This arrangement holds the bottles end to end firmly and safely. The frames are staggered along the shaft to form a sort of screw propeller and create a powerful stirring effect on the water in the tank. As many as twenty bottles can be rotated at one time, but it was found advisable to remove one frame to make room for a settling rack, leaving sixteen bottles in motion and five on the rack. The gear ratio was designed to give the main shaft a speed of 10 r.p.m., since too great a speed would defeat the purpose, by causing centrifugal action.

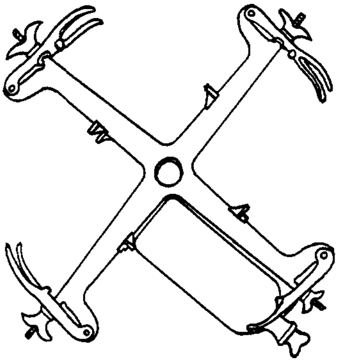

Fig. 1.—Bottle frame.

The thermoregulator is of the bimetallic type, made by the Thermo-Electric Instrument Company, of Newark, New Jersey. A constancy within 0.1° was desired, but a fluctuation of 1° was found, and a discharge across the contact points fused them together at times so that they had to be pulled apart with the fingers. A magnetic relay operated by a 6v. Edison storage battery was then installed, so only a very small current passed through the regulator itself, the heavy heating current passing through the carbon contacts of the relay. This arrangement worked beautifully, giving a constancy within less than 0.1° over long periods of time. The heating was effected by 250-watt heater bulbs, one being sufficient for ordinary regulation.

It is believed that this thermostat, developed after a great amount of tedious experiment, is more suitable for work of this kind than any other which has so far been described. Acknowledgment is gratefully made to Mr. F. W. Fullerton, Mechanician of the School of Chemistry of the University of Minnesota, for its skilful construction and for valuable suggestions during the period of development.

Bottles.—The bottles, which had been aged for over a year with distilled water, were tested for leakage and stoppers ground in where necessary. The tops of the stoppers were ground flat and a little groove was ground in so they could be wired on, and wire collars with loops were placed permanently on the necks of the bottles. A blank showed a specific conductance of 1.7×10^{-6} mho on a sample of conductivity water which had been kept in one of these bottles for several weeks.

Experimental Part

Saturation.—The water or acid of known concentration was placed in a bottle and a considerable excess of powdered oxalate added, the stopper wired on and paraffined, and the bottle then rotated in the bath for several days. (It was found by experiment that at least 24 hours' agitation was necessary under the most favorable conditions, and a longer time was needed where only small amounts of material were available.) At the end of that time the bottle was removed from the rotating shaft and placed in the settling rack in the bath for eight or ten hours. Some samples settled clear in an hour, while others, especially the water solutions and low acid concentrations, settled very slowly.

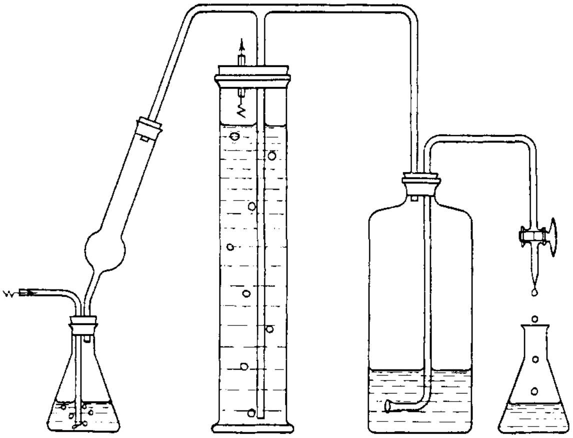

Fig. 2.—Pressure pipet.

Samples.—The removal of suspended solid from the solutions presented quite a serious problem. At first filtration was attempted, discarding the first portions passing through, but this was soon found to be hopeless. The long grinding in the rotating bottles reduced the oxalates to an extremely fine state of subdivision, so that the filtrate, even through hardened filter paper, was opalescent. Furthermore, filtration was slow and messy, introducing disturbing factors like adsorption in the pores of the paper, evaporation and temperature changes. Therefore, filtration was definitely abandoned. Next, cautious pipetting by slow mechanical suction was tried with fair success, but where more than one pipetful was required the least amount of liquid flowing back into the bottle disturbed the solid so that a further settling period was necessary; the same factor rendered it difficult to take duplicates.

By far the fastest, most convenient and accurate way of removing solution from excess of solid phase was found to be by means of a simple pressure pipet (Fig. 2). The glass tube was bent so as to lie flat near the bottom inside the bottle, its mouth being spread to a fan shape and pointed slightly upward. This draws a wide, flat stream of solution toward the solid rather than away from it, thus minimizing the danger of drawing some of the latter out with the sample. Furthermore, it permits the taking of a large sample at a single operation, with great economy of time. A separate pipet was used for each element to lessen risk of contamination, and they were always washed and dried immediately after use. To take a sample then, the siphon was adjusted in a bottle and its stopcock closed, the washed, dried air escaping through the pressure regulator; a tared flask was placed in position, the stopcock opened until the desired amount had passed over, and then closed again. The flask containing the sample was then weighed, and a duplicate immediately taken in like manner. When finished, the pressure was disconnected and the stopcock opened, whereupon the contents of the tube siphoned back into the bottle, an important feature where materials were so rare and valuable.

A few samples were purposely taken before the liquid settled quite clear and then filtered through the finest paper, but the results were much too high, demonstrating the utter inadequacy of filtration for the removal of suspended oxalates. Thus it seems that the method here described is the best for the purpose. Every sample was held up to a bright light and examined for suspended solid before being used. Amounts varied from 50–1000 g. according to the nature of the solvent, a large analytical balance specially constructed by Bünge for heavy loads being used for the weighings.

Evaporation and Ignition.—The samples were transferred a little at a time to small porcelain evaporating dishes of about 60 cc. capacity which had been tared against other dishes of similar size, and evaporated to dryness over distilled water on an electrically heated water-bath which was protected from dust by a reinforced plate-glass cover. These dishes weighed only about 45 g., so the sensitivity of the balance was not materially affected, and by evaporating large samples in small portions, the difficulty of obtaining the weights of small residues in large dishes was avoided.

The residues were first gently ignited to change oxalates to carbonates, and then evaporated with a little concd., redistilled nitric acid to expel chlorides when present, and to assist in oxidizing the carbon in all cases; it was found very difficult to get the dishes hot enough to oxidize the carbon completely, by heat alone. After this treatment the residues were generally ignited and weighed as oxides.

The conversion of rare-earth sulfates to oxides is by no means as easy as is frequently thought. The first determination in this investigation was that of praseodymium, where the conversion of sulfate to oxide would be accompanied by a color change from light green to dark brown, but neither Meker burner nor blast lamp was able to bring about an appreciable change in color. This directed attention to statements in the literature that it is only at white heat that a rare earth sulfate can be converted to oxide, and that with the exception of cerium they form basic sulfates stable at 1000°.[13] Since these porcelain dishes are difficult to heat to a high temperature, one was tested with a thermocouple and about 700° was obtained over the blast with the dish covered, and 600–650° when uncovered. This was entirely inadequate for the complete conversion to oxides, so it was decided to weigh as anhydrous sulfates. This weighing form has been criticized in the case of atomic-weight determinations on account of its great hygroscopicity, but by weighing rapidly it was possible to obtain results accurate enough for this work. The samples were heated for several hours in a muffle furnace at 500°, the temperature being observed with a calibrated thermocouple. These ignitions were tedious, but it is believed the results are good. The formula $R_2(SO_4)_3$ was used in making calculations.

In all ignitions to oxide considerable difficulty was experienced in obtaining constant weight; all the oxides except that of cerium showed a well defined tendency to descend to a minimum, and then gradually to register considerable gains on subsequent ignitions. Some samples were ignited as long as 50 hours and weighed 30 times. The gain on each new ignition was small, 0.1–0.2 mg., and might easily be overlooked. On reviewing some work done several years ago it was seen that weights then accepted as constant had really shown slight gains on the last ignition. The explanation which first suggested itself was the formation of higher oxides, and on this subject the literature[14] is contradictory. In order to test this point, some gadolinium oxide was heated under varying conditions in a small porcelain boat, along with a similar boat for a tare. After 13 hours in a current of hydrogen in an electric combustion furnace at 700°, it lost 0.7% of its weight, which was not regained upon heating for nine hours in oxygen; upon heating for ten hours over a Meker burner at 900°, it gained 0.33%; another small gain of 0.1% was registered after heating in a current of dry air in an electric muffle at 700° for nine

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[13] (a) Matignon, *Compt. rend.*, **134,** 657 (1902); (b) **141,** 1230 (1905); (c) **142,** 394 (1906). (d) Wild, *Z. anorg. Chem.*, **47,** 464 (1905). (e) Wöhler and Gründzweig, *Ber.*, **46,** 1726 (1913).

[14] (a) Marc, *Ber.*, **35,** 2370 (1902). (b) Hermann, *Z. prakt. Chem.*, **82,** 385 (1861). (c) Zschiesche, *ibid.*, **107,** 65 (1869). (d) Jones, *Am. Chem. J.*, **20,** 345 (1898). (e) Meyer and Koss, *Ber.*, **35,** 3740 (1902). (f) Meyer, *Z. anorg. Chem.*, **41,** 119 (1904). (g) Waegner, *ibid.*, **42,** 118 (1904). (h) Joye and Garnier, *Compt. rend.*, **154,** 510 (1912). (i) Joye, *Arch. sci. phys. nat.*, [IV] **36,** 41 (1913). (j) Brauner, *Proc. Chem. Soc.*, **14,** 72 (1898); (k) **17,** 66 (1901); (l) *Z. anorg. Chem.*, **32,** 1 (1902). (m) Cleve, *Chem. News*, **53,** 30 (1886); (n) *Compt. rend.*, **97,** 94 (1883); (o) *Bull. soc. chim.*, [II] **43,** 162 (1885); (p) *J. Chem. Soc.*, **43,** 362 (1883). (q) Ref. 5. (r) Brinton and Pagel, THIS JOURNAL, **45,** 1460 (1923).

hours, and it then remained stationary through ten more hours of similar treatment; finally, after four more hours in open air over the Meker burner it gained another 0.1%. No appreciable amount of sulfate was found, so the gain could not be due to sulfur in the illuminating gas. The boat was cooled in a desiccator containing fresh sticks of potassium hydroxide and then weighed very rapidly, to protect from carbon dioxide. The whole question of adsorption and higher oxides is now being studied in the laboratories of the University of Minnesota, so no attempt to explain this peculiar behavior will be made in this paper. The minimum weight has been accepted as the true weight of the oxides, and the formulas used as the basis of calculations are La_2O_3, CeO_2, Pr_6O_{11}, Nd_2O_3, Sm_2O_3 and Gd_2O_3. Evidence for the formula Pr_6O_{11} instead of the formerly accepted Pr_4O_7 has been clearly established.[14r]

Conductivity Measurements.—Precision instruments were used for these, including the Vreeland oscillator, Curtis coil resistances, Kohlrausch drum-wound slide-wire bridge with extension coils, cell, variable air condensers, and Western Electric 2200-ohm radio head-phones.

The oxalates were placed in bottles with conductivity water, sealed, and turned over in the bath for several weeks, along with a bottle of pure water as a blank. At the end of this time the water gave a zero gravimetric blank from a 1-liter sample, and had a specific conductance of 1.67×10^{-6} mho at 25°. Gravimetric and conductivity determinations were then made, using 1-liter portions for the former. Determinations were also run according to the technique used by Rimbach and Schubert[9] in their conductivity work, placing the solid with conductivity water in the cell and making readings with occasional agitations until equilibrium was attained. They stopped at the end of 20 minutes, but we found that at the end of an hour and a half the conductance was still increasing more rapidly than could be accounted for by the absorption of atmospheric gases by the solution. It is felt that while 20 minutes may be long enough for salts of low valence to come to equilibrium in solution, such a technique can scarcely be approved for the trivalent rare-earth salts. Table I shows that we obtained fairly good concordance between gravimetric and conductivity determinations, and that both sets were much higher than those reported by Rimbach and Schubert.

TABLE I

SOLUBILITIES IN WATER AT 25°

(Milligrams of anhydrous oxalate per liter)

	La	Ce	Pr	Nd	Sm
Gravimetric detn.	2.14	1.09	1.49	1.48	1.48
Conductivity detn.	2.06	0.80	2.15	1.98	1.37
Conductivity detn. (Rimbach and Schubert)	0.62	.41	0.74	0.49	0.54

The conductivity values were calculated from the equation $n = 1000k/$-

Λ_∞, where n equals the number of gram equivalents of the salt per liter, k the specific conductance of the solution and Λ_∞ the sum of the ionic conductances at infinite dilution. Values for Λ_∞ have been determined by Aufrecht[15] for cerium (72.1), praseodymium (71.4), and neodymium (71.1); by Ley[16] for lanthanum (67.3); and by Rimbach and Schubert[9] for samarium (71.7). These are the same values used by Rimbach and Schubert in their conductivity determinations. The ionic conductance for gadolinium at infinite dilution has not been determined as yet, but this will be done, and the solubility of gadolinium oxalate in water reported in a later paper.

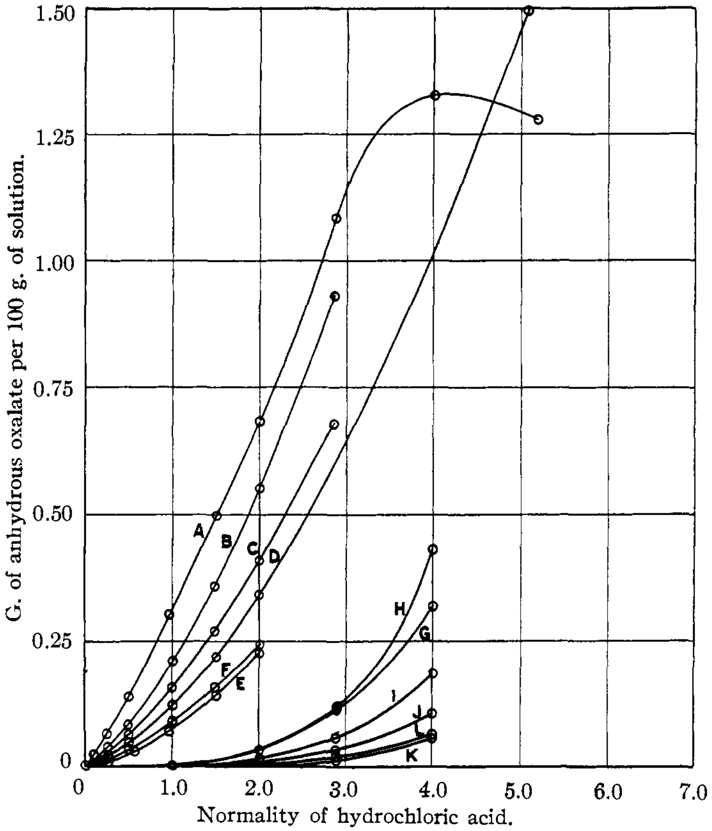

Fig. 3.—*A*, lanthanum oxalate; *B*, cerous oxalate; *C*, praseodymium oxalate; *D*, neodymium oxalate; *E*, samarium oxalate; *F*, gadolinium oxalate. 0.5 *N* oxalic acid: *G*, lanthanum oxalate; *H*, cerous oxalate; *I*, praseodymium oxalate; *J*, neodymium oxalate; *K*, samarium oxalate; *L*, gadolinium oxalate.

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[15] Aufrecht, *Inaugural Dissertation*, Berlin, **1904**.

[16] Ley, *Z. physik. Chem.*, **193**, 257 (1899).

The other solubility values are given in Table II, and the results shown graphically by a number of curves, Figs. 3–7.

TABLE II

SOLUBILITIES IN ACIDS AT 25°

(G. of anhydrous oxalate per 100 g. of solution)

Mineral acid, *N*	Oxalic acid, *N*	La	Ce	Pr	Nd	Sm	Gd
HCl							
0.1008	...	0.0208	0.0131	0.0098	0.0076	0.0052	0.0024
.2576	...	.0567	.0376	.0279	.0217	.0181	.0099
.5004	...	.1384	.0834	.0625	.0442	...	.0329
.5702	...	...	...	...	...	.0267	...
.978	...	.3074	...	...	...	.0712	...
1.018	...	...	.2174	.1603	.1260	...	.0938
1.484	...	.4937	.3552	.2658	.2222	.1452	.1563
2.000	...	.6770	.5518	.4108	.3318	.2296	.2457
2.865	...	1.082	.9354	.6799	...	...	...
4.000	...	1.327	...	...	...	...	...
5.20	...	1.285	...	...	1.533	...	...
0.978	0.1	0.0532	.0272	.0128	0.0082	.0061	.0061
2.000	.1	.2998	.2120	.1163	.0747	.0421	.0525
2.865	.1	.6330	.5486	.3255	.2167	.1228	.1448
3.965	.1	1.026	1.152	.7021	.5570	.3202	.3777
0.978	.5	0.0062	0.0049	.0026	.0020	.0010	.0011
2.000	.5	...	.0338	.0173	.0112	.0061	.0037
2.865	.5	.1098	.1142	.0548	.0352	.0175	.0215
3.965	.5	.3127	.3808	.1833	.1047	.0594	.0676
1.484	Satd.	.0058	.0068	.0046	.0033	.0031	.0026
4.00	Satd.	.1782	.3130	.0986	.0775	.0285	.0475
6.00	Satd.	...	.1862	.1492	.1814	.1165	.1921
6.20	Satd.	...	.1604	.1338	.1785	...	...
HNO_3							
0.2482	...	.0354	.0355	.0289	.0238	.0189	.0219
1.992	...	.9256	.6808	.5102	.4287	.3408	.2785
4.054	...	2.660	2.264	1.656	1.353	1.062	.9032
2.000	0.1	0.3908	0.3160	0.1295	0.1138	0.0905	.0768
3.03	.1	1.227	.9328	.5712	.4606	.2898	.2813
4.00	.1	1.568	1.738	1.057	...	.6327	.5498
2.00	.5	0.1292	0.0526	0.0292	.0195	.0134	.0128
3.03	.5	.3576	.2604	.1323	.0811	.0504	.0463
4.00	.5	.7200	.7934	.3987	.2528	.1603	.1397
4.00	Satd.	.7664	.4014	.0663	.0972	...	.0383
6.00	Satd.	1.304	1.328	.912	.3413	...	.1227
H_2SO_4							
0.086	...	0.0222	0.0142	.0103	.0091	.0090	.0086
.419	...	.1078	.0683	.0512	.0415	.0424	.0401
.958	...	.2523	.1738	.1294	.1037	.1042	.0988
1.846	...	.5128	.3820	.2808	.2237	.2189	.2047
2.612	...	.6840	.5904	.4213	.3702	...	.2970

Discussion

Fig. 3 shows the solubilities of the six elements in hydrochloric acid, and in hydrochloric acid which is 0.5 *N* with oxalic acid, while Fig. 4 gives the same information for hydrochloric acid which is 0.1 *N* with oxalic acid, and for hydrochloric acid which is saturated with oxalic acid. In all four sets the lanthanum curve tends to cross the others at higher mineral acid concentrations and the serial order is lanthanum, cerium, praseodymium, neodymium, gadolinium, samarium; at low mineral acid concentrations samarium comes ahead of gadolinium. Not very much work has been done at high acid concentrations since it was not regarded as important from an analytical standpoint, but it is seen from Fig. 4 that in saturated oxalic acid solutions the solubilities seem to increase

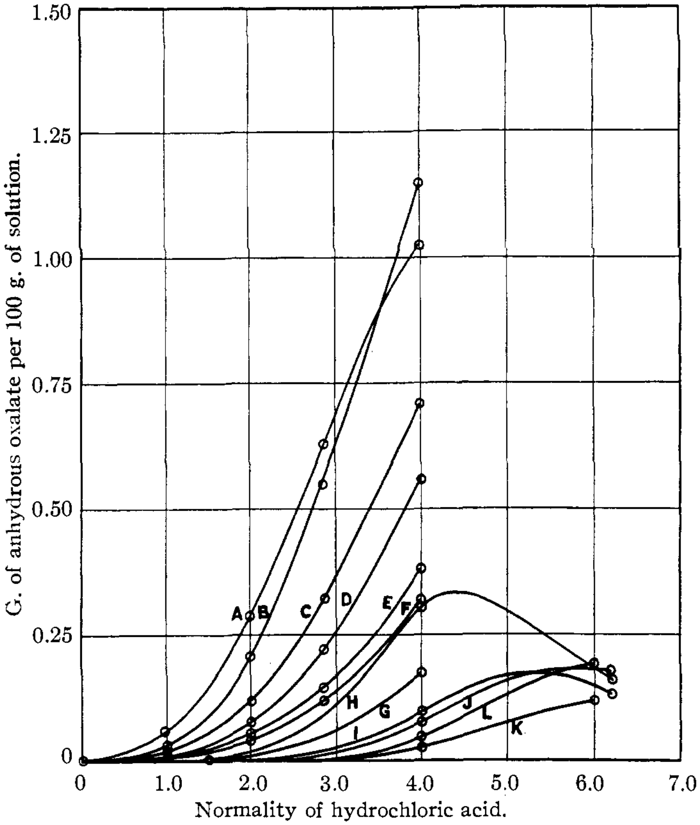

Fig. 4.—0.1 *N* oxalic acid: *A*, lanthanum oxalate; *B*, cerous oxalate; *C*, praseodymium oxalate; *D*, neodymium oxalate; *E*, samarium oxalate; *F*, gadolinium oxalate. Saturated oxalic acid: *G*, lanthanum oxalate; *H*, cerous oxalate; *I*, praseodymium oxalate; *J*, neodymium oxalate; *K*, samarium oxalate; *L*, gadolinium oxalate.

with growing hydrochloric acid concentrations up to a maximum, and then fall. Even a small excess of oxalic acid causes a large solubility depression, while saturated oxalic acid solutions show no evidence of appreciable complex formation.

Fig. 5 shows the solubility curves for nitric acid alone, and for nitric acid which is 0.5 *N* with oxalic acid; Fig. 6 gives the curves for nitric acid which is 0.1 *N* with oxalic acid and for nitric acid which is saturated with oxalic acid. In pure nitric acid solutions the lanthanum curve does not begin to cross the others within the range studied, but it does in the nitric acid-oxalic acid mixtures. The serial order is lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium. The depression caused by oxalic acid is much less than for the hydrochloric acid

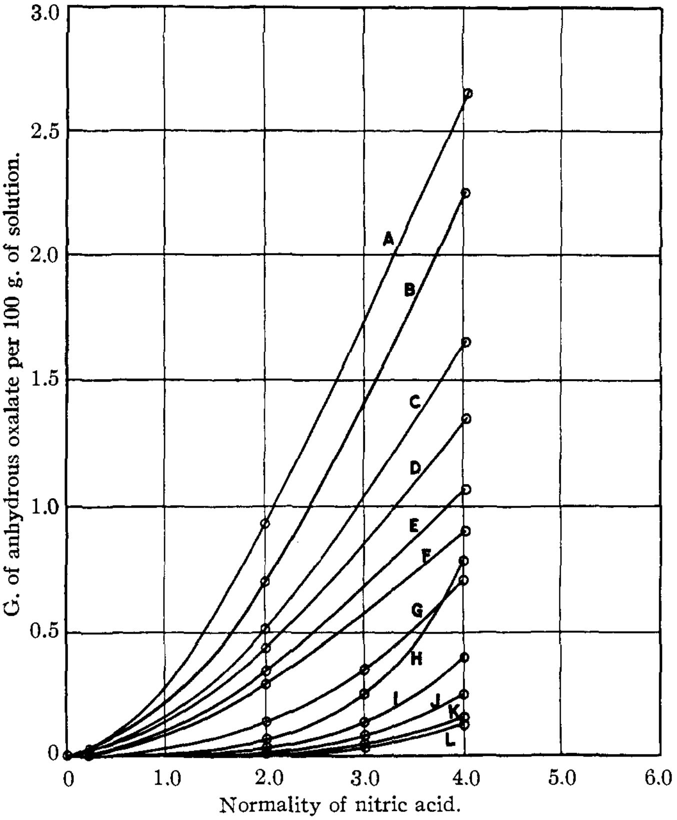

Fig. 5.—*A*, lanthanum oxalate; *B*, cerous oxalate; *C*, praseodymium oxalate; *D*, neodymium oxalate; *E*, samarium oxalate; *F*, gadolinium oxalate. 0.5 *N* oxalic acid: *G*, lanthanum oxalate; *H*, cerous oxalate; *I*, praseodymium oxalate; *J*, neodymium oxalate; *K*, samarium oxalate; *L*, gadolinium oxalate.

mixtures; the solubility of lanthanum oxalate in 1 *N* hydrochloric acid is lowered to 16.5% of its value by 0.1 *N* oxalic acid, and to 1.95% of its value by 0.5 *N* oxalic acid, while in nitric acid it is lowered only to 25% of its value by 0.1 *N* oxalic acid, and to 10.7% of its value by 0.5 *N* oxalic acid. Nitric acid is, then, a less suitable medium for analytical separations because the acid concentration would have to be limited so carefully.

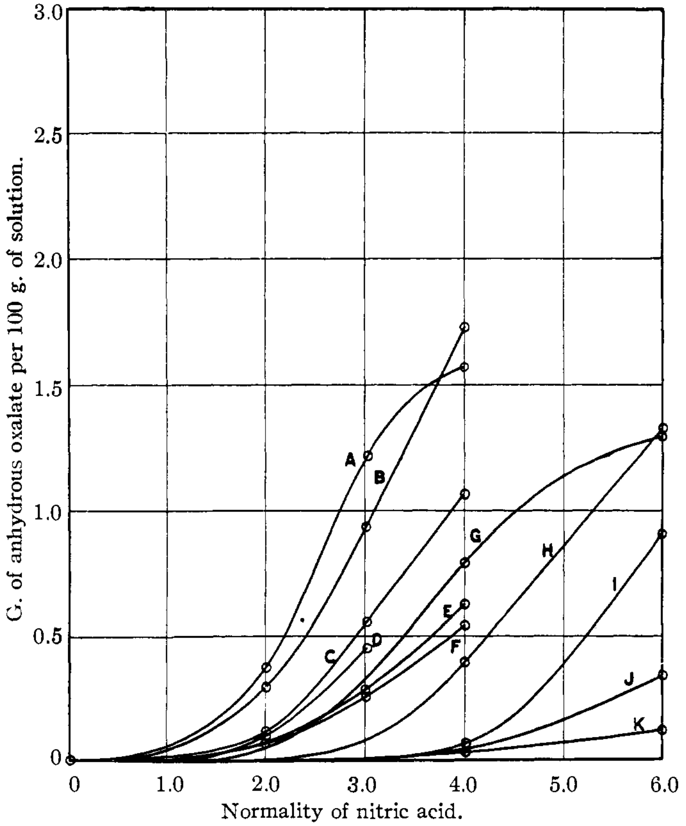

Fig. 6.—0.1 *N* oxalic acid: *A*, lanthanum oxalate; *B*, cerous oxalate; *C*, praseodymium oxalate; *D*, neodymium oxalate; *E*, samarium oxalate; *F*, gadolinium oxalate. Saturated oxalic acid: *G*, lanthanum oxalate; *H*, cerous oxalate; *I*, praseodymium oxalate; *J*, neodymium oxalate; *K*, gadolinium oxalate.

Fig. 7 gives the curves for the solubilities in various concentrations of sulfuric acid, and here too the lanthanum curve flattens out toward the top. The serial order of the elements is lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium.

As already pointed out, information on these elements in the literature is both meager and somewhat contradictory. The values for cerous oxalate and neodymium oxalate in hydrochloric acid agree with ours fairly well. The solubilities of lanthanum and praseodymium oxalates in two concentrations of nitric acid show bad agreement between duplicates, and are not very near to our values, but are of the same order of magnitude. A large number of determinations have been run in a sulfuric acid medium, but unfortunately the great stability of the basic sulfates has not been generally realized. The sulfates of cerium and samarium decompose fairly easily, but we are forced to the conclusion that previous determinations of the solubilities of lanthanum, praseodymium, neodymium and gadolinium oxalates in sulfuric acid solutions are not even approximately correct.

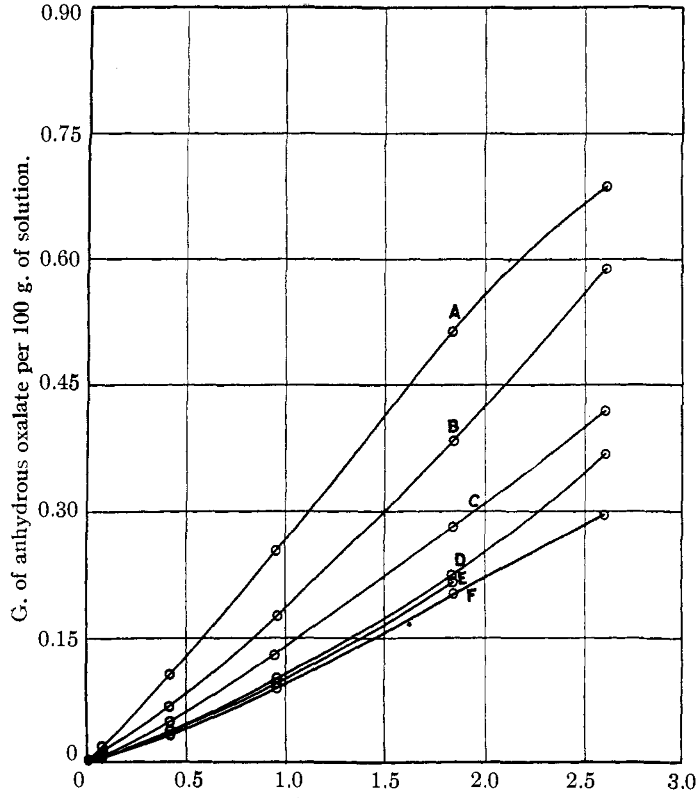

Fig. 7.—*A*, lanthanum oxalate; *B*, cerous oxalate; *C*, praseodymium oxalate; *D*, neodymium oxalate; *E*, samarium oxalate; *F*, gadolinium oxalate.

It is of interest to note that gadolinium oxalate is more soluble than samarium oxalate in hydrochloric acid, and that gadolinium sulfate seems to be more stable than samarium sulfate, although solubility considerations in general place it between europium and terbium in the serial order, and the hydrolyses of the sulfates and carbonates[17] accord it the same position. On the other hand, the dissociation of the anhydrous sulfates[13e] and the fractional precipitation with ammonium hydroxide[18] place it between neodymium and samarium. Gadolinium presents a number of abnormalities in its chemical and physical properties, so it is not surprising that the solubility evidence is not completely in accord with the serial order of increasing atomic weights.

Since the sulfates are decomposed to oxides with such great difficulty and are comparatively so difficultly soluble, sulfuric acid is in general not an ideal medium for analytical work with the rare earths. Neither would nitric acid be satisfactory because of the magnitude of the solubility values; lanthanum oxalate is about six times as soluble in normal nitric acid which is 0.5 *N* with oxalic acid as it is in 1 *N* hydrochloric acid which is 0.5 *N* with oxalic acid. In fact, the solution would have to be saturated with oxalic acid to obtain as complete a separation as half-normal oxalic acid would give from hydrochloric acid. Even in hydrochloric acid the solubility of lanthanum and cerous oxalates is appreciable; in 100 g. of a solution which is 0.5 *N* with respect to both hydrochloric and oxalic acids about 2 mg. of lanthanum oxalate and 1.5 mg. of cerous oxalate would remain unprecipitated; only a few tenths of a milligram of praseodymium, neodymium, samarium or gadolinium oxalate would remain in solution. Some mineral acid is necessary to avoid the formation of basic compounds, so it is recommended that 0.5 *N* hydrochloric acid be used in all cases, and that the solution be almost saturated with oxalic acid for the separation of lanthanum and cerium, while 0.5 *N* oxalic acid is sufficient to precipitate praseodymium, neodymium, samarium and gadolinium quantitatively. A hot, concentrated solution of oxalic acid should be added with stirring to the boiling solution of rare earths which is 0.5 *N* with respect to hydrochloric acid, and the precipitate allowed to stand several hours before filtering. The oxalate must then be ignited until a constant or minimum weight has been obtained.

Summary

The solubilities in water of the oxalates of the five rare-earth elements lanthanum, cerium, praseodymium, neodymium and samarium have been measured by gravimetric and conductivity methods; the solubilities of these same oxalates, as well as that of gadolinium, in hydrochloric, nitric and sulfuric acids, mixtures of hydrochloric and oxalic acids and mixtures of nitric and oxalic acids, have been determined by gravimetric methods.

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[17] Katz and James, This Journal, **36**, 779 (1914). Ref. 12.

[18] de Boisbaudran, *Compt. rend.*, **3**, 393 (1890). Ref. 14 q.

Analytical conditions for the quantitative estimation of these elements have been determined and their limitations discussed.

Apparatus and procedure for the rapid and accurate determination of solubilities have been developed for future work.

MINNESOTA, MINNEAPOLIS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, RESEARCH INSTITUTE OF CUTANEOUS MEDICINE]

SODIUM AUROTHIOSULFATE. A SIMPLE METHOD FOR ITS PREPARATION

BY HERMAN BROWN

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The preparation first described by Fordos and Gélis[1] as sodium aurothiosulfate has recently attained considerable prominence through the claims by Møllgaard and his associates[2] for its curative properties in tuberculosis. The value of the compound in the treatment of *lupus erythematosus*, which is believed by many to be of tuberculous origin, has been indicated by Schamberg and Wright[3] and during the past year hundreds of ampoules of sodium aurothiosulfate have been distributed from this Institute to various dermatologists.

In view of the increasing demand, an economical method for preparing this compound assumed considerable importance. Møllgaard's method not being available, the procedure of McCluskey and Eichelberger,[4] employing cesium auric chloride as the intermediate, was used at first. However, the price of cesium nitrate soon increased enormously and it became difficult to obtain, making desirable the development of a method of preparation which would not require cesium. The procedure described below presents several advantages over that of McCluskey and Eichelberger, in that the use of cesium is eliminated, the process is carried out in one continuous operation and is completed within a few hours. The yields are over 95%.

To 41.2 g. (0.1 mole) of hydrochloro-auric acid dissolved in 75 cc. of water is added 40% of sodium hydroxide solution, dropwise, until a faint alkaline reaction is obtained to litmus, and the gold hydroxide is precipitated. The entire contents of the beaker is then added to 102 g. (0.4 mole plus 10% excess) of hydrated sodium thiosulfate dissolved in 200 cc. of water, and the mixture is stirred mechanically. At this point no apparent change takes place in the gold hydroxide suspension. After about five minutes, and while stirring, approximately 4 *M* nitric acid is

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[1] Fordos and Gélis, *Ann. chim. phys.*, **13**, 394 (1845).

[2] Møllgaard, "Chemotherapy of Tuberculosis," *Nyt Nordisk Forlag*, **1924.**

[3] Schamberg and Wright, *Arch. Derm. Syph.*, **15**, 119 (1927).

[4] McCluskey and Eichelberger, THIS JOURNAL, **48**, 136 (1926).