214. *The Selenates of Lanthanum and their Solubilities in Water.*

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SEVERAL hydrates of lanthanum selenate were described by Cleve (*Bull. Soc. chim.*, 1874, **21**, 196) and by Frerichs and Smith (*Annalen*, 1878, **191**, 361). As in several cases the analyses are either not given or are incomplete, and as the data are somewhat at variance, it seemed desirable to check and extend this early work and to determine the solubilities of the salts in water.

The lanthanum selenate was prepared by dissolving ignited lanthana in diluted selenic acid and crystallising it on the water-bath. The salt is only slightly soluble in boiling water, and the dilute mother-liquor was poured off and used in preparing further batches.

The lanthana was purchased from Messrs. Hilger; spectroscopic examination by Dr. S. Judd Lewis showed that it contained only the merest traces of cerium, praseodymium, and neodymium. Traces of terbium were also present, but chemical analysis showed that thorium was absent. In order to ensure the removal of any other contamination, such as chloride, which cannot be readily detected with the spectroscope, the lanthana was dissolved in dilute nitric acid and the clear solution, which did not require filtration, was raised to boiling, lanthanum oxalate being precipitated with boiling oxalic acid solution. After being filtered, washed and dried, the oxalate was ignited to oxide.

The selenic acid was purchased as pure and found to be free from sulphuric acid and halogen derivatives.

Solutions of lanthanum selenate proved to be slightly more stable than those of neodymium selenate, but analysis of both the solid and the liquid content of the saturation bottle after certain solubility determinations, particularly those at the higher temperatures, showed that hydrolysis had taken palce. This is referred to later.

Some acid solutions on warming gave an appreciable deposit of insoluble lanthanum selenite, as though some catalyst were present accelerating the reduction. One batch of material was discarded for this reason although it appeared to be quite pure. A similar reduction was noticed with neodymium selenate (Friend, J., 1931, 1802).

As with the selenates of neodymium, the rate of transformation of one hydrate into another is often slow, some of the hydrates existing very persistently in the metastable region. This is well indicated in one case by the broken line in the figure.

Method of Analysis.—One of the most convenient and accurate methods of estimating lanthanum consists in precipitation with excess of oxalic acid and ignition to oxide, with observance of the precautions already given in connexion with neodymium salts (Friend, J., 1930, 1633). The precipitate of lanthanum oxalate was neither so granular nor quite so easy to filter and wash free from adsorbed material as neodymium oxalate. Considerable excess of oxalic acid was taken, as recommended by Kolthoff and Elmquist (*J. Amer. Chem. Soc.*, 1931, **53**, 1225; see also Backer and Klaassens, *Z. anal. Chem.*, 1930, **81**, 104; Sarver and Brinton, *J. Amer. Chem. Soc.*, 1927, **49**, 943). The volumetric method of precipitating as oxalate and titrating with permanganate (Kolthoff and Elmquist) was not adopted because contamination of the solution with manganese salts renders the subsequent recovery of the lanthana more arduous owing to adsorption of manganese compounds. The selenium was usually determined in separate samples by boiling with concentrated hydrochloric acid to reduce to selenite, precipitating the element with sulphur dioxide, and collecting it on a sintered-glass filter. The selenium was washed with hot water and alcohol, dried in an electric oven at 120—130°, and weighed.

In order to conserve material, it was hoped that it might be possible to estimate both lanthanum and selenium in the same sample, as was done with the corresponding neodymium salts (Friend, J., 1931, 1802). The method worked satisfactorily if the selenium were removed first, in which case the filtrate was taken to dryness on the water-bath, the residue dissolved in water, and the lanthanum precipitated with oxalic acid or a mixture of this with ammonium oxalate. Alkali-metal oxalates were not used owing to their tendency to be adsorbed by the precipitate (Kolthoff and Elmquist, *loc. cit.*). The following results are typical:

Direct pptn. from selenate (g. La_2O_3) ...	0·3526	0·3180	0·3614	0·2286
Pptn. after removal of Se (g. La_2O_3) ...	0·3523	0·3169	0·3604	0·2271

The results were invariably about 1 mg. too low by the second method, but the difference was too minute to affect the solubility data. Precipitation of the selenium after removal of the lanthanum did not proceed so satisfactorily as with the neodymium salts. Sometimes the results were good but sometimes they were appreciably too low, probably on account of adsorption by the precipitated oxalate. The subject was not further investigated, but the following results are typical of the best:

Direct pptn. from selenate (g. Se)	0·2842	0·1735	0·0688	0·1353
Pptn. after removal of La (g. Se)	0·2848	0·1728	0·0670	0·1310

This method, therefore, was only used as a check.

Anhydrous Lanthanum Selenate, $La_2(SeO_4)_3$.—According to Cleve (*loc. cit.*), this salt is obtained by heating one of the hydrates to 185°. This was found to be substantially true, although it is difficult if not impossible by mere heating to remove the last traces of water without causing partial decomposition of the salt, as was found to be the case with neodymium selenate. In one experiment, 0·8 g. of the pentahydrate was heated for 8 hours in a platinum dish in an electric oven at 180° and for a further 4 hours at 200°. At intervals the dish was removed and weighed and after each heating showed further small losses.

Pentahydrate, $La_2(SeO_4)_3,5H_2O$.—Cleve stated that the hexahydrate loses 1 mol. of water at 100°, but gave no analytical data. On taking a solution of lanthanum selenate to dryness on a water-bath in a platinum dish, a residue of constant weight is rapidly obtained consisting of minute, needle-shaped, colourless crystals. A few typical analyses are as follows:

	(1).	(2).	(3).	Calc. for $La_2(SeO_4)_3,5H_2O$.
La_2O_3, %	40·64	39·97	40·22	40·85
SeO_3, %	47·48	49·00	48·31	47·85
Water (by diff.), %	11·88	11·03	11·47	11·30
Ratio La_2O_3 : Se	1·373	1·354	1·337	1·371

The salt dissolves in water with considerable heat evolution.

Hexahydrate, $La_2(SeO_4)_3,6H_2O$.—Cleve obtained and analysed a substance corresponding to this composition. It gradually results upon spontaneous evaporation of an aqueous solution or by exposure of the pentahydrate to moist air. In dry air it loses water, and on the water-bath readily yields the pentahydrate. The following analyses are typical :

			Calc. for $La_2(SeO_4)_3,6H_2O$.
La_2O_3, %	40·21	39·12	39·95
SeO_3, %	47·00	46·98	46·79
H_2O (by diff.), %	12·79	13·90	13·26
Ratio La_2O_3 : Se	1·373	1·337	1·371

The results fluctuate considerably with the humidity of the air.

Dodecahydrate, $La_2(SeO_4)_3,12H_2O$.—This salt was stated by Frerichs and Smith to be obtained by dissolving lanthana in selenic acid and evaporating it on the water-bath. They gave an analysis in which the lanthanum but not the selenium was estimated. The description of the method of preparation is misleading, for evaporation to dryness on the water-bath yields the pentahydrate, as mentioned above. The dodecahydrate is only stable in contact with its saturated solution above 43° ; its solubility rapidly falls with rise of temperature, as shown in the figure, so that it is readily obtained in a pure condition when a slightly acid, concentrated solution below 40° is heated to about 80°, as shown by the first analysis below. The remaining analyses represent the composition of the solid phases in the saturation bottle at the temperatures given ; the basic nature of the salts, particularly that obtained at 100°, due to hydrolysis, will be noted.

Temp.	—	81·6°.	83·6°.	93·4°.	93·4°.	100°.	Calc. for $La_2(SeO_4)_3,12H_2O$.
La_2O_3, %	35·60	36·28*	34·67	36·68*	35·56	35·41	35·28
SeO_3, %	41·24	41·41	39·78	41·83	40·53	39·66	41·32
H_2O (by diff.), %	23·16	22·31	25·58	21·49	23·91	24·93	23·40
Ratio La_2O_3 : Se	1·387	1·406	1·399	1·409	1·409	1·434	1·371

* Calc. for $La_2(SeO_4)_3,10H_2O$: La_2O_3, 36·71%.

Normally, upon exposure to air, even very moist air, the salt loses water, being slowly converted into the hexahydrate. Transformation of the pure salt may be suspended, however, for prolonged periods. In one case the salt was kept for several days in the dry air of the author's office without change ; but this only happened once.

It is probable that the (apparently unanalysed) salt stated by Cleve to be the decahydrate and obtained by spontaneous evaporation of the aqueous solution was in reality this dodecahydrate. No clear evidence has been obtained of the existence of a hydrate intermediate between this and the hexahydrate, although on two occasions analyses of salt believed to be the dodecahydrate approximated more closely to the decahydrate. Probably this was due to partial dehydration, but the possible existence of a decahydrate is not excluded.

Higher Hydrates.—More highly hydrated salts do not crystallise easily. The putty-like residues in the saturation bottle after determination of the solubilities at the temperatures mentioned below were dried between filter papers and analysed.

						Calc. for	
Temp.	0°.	0·6°.	9·6°.	25·4°.	35°.	$22H_2O$.	$24H_2O$.
La_2O_3, %	30·61	28·84	29·77	29·55	28·13	29·52	28·58
SeO_3, %	33·70	33·98	33·62	33·57	34·69	34·57	33·48
H_2O (by diff.), %	35·69	37·18	36·61	36·88	37·18	35·91	37·94
Ratio La_2O_3 : Se	1·460	1·363	1·422	1·414	1·297	1·371	1·371

Several of the salts are distinctly basic. The analyses approximate to that calculated for the 22-hydrate, thus closely resembling those of the neodymium residues at similar temperatures. The fifth salt at 35° was distinctly acid, and was obtained from the 7·8% acid solution shown in the solubility table.

Determination of Solubility.—The apparatus used was similar to that described for neodymium sulphate (Friend, J., 1930, 1633). In general the saturated solution, after being weighed, was diluted to 250 c.c., and two lots of 50 c.c. each were taken for analysis. In the one the lanthanum was precipitated, in the other selenium. Usually the filtrates were worked for selenium and lanthanum respectively as a check on the results. When the differences were slight, the first data were regarded as correct; when the results diverged appreciably the estimations were repeated with fresh lots of solution. In every case the amount of selenium in solution was determined as well as the lanthanum. Owing to hydrolysis, the saturated solutions were usually slightly acid when crystals of pure neutral salt had been initially taken; the extent of acidity appeared to vary with the temperature and with the relative amount of solution and excess salt; probably a true equilibrium was not attained between the solid and liquid phases in the 4—5 hours' stirring allowed for saturation; if so, this would account for the difficulty experienced in obtaining accurate repeat results. In the following table, *S* represents the solubility as g. of anhydrous lanthanum selenate per 100 g. of solution. The theoretical value for the ratio La_2O_3 : Se is 1·371.

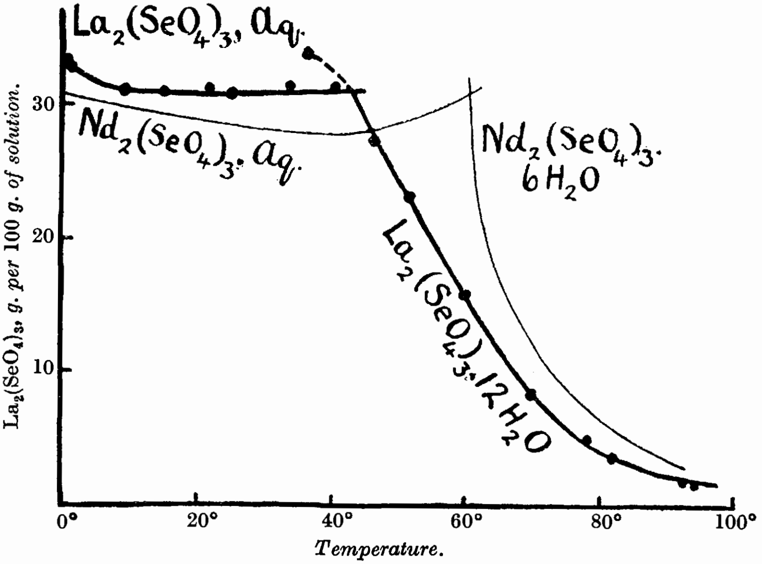
(*Crystals initially neutral or very slightly basic.*)

Solid phase $La_2(SeO_4)_3$,Aq.			Solid phase $La_2(SeO_4)_3,12H_2O$.		
Temp.	*S*.	La_2O_3 : Se.	Temp.	*S*.	La_2O_3 : Se.
0·0°	33·55	1·380	36·4°	34·00	1·373
0·6	32·87	1·377	46·2	27·54	1·347
9·6	30·90	1·387	51·4	23·37	1·395
15·0	30·84	1·378	59·4	15·92	1·342
21·8	31·31	1·389	69·4	8·51	1·318
25·4	30·54	1·398	78·2	5·02	1·269
33·6	31·29	1·385	81·6	3·78	1·275
40·6	31·15	1·354	92·4	1·93	1·568
			93·4	1·97	1·319

(*Free selenic acid added to solution.*)

Temp.	35°	35°	35°	83·6°	83·6°
Free H_2SeO_4, %	0	2·08	7·80	0	1·68
S	31·2*	28·96	24·07	3·25*	4·81

* Calculated.



The foregoing results are shown in the figure, together with the solubility curve for neodymium selenate. Although neodymium sulphate is 2·5—3 times as soluble as lanthanum sulphate between 0° and 45°, there is little difference between their selenates at these temperatures. The transition point between the dodeca- and the higher hydrate lies at approximately 43°.

Increase in the concentration of free acid at 35° reduces the solubility. The results do not indicate whether or not traces of acid increase the solubility, as was observed with lanthanum sulphate (Wirth, *Z. anorg. Chem.*, 1912, **76**, 174) and neodymium sulphate (Friend, J., 1930, 1633) at these lower temperatures. At higher temperatures, *e.g.*, 83·6°, the solubility is increased by the presence of acid, as was observed with neodymium sulphate.

In conclusion, the author desires to acknowledge the assistance of Mr. D. J. Munns, who has carried out several of the analyses.

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