

as a catalyst was tried,¹⁴ but at present no definite information on the conditions of formation of the higher oxide has been obtained.

The results so far, however, show definitely that lanthanum oxide heated for long periods of time at very high temperature in an electric furnace and exposed to the air can be transformed into the higher oxides La_2O_5 and La_2O_7 .

Summary

1. A precise volumetric procedure has been described for the determination of lanthanum as lanthanum oxalate. The oxalate can be estimated gravimetrically as oxide if ignited to constant weight in an electric furnace at 800 to 900° and weighed in a well-closed weighing bottle.

2. In the precipitation of lanthanum chloride with sodium hydroxide or ammonia basic chloride is formed. This is avoided by adding the lanthanum solution slowly to an excess of the base. Use of this fact is made in the volumetric and gravimetric determinations of lanthanum by precipitation as hydrous oxide.

3. Lanthanum oxide heated for long periods of time at white heat in an electric muffle furnace in air can be transformed into higher oxides La_2O_5 and La_2O_7 .

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LANTHANUM ALKALI OXALATES¹

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The fact that alkali oxalates are carried down by lanthanum oxalate was first observed by Th. Sheerer.² G. P. Baxter and R. C. Griffin³ stated that ammonium oxalate, but not oxalic acid, was carried down in considerable quantities by rare earth oxalates and that occlusion of ammonium oxalate was made negligible by acidifying the solution with twice the equivalent amount of nitric acid. G. P. Baxter and H. W. Daudt⁴ reported that potassium oxalate was occluded to the same extent as ammonium oxalate (5–18%) but that sodium oxalate was occluded only slightly even in neutral solution. Since the occluded oxalate was determined after washing the lanthanum oxalate, part of the occluded salt may be removed from the precipitate. For this reason a series of experi-

¹⁴ Ref. 12, p. 82–87.

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

² Sheerer, *Ann. phys. chim.*, [II] 56, 479 (1842).

³ Baxter and Griffin, *THIS JOURNAL*, 28, 1684 (1906).

⁴ Baxter and Daudt, *ibid.*, 30, 563 (1908).

ments was carried out in which an excess of alkali oxalate was added to a lanthanum chloride solution. The excess of oxalate was determined in an aliquot part of the filtrate by titration with potassium permanganate. The precipitates obtained with ammonium oxalate were washed out with distilled water containing a trace of potassium sulfate in order to prevent them from going into colloidal solution, and after dissolving in warm sulfuric acid titrated with permanganate. The procedure was the same as that described in a previous paper⁵ for the experiments with oxalic acid. As may be seen from the results in Table I, the greater part of the alkali oxalate carried down by lanthanum oxalate is removed by washing out. The low results obtained with sodium and potassium oxalate which are given in the last column are explained by the fact that at the end of the washing a trace of the precipitate ran through the filter in a colloidal state.

TABLE I
COPRECIPITATION OF ALKALI OXALATES BY LANTHANUM OXALATE

Precipitant oxalate	M. equiv. of LaCl ₃ taken	M. equiv. of oxalate added	Equiv. of alkali oxalate carried down by 100 equivs. of lanthanum oxalate	Equiv. of alkali oxalate in 100 equivs. of the ppt. after washing out
Sodium	2.999	4.024	5.53	(-1.10)
Sodium	2.990	7.555	15.15	(-0.27)
Potassium	2.993	3.993	13.1	(- .90)
Potassium	2.991	7.487	48.2	(- .50)
Potassium	2.986	9.983	66.5	(-1.2)
Ammonium	2.993	3.982	18.5	+2.2
Ammonium	2.992	9.954	33.0	+3.6

The order of the coprecipitation found is potassium oxalate > sodium oxalate > ammonium oxalate.

This carrying down of alkali oxalates can be explained as due to the ordinary causes of coprecipitation or by the formation of definite double salts of lanthanum oxalate with alkali oxalate. The large extent to which the alkali oxalates are carried down indicates double salt formation. No double oxalates of the cerium group of rare earth elements have been described in the literature;⁶ the following study, however, shows that even at relatively low concentrations of alkali oxalates in the solution lanthanum oxalate is transformed into a double salt. In the present investigation weighed amounts of lanthanum oxalate were shaken in paraffined oil bottles in a thermostat at 25° with 75 to 100 cc. portions of solution of ammonium oxalate, sodium oxalate and potassium oxalate of various but known concentrations. After shaking for a definite time the bottles were clamped in

⁵ Kolthoff and Elmquist, *THIS JOURNAL*, **53**, 1225 (1931).

⁶ Double alkali oxalates of the yttrium group of rare earth elements are known; see P. T. Cleve and O. Hoeglund, *Bull. soc. chim.*, **18**, 289 (1872); C. A. von Welsbach, *Monatsh.*, **27**, 935 (1906); L. A. Pratt and C. James, *THIS JOURNAL*, **34**, 488 (1911).

an upright position in the thermostat. Although a few samples settled quickly, considerable difficulty was usually experienced in removing the suspended solid from the solution. Filtration through various materials gave opalescent filtrates. The best method for obtaining a clear solution was to place the oil bottles in which the experiments were made in a centrifuge. They were rotated for several minutes and the clear solution removed by cautious pipetting with slow mechanical suction. Every sample was examined for suspended solid and discarded if any was found. Aliquot portions of both samples and blanks were titrated with permanganate. From the difference in concentration the number of moles of alkali oxalate removed by one mole of lanthanum oxalate was calculated.

The lanthanum oxalate used was prepared by precipitating a pure lanthanum chloride solution with an excess of oxalic acid. The precipitate was washed with distilled water until methyl orange gave the wash liquid the same color that it gives to the water. The lanthanum oxalate was air-dried and analyzed by titrating with a standard solution of potassium permanganate (weight buret) just before the shaking experiments were started. The results are given in the tables. The formation of the double salts is very slow, especially at low concentrations of alkali oxalate; in some cases equilibrium had not been attained even after four weeks of shaking.

Discussion of the Results.—Even at low concentrations of alkali oxalates, lanthanum oxalate is slowly transformed into a double salt of the general composition $1\text{La}_2\text{Ox}_3 \cdot 1\text{Alk}_2\text{Ox} \cdot x\text{H}_2\text{O}$ (1:1 compound). At concentrations of ammonium oxalate smaller than 0.012 *N*, lanthanum oxalate is the stable solid body; at higher concentrations it is transformed into the double salt 1:1 (Table II, Expts. 3 and 4). At a concentration of

TABLE II

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH AMMONIUM OXALATE

Expt.	Initial concn. of Am_2Ox <i>N</i>	Final concn. of Am_2Ox , <i>N</i>	Vol. of soln. shaken, cc.	Millimoles of La_2Ox_3 taken	Time shaken, weeks	Moles of Am_2Ox removed by 1 mole of La_2Ox_3
1	0.01	0.01	75	0.4155	5	0.00
2	.01	.01	75	.4194	7	.01
3	.0191	.0122	75	.6925	5	.37
4	.0191	.0120	75	.6884	7	.39
5	.0302	.0128	75	.6840	5	.95
6	.0302	.0126	75	.6881	7	.96
7	.0291	.0215	100	.412	1	.92
8	.0432	.0292	100	.692	4	1.02
9	.0693	.0553	100	.683	1	1.02
10	.0996	.0861	100	.679	1	1.00
11	.1990	.1722	100	1.366	1	0.98
12	.3905	.3637	100	1.366	1	.98
13	.5279	.5144	100	0.692	4	.98
14	.5442	.5315	100	.692	4	.92

TABLE III

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH POTASSIUM OXALATE

Expt.	Initial concn. of K_2Ox , N	Final concn. of K_2Ox , N	Vol. of soln. shaken, cc.	Millimoles of La_2Ox_3 taken	Time shaken, weeks	Moles of K_2Ox removed by 1 mole of La_2Ox_3
1	0.0101	0.0101	75	0.4159	5	0.00
2	.0101	.00922	75	.4118	7	.11
3	.0281	.0279	100	.679	1	.016
4	.0293	.0162	100	.692	4	.95
5	.0483	.0349	100	.679	1	.99
6	.0682	.0556	100	.683	1	.93
7	.0985	.0849	100	.679	1	1.00
8	.1406	.1259	100	.692	4	1.06
9	.1470	.1220	100	.684	4	1.83
10	.1989	.1466	100	1.366	1	1.92
11	.2993	.2476	100	1.366	1	1.90
12	.3990	.3460	100	1.366	1	1.95
13	.4978	.4708	100	0.679	1	1.99
14	.9915	.8858	100	2.730	1	1.94
15	1.718	1.662	100	1.372	1	2.01
16	3.853	3.745	100	1.366	1	1.96

TABLE IV

DOUBLE SALT FORMATION OF LANTHANUM OXALATE WITH SODIUM OXALATE

Expt.	Initial concn. of Na_2Ox , N	Final concn. of Na_2Ox , N	Vol. of soln., shaken, cc.	Millimoles of La_2Ox_3 taken	Time, shaken, weeks	Moles of Na_2Ox removed by 1 mole of La_2Ox_3
1	0.01	0.01	75	0.4120	5	0.00
2	.01	.01	75	.4145	7	.00
3	.02	.02	75	.4190	7	.00
4	.0374	.0216	100	.692	4	1.14
5	.0498	.0363	100	.692	4	0.99
6	.1002	.0866	100	.679	1	1.00
7	.1985	.1851	100	.679	1	0.99
8	.2372	.2233	100	.692	4	1.01
9	.2449	.2263	100	.692	4	1.34
10	.2479	.2249	100	.692	4	1.66
11	.3014	.2716	100	.692	4	1.96
12	.4012	.3492	100	1.366	1	1.90
13	.4993	.4721	100	0.679	1	2.00

about 0.01 N potassium oxalate both lanthanum oxalate and the double salt 1:1 can exist as solid bodies, whereas the former seems to be stable in sodium oxalate solutions up to a concentration of about 0.02 N Na_2Ox .

It is desirable to determine the equilibrium concentration of alkali oxalate at which lanthanum oxalate and the double compound 1:1 can exist as solid bodies from the other side by starting with the double salt. As the formation of the double salt, especially at relatively low oxalate concentrations, is slow, it is not quite certain whether in all cases equilibrium had been attained even after shaking for seven weeks.

Sodium and potassium oxalate can form two kinds of double salts, $\text{La}_2\text{Ox}_3 \cdot 1\text{K}_2(\text{Na}_2)\text{Ox} \cdot x\text{H}_2\text{O}$ and $\text{La}_2\text{Ox}_3 \cdot 2\text{K}_2(\text{Na}_2)\text{Ox} \cdot y\text{H}_2\text{O}$. Both solid phases are in equilibrium with the solution at a potassium oxalate concentration of 0.125 *N* (Table III, Expts. 8 and 9) or a sodium oxalate concentration of 0.225 *N* (Table IV, Expts. 9 and 10). No indication has been obtained that a similar compound 1:2 of ammonium oxalate exists.

Lanthanum oxalate was also shaken with solutions of oxalic acid of concentrations varying between 0.01 and 1.01 *N*. After shaking for a few weeks the filtrates were analyzed by titration with sodium hydroxide and with permanganate. Under no conditions was there a double compound formation. At higher oxalic acid concentrations (0.1 *N*) a slight adsorption of the acid by the lanthanum oxalate of the order of one equivalent per cent. was found.

The above results explain why oxalic acid and not alkali oxalates must be used as a precipitant in the determination of lanthanum.

Summary

The so-called coprecipitation of alkali oxalate with lanthanum oxalate is to be attributed to a double salt formation. Lanthanum oxalate is in equilibrium with the double salt $\text{La}_2\text{Ox}_3 \cdot (\text{Alk})_2\text{Ox} \cdot x\text{H}_2\text{O}$ at a concentration of about 0.012 *N* ammonium oxalate, 0.01 *N* potassium oxalate or 0.02 *N* sodium oxalate.

Potassium and sodium oxalate also form double salts of the composition $\text{La}_2\text{Ox}_3 \cdot 2\text{K}_2(\text{Na}_2)\text{Ox} \cdot y\text{H}_2\text{O}$ at a concentration of 0.125 *N* potassium oxalate and 0.225 *N* sodium oxalate, respectively. No double compounds of lanthanum oxalate and oxalic acid are formed.

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

THE DECOMPOSITION OF HYDROCARBONS IN THE POSITIVE RAY TUBE

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Some time ago, Olson and Meyers¹ investigated the reactions produced by excited mercury atoms in mixtures of hydrogen and ethylene. The products were analyzed by Dr. H. M. Kvalnes using the positive ray apparatus which Dr. Hogness and his students had constructed. By making some assumptions which were stated in the above paper, Olson and Meyers were able to postulate a reaction mechanism which accounted for the results of the analysis. The desirability of determining the trustworthiness of such an analysis was discussed privately at that time, but the actual investigation had to be postponed until a new apparatus could be built.

¹ Olson and Meyers, *THIS JOURNAL*, 49, 3131 (1927).