

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

**THE SOLUBILITIES OF LANTHANUM OXALATE AND
OF LANTHANUM HYDROXIDE IN WATER.
THE MOBILITY OF THE LANTHANUM ION AT 25°**BY I. M. KOLTHOFF AND RUTH ELMQUIST¹

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In a study of the quantitative determination of lanthanum by precipitation as lanthanum oxalate and as hydrous lanthanum oxide—the results of which will be discussed in a later paper—it was of interest to know the solubilities of the two slightly soluble compounds in water. Since the saturation values are extremely small, the electrical conductance method can be applied advantageously. As will be shown later, the results of the latter method have to be accepted with caution and, therefore, the data have been verified by volumetric and sometimes by colorimetric procedures.

Materials Used.—The lanthanum compounds were prepared from lanthanum ammonium nitrate procured through the courtesy of Dr. H. S. Miner of the Welsbach Company, Gloucester, New Jersey. The arc spectrum of this material photographed with a quartz spectrograph showed entire freedom from any other rare earth elements. It was treated with ammonium hydroxide and hydrogen peroxide to insure absence of any cerium, using sufficient excess of ammonia to precipitate a small amount of lanthanum with any cerium that might be present. Following this, the lanthanum was precipitated with oxalic acid a number of times with thorough washing each time. The air-dry oxalate was converted into the oxide by ignition in an electric furnace at 800° to constant weight. An excess of this oxide was added to hydrochloric acid which had been prepared by bubbling hydrogen chloride into redistilled water. After the excess had been filtered off, the lanthanum chloride was crystallized from the solution and then twice recrystallized from conductivity water. The crystals containing seven molecules of water were kept in a desiccator over deliquescent calcium chloride. Lanthanum and chloride were determined quantitatively; the results agreed within 0.1%. The *PH* of the 0.1 molar solution, determined colorimetrically with adjusted brom thymol blue as an indicator in carbon dioxide-free water as a solvent was 6.2.²

¹ From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² The data reported by J. H. Kleinheksel and H. C. Kremers [THIS JOURNAL, 50, 959 (1928)] are not in agreement with our results. Their figures on the hydrolysis of salts of rare earth elements cannot be accepted as being reliable since they prepared the anhydrous salts in a stream of hydrochloric acid and did not give any proof that no free acid was adsorbed or occluded by the crystals. From their experimental figures (p. 965) it is quite evident that the acidity of lanthanum chloride reported was due to the presence of free hydrochloric acid.

Lanthanum Oxalate.—This was prepared by precipitating a solution of pure lanthanum chloride with pure oxalic acid. The precipitated lanthanum oxalate was washed with distilled water until the *PH* of the wash water remained unchanged (methyl red as indicator) and then repeatedly washed with conductivity water. The air-dried crystals contained ten molecules of water.

Lanthanum Oxide and Hydrrous Lanthanum Oxide.—Three samples of lanthanum oxide were used, one prepared from lanthanum hydroxide, the second from lanthanum oxalate and the third from lanthanum nitrate. All three had been ignited to constant weight in an electric furnace at 800°. Also freshly precipitated hydrrous lanthanum oxide was used. It was prepared by slowly adding a solution of pure lanthanum chloride to an excess of ammonium hydroxide. An attempt was made to wash the hydrrous oxide free from electrolytes in the filtering apparatus of Bachmeyer and thus protect it from carbon dioxide of the air. On account of the gelatinous character of the precipitate this purification method had to be given up. Good results were obtained by centrifuging the precipitate several times with carbon dioxide-free water until the conductance of the saturated solution remained unchanged upon further washing. The wet precipitate was quickly transferred to the conductance cell. The various oxides and the hydrrous oxide absorb carbon dioxide from the air very readily; the order of the solubility is changed entirely even by traces of this impurity.

Conductivity Water.—Conductivity water was distilled over sulfuric acid, then over barium hydroxide and finally without any addition to remove traces of acid and alkaline impurities. It was collected in aged Pyrex flasks with precautions against contamination from the air. In equilibrium with the air it had a conductivity of 0.80 to 0.85×10^{-9} rec. ohms. It could be kept for a week in the Pyrex flasks without change in conductance.

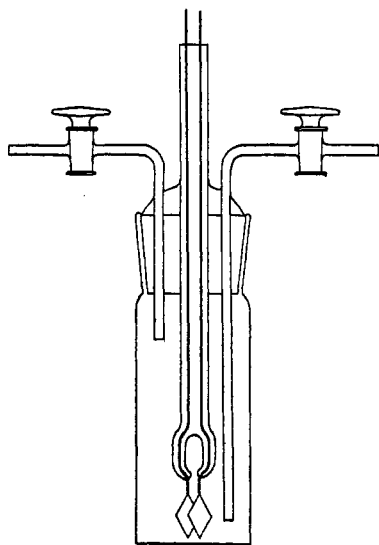


Fig. 1.

Arrangement for the Measurement of the Conductance.—A Leeds and Northrup Wheatstone bridge (rheostat with ratio arms, accuracy 0.1%) was used in this work. Although a condenser was used to balance most of the interference by capacitance, some error was introduced by the latter and by induction. These errors, however, are small compared with other experimental errors in measuring extremely dilute electrolyte solutions.

Conductivity cells of the Washburn type were used for the measurement of solutions with a concentration greater than 0.001. Special cells were constructed for the measurement of the conductance of extremely dilute solutions. The type of cell is given in Fig. 1. The platinum electrodes, which had a diameter of about 25 mm., were placed at a small distance from each other, making the constants of all the cells of the order of 0.01. The electrodes were kept in position by four glass beads at the corner.

Air could be passed through the cell to make the water or solution carbon dioxide free or to put it in equilibrium with the normal air. When equilibrium water was prepared the air from the air pressure in the laboratory was bubbled through a train of two wash bottles containing dilute permanganate, two bottles containing 0.01 *N* sulfuric acid and three with pure water, the last one being mounted in the thermostat. A similar arrangement was used when the water had to be made carbon dioxide free, but three large towers filled with soda lime were then placed between the permanganate and sulfuric acid bottles and a fourth tower after the last flask in the thermostat. The thermostat was kept at $25 \pm 0.05^\circ$.

For solutions with a concentration smaller than 0.0001 *N*, bright platinum electrodes have to be used, with slightly platinized electrodes irregularities and deviations of the order of 1% are observed. The effect is much smaller than L. de Broeckère³ noted. With dilute hydrochloric acid solutions the effect is slightly greater than with neutral salts. When using even slightly platinized electrodes, dilute alkaline solutions cannot be measured with any degree of accuracy on account of the relatively strong adsorbent power of the platinum black.⁴ In working with extremely dilute alkaline solutions the Pyrex vessels must be paraffined or coated with some other inert material to prevent the attack of the glass by alkali. After the coat has been thoroughly cleaned, constant and reproducible results are obtained even with sodium hydroxide solutions more dilute than 0.0001 *N*. Some measurements were made in the following way. A measured volume of water (about 200 cc.) was placed in the cell and made carbon dioxide free by passing through purified air. A 0.01 *N* sodium hydroxide solution was added from a microburet with the air still bubbling through. The inlet and outlet tubes were closed by the glass stopcocks and the readings made. After subtracting the conductivity of the carbon dioxide-free water (0.12×10^{-6} rec. ohms) an equivalent conductance of 250 was found for 0.0001 *N* sodium hydroxide and of 249.2 for 0.00005 *N* base at 25° .

In determining the conductivity of a saturated solution of lanthanum hydroxide, the water was made carbon dioxide free and the pure oxide or hydrous oxide was added quickly with the air still bubbling through. Readings were taken until the resistance was constant.

The Water Correction.—An excellent review on the "water correction"

³ L. de Broeckère, *J. chim. phys.*, **25**, 294 (1928).

⁴ Cf., e. g., Wi. Ostwald, *J. prakt. Chem.*, **33**, 352 (1886); **35**, 112 (1887); Bredig, *Z. physik. Chem.*, **13**, 289 (1894); Jones, *Am. Chem. J.*, **26**, 428 (1901); Bousfield and Lowry, *Phil. Trans.*, **204**, 292 (1905); A. A. Noyes, *Publ. Carnegie Inst.*, 262 (1907); Fray and Nietz, *THIS JOURNAL*, **37**, 2263 (1915); Raikes, Yorke and Ewart, *J. Chem. Soc.*, **128**, 635 (1926); Ferguson and Vogel, *Phil. Mag.*, [7] **4**, 300 (1927); M. Randall and C. C. Scalione, *THIS JOURNAL*, **49**, 1486 (1927).

has been written by J. Kendall.⁵ He prefers to work with pure water which is a saturated solution of carbon dioxide under atmospheric conditions (equilibrium water). E. W. Washburn⁶ showed, however, that it is impracticable to extend conductivity measurements in equilibrium water as long as the slightest uncertainty exists as to the exact purity of the water to such high dilutions. Therefore, he worked under those conditions with ultra pure water having a conductivity of 0.06×10^{-6} rec. ohms at 18°. From Kendall's work different authors⁷ improperly concluded that carbon dioxide is the only contaminant of good conductivity water, and that the carbonic acid content can be computed from the conductance by means of Kendall's table. Hence they use this water even if not in equilibrium with the air. There are various objections to such a procedure. Even if the equilibrium water at 25° has a conductance of 0.8×10^{-6} rec. ohms (which is the theoretical value if carbon dioxide is the only impurity of electrolytic nature), there is no guarantee that carbon dioxide is the only contamination. In our experiments equilibrium water with a conductance of 0.80 to 0.85×10^{-6} at 25° had a residual conductance of 0.11 to 0.14×10^{-6} after removing all the carbon dioxide. In working with extremely dilute solutions of neutral salts there is no objection to the use of equilibrium water if the water is brought *into equilibrium with air at the temperature at which the measurements are made*. This point is often overlooked, and if the above condition is not fulfilled the water correction will become uncertain, for the conductance of the water will change when exposed to the air. As an illustration some values of the cell constant determined with extremely dilute solutions of potassium chloride in equilibrium water (conductance 0.85×10^{-6}) and in the same water when carbon dioxide free (cond. 0.12×10^{-6}) will be given. The conductance of the water is subtracted as a correction. The agreement is satisfactory.

Concentration of KCl	Cell constant using equilibrium water	Cell constant using carbon dioxide-free water
0.0005 N	0.01242	0.01240
.00025 N	.01240	.01239
.0001 N	.01241	.01239
.00005 N	.01238	.01241

In the measurements of the conductance of extremely dilute lanthanum chloride solutions and in the determination of the solubility of lanthanum oxalate, both equilibrium water and the latter freed from carbon dioxide have been used. The conductivity of the water was subtracted as a correction and the results of both sets of measurements as a rule agree to

⁵ J. Kendall, *THIS JOURNAL*, **38**, 2460 (1916); **39**, 7 (1917); see also, I. M. Kolthoff, *Rec. trav. chim.*, **48**, 664 (1929).

⁶ E. W. Washburn, *THIS JOURNAL*, **40**, 106 (1918).

⁷ H. Remy, *Z. Elektrochem.*, **31**, 88 (1925); Remy and Kuhlmann, *Z. anal. Chem.*, **65**, 1 (1924); E. Laue, *Z. anorg. allgem. Chem.*, **165**, 305 (1927).

within 0.3%. In order to get reliable results from the conductance measurements of a saturated solution of the slightly soluble lanthanum hydroxide, carbon dioxide-free water has to be used as a solvent. Its conductivity was subtracted from the figure, which may cause a slight uncertainty in the result.

The Conductance of Lanthanum Chloride Solutions and the Mobility of the Lanthanum Ion.—The conductance of lanthanum chloride solutions was measured at different dilutions in various cells. The duplicates agreed within 0.1%.

Conductance of Lanthanum Chloride at 25°.—Conductivity of equilibrium water, 0.8×10^{-6} ; of carbon dioxide-free water, 0.15×10^{-6} rec. ohms. These figures have been subtracted from the conductances of the solution.

Normality of LaCl ₃	Cond. $\times 10^6$ in equilibrium water	Cond. $\times 10^6$ in carbon dioxide-free water	Normality of LaCl ₃	Cond. $\times 10^6$ in equilibrium water	Cond. $\times 10^6$ in carbon dioxide-free water
0.0100	1220	...	0.000599	84.75	84.66
.0050	639000435	62.17	61.97
.0025	331.7000261	37.74	37.65
.001501	204.2	203.8	.000150	22.02	22.00
.0010	138.2	138.2	.000075	11.13	11.07
.000745	104.3	104.4	.000060	8.97	8.43

The empirical equation of Kohlrausch⁸ in which Λ is the equivalent

$$\Lambda = \Lambda_{\infty} - A \sqrt{c}$$

conductivity at a normality c , and Λ_{∞} the same at infinitely dilute solution, is theoretically the limiting expression to which the data will approach

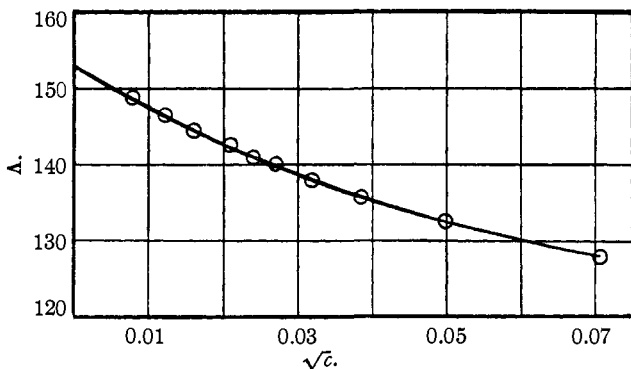


Fig. 2.

more and more closely as the concentration approaches zero.⁹ In Fig. 2 the equivalent conductance is plotted against the square root of the

⁸ F. E. Kohlrausch and M. E. Maltby, *Wiss. Abh. Physik.-Techn.*, Reichsanstalt, 3, 156 (1900).

⁹ L. Onsager, *Physik. Z.*, 27, 388 (1926); 28, 277 (1927); *Trans. Faraday Soc.*, 23, 341 (1927).

normality c ; the line is straight at concentrations smaller than 0.0008 N . From the graph it can be seen that up to concentrations of 0.0008 to 0.001 N the following relation holds for lanthanum chloride

$$\Lambda = 152.8 - 475 \sqrt{c}$$

The following table shows the calculated and experimental data of the equivalent conductance up to a normality of 0.001 N .

EQUIVALENT CONDUCTANCE OF LANTHANUM CHLORIDE

$$\Lambda_{\text{calcd.}} = 152.8 - 475 \sqrt{c}$$

Normality of LaCl ₃	$\Lambda_{\text{exptl.}}$	$\Lambda_{\text{calcd.}}$	Difference in %
0.001	138.2	137.8	+0.3
.000745	140.0	140.0	0.0
.000599	141.3	141.3	0.0
.000435	142.6	143.0	-0.3
.000261	144.7	145.3	-0.4
.000150	146.6	147.1	-0.3
.000075	148.8	148.8	0.0
.000060	149.4	149.2	+0.1

At concentrations between 0.001 and 0.01 N the following relation holds

$$\Lambda = 152.8 - 146 \sqrt{c}$$

Using the value 75.8 for the mobility of the chloride ion at infinite dilution¹⁰ a value of 77 is found for the equivalent conductance of the lanthanum ion at an ionic strength of zero. This value is higher than those reported in the literature. H. Ley¹¹ found 67.3, A. A. Noyes and J. Johnston¹² 72.0, and Rimbach and Schubert,¹³ 67.3. The measurements described in this paper have been extended to extremely high dilutions and the extrapolated figure of Λ_{∞} therefore is more certain than that of previous authors.

The Solubility of Lanthanum Oxalate in Water at 25°

(a) **Conductivity Method.**—The conductance of a saturated solution of lanthanum oxalate (three different products) in equilibrium water and carbon dioxide-free water was determined at 25°. After subtracting the conductivity of the solvent, a specific conductance of $9.97 (\pm 0.1) \times 10^{-6}$ rec. ohms was found. Assuming complete ionization and a value of 77 for the mobility of the lanthanum ion and of 72.7 of the oxalate ion,¹⁴ this conductance corresponds to a solubility of 0.60 mg. of the anhydrous salt per liter or a molarity of 3.35×10^{-6} .

(b) **Volumetric Method.**—Saturated solutions of three different products of lanthanum oxalate were prepared in conductivity water by shaking an excess of the solid with 2.5 liters of water for a week in a thermostat at $25 \pm 0.05^\circ$. After settling in the thermostat, large samples were removed by means of a pressure pipet and each sample examined in a strong light to make sure of the absence of any suspended solid. Two

¹⁰ F. L. Hunt, *THIS JOURNAL*, **33**, 795 (1911).

¹¹ H. Ley, *Z. physik. Chem.*, **30**, 193 (1899).

¹² A. A. Noyes and J. Johnston, *THIS JOURNAL*, **31**, 987 (1909).

¹³ Rimbach and Schubert, *Z. physik. Chem.*, **67**, 183 (1909).

¹⁴ F. Kohlrausch and Holborn, "Leitvermögen der Elektrolyte," 1916.

liters were evaporated to a small volume (about 25 cc.) and the oxalate titrated with 0.01 *N* permanganate. A solubility of 2.08 ± 0.03 mg. of anhydrous oxalate per liter was found in this way.

(c) **Colorimetric Method.**—As there was a large discrepancy between the conductimetric and volumetric methods, the solubility was approximated in a colorimetric way. It was found that a dilute solution of sodium alizarinate gives a bright violet color to a solution of lanthanum containing as little as 1 mg. of the latter in a liter. This test can be applied successfully to the colorimetric estimation of lanthanum in extremely small concentrations down to 0.1 mg. of lanthanum per liter. At a definite lanthanum content the sensitivity and the color observed are dependent upon the hydrogen-ion concentration. In order to get comparable conditions, 1 cc. of an acetate buffer containing 2 *N* ammonium acetate and 2 *N* acetic acid is added to 10 cc. of the nearly neutral solution to be tested. Then 0.4 cc. of a 0.1% sodium alizarinate solution is added and comparison made with lanthanum solutions of known content. The method gives good results for concentrations between 0.1 and 2 mg. of lanthanum per liter. The solutions for comparison cannot be kept for a long time as the lanthanum alizarinate compound flocculates as a purple precipitate after standing for ten to twenty hours. Oxalate interferes somewhat with this color test; therefore, in the determination of the solubility of lanthanum oxalate the anion was replaced by sulfate. Five, 10 and 20 cc. samples of the saturated solution were evaporated to dryness. A little sulfuric acid was added to the residue, which was then heated until no more fumes were given off. After cooling, 1 cc. of the acetate buffer was added and the colorimetric measurement made as described before. In this way a solubility was found corresponding to 1.95 mg. of anhydrous lanthanum oxalate per liter. This figure is about 6% smaller than that found by the volumetric method, which is a satisfactory agreement considering the approximate character of the colorimetric reading. The following table gives a summary of the data on the solubility of lanthanum oxalate described in the literature.

SOLUBILITY OF LANTHANUM OXALATE

Mg. of Anhydrous Oxalate per Liter

Investigator	Conductivity method	Gravimetric method	Volumetric method	Colorimetric method
Rimbach and Schubert ¹³	0.62			
Hauser and Herzfeld ¹⁵	0.70	0.96	1.21	
Sarver and Brinton ¹⁶	2.07	2.14		
Kolthoff and Elmquist	0.60		2.08	1.95

The agreement between Sarver and Brinton's gravimetric figure and our volumetric one is very satisfactory. The conductivity method undoubtedly gives much too low results, which is not surprising considering the tendency of various earth alkali oxalates to form complex ions in the solution.¹⁷

The Solubility of Lanthanum Oxide and Hydrus Lanthanum Oxide

Conductivity Method.—At the beginning of this paper, it was mentioned that the hydrolysis of lanthanum chloride is negligibly small. Therefore, lanthanum hydroxide

¹⁵ R. J. Meyer and O. Hauser, "Die Seltenen Erden und Erdsäuren," p. 61.

¹⁶ L. A. Sarver and P. H. M.-P. Brinton, *THIS JOURNAL*, 49, 943 (1927).

¹⁷ Cf. R. Scholder, E. Gadenne and H. Niemann, *Ber.*, 60, 1510 (1927). Recently Mr. Sandell found in this Laboratory a much lower value for the solubility of magnesium oxalate by the conductivity method than by direct determinations and even in the case of calcium oxalate there was a small but distinct difference.

must be a strong base and the saturated, extremely dilute solution can be considered as being completely ionized.

Various products of lanthanum oxide (*cf.* under materials used) were added to the water which had been made carbon dioxide free in the conductivity cell. The passage of carbon dioxide-free air was continued until the conductance was constant. As a rule this was the case after one-half to three hours and then it remained constant for at least a day. If some more oxide was added to the saturated solution, the conductance did not change, which is a good proof of the absence of foreign electrolytes. As lanthanum oxide absorbs carbon dioxide very readily, the products were ignited in an electric furnace at 800° and while still hot introduced into the cell. The saturated solution of the various products had the same conductivity; after subtracting the conductivity of the carbon dioxide-free water, a value of 3.34×10^{-6} rec. ohms was found, corresponding to a solubility of 0.67 mg. of La_2O_3 per liter. For the conductance of the saturated solution of precipitated and washed hydrous lanthanum oxide a lower value was found, probably on account of a slight contamination by carbon dioxide. A solubility of 0.3 mg. of La_2O_3 per liter was derived from the conductivity figures.

Volumetric Method.—The solubilities of the three oxides and the hydrous oxides were also determined in a volumetric way. Water was made carbon dioxide free in 2.5-liter paraffin-lined bottles (the paraffin coat was washed with a solution of ammonia in 50% alcohol to remove traces of acids), the oxide or hydrous oxide was added quickly and the bottles rotated in a thermostat for ten days. After the settling of the precipitate in the thermostat, large samples were collected with a pressure pipet. One liter of each solution and the same volume of a blank were evaporated to a small volume, a known excess of 0.01 *N* hydrochloric acid was added, and after removing all carbon dioxide, back titrated with 0.01 *N* base, using brom cresol green as an indicator. The titration error was corrected for in an empirical way. In all cases it was found that 1 liter of solution required 1.29 to 1.36 cc. of 0.01 *N* acid for its neutralization, corresponding to a solubility of 0.73 mg. of La_2O_3 per liter. This is in satisfactory agreement with the conductimetric data considering the extremely slight solubility. W. Busch¹⁸ found by the volumetric method a solubility of 4 mg. of La_2O_3 per liter at 25°. However, he mentions that the accuracy of his method is dependent upon the rapidity and the thoroughness of the filtration. E. Sadolin¹⁹ calculated from potentiometric determinations of *P_H* in mixtures of lanthanum chloride and hydrous lanthanum oxide at 18° a solubility product $[\text{La}^{+++}][\text{OH}^-]^3 = 10^{-20.98}$, corresponding to a solubility of 0.405 mg. of lanthanum oxide per liter. From our figures a solubility product of aged lanthanum hydroxide of $10^{-20.04}$ is derived.

Summary

1. The mobility of the lanthanum ion at infinite dilution and at 25° is 77.
2. A colorimetric method with sodium alizarinate as reagent has been developed for the determination of traces of lanthanum.
3. At 25° the solubility of lanthanum oxalate is equal to 2.08 mg. of the anhydrous salt per liter. The conductivity method gives much too low results on account of a complex dissociation of the dissolved lanthanum oxalate.
4. The solubility of lanthanum oxide and aged hydrous lanthanum

¹⁸ W. Busch, *Z. anorg. allgem. Chem.*, **161**, 161 (1927).

¹⁹ E. Sadolin, *ibid.*, **160**, 133 (1927).

oxide is found to be 0.7 mg. of La_2O_3 per liter at 25° . The data from the conductivity and volumetric methods agree within 10%.

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]
**THE QUANTITATIVE DETERMINATION OF LANTHANUM BY
PRECIPITATION AS OXALATE OR AS HYDROXIDE AND THE
HIGHER OXIDE FORMATION OF LANTHANUM**

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The Determination of Lanthanum by Precipitation as Oxalate.—As lanthanum oxalate carries down alkali oxalates² oxalic acid must be used as a precipitating agent. The determination can be made volumetrically or gravimetrically. All experiments have been carried out with lanthanum chloride solutions. Pure³ lanthanum chloride ($\text{LaCl}_3 \cdot 6\text{H}_2\text{O}$) was prepared and a standard solution of this product made up in a known weight of water. The latter was standardized by gravimetric chloride and lanthanum determinations according to precision methods, and contained 0.2946 equivalent of LaCl_3 per 1000 g. of solution (chloride analysis). In all further experiments a known volume was pipetted out and weighed. All reagents used were purified and tested for purity according to precision methods.

Volumetric Determination.—(a) The excess of oxalic acid is titrated in an aliquot part of the filtrate. (b) After washing out with water the precipitate is dissolved in warm dilute sulfuric acid and titrated according to the standard procedure with permanganate.

Ten-cc. portions of the stock solution of lanthanum chloride were pipetted into iodine flasks of known weight. Afterward the flasks were reweighed, varying amounts of a pure 0.05 molal oxalic acid solution were added and the flasks and contents again weighed. After standing overnight, weighed portions of the filtrates were titrated with a standard permanganate solution added from a weight buret. In all cases the titration error was determined by experiment. The precipitated lanthanum oxalate was collected on a filter and washed with cold water until the filtrate turned methyl orange the same shade as the water. The precipitate was

¹ From a thesis submitted by Ruth Elmquist to the Graduate School of the University of Minnesota in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

² Th. Sheerer, *Ann. phys. chim.*, [II] 56, 479 (1842); G. P. Baxter and R. C. Griffin, *THIS JOURNAL*, 28, 1684 (1906); G. P. Baxter and H. W. Daudt, *ibid.*, 30, 563 (1908); compare next paper in this series, where an interpretation of this so-called coprecipitation has been given.

³ Cf. I. M. Kolthoff and Ruth Elmquist, *THIS JOURNAL*, 53, 1217 (1931).