188. *The Nitrates of Lanthanum, and their Solubilities in Water.*

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Although the simple nitrates of the rare-earth elements yield crystalline nitrates readily soluble in water, it is unusual for them to be used for the separation of the elements of the cerium group (Nos. 57 to 62) by fractional crystallisation, the double magnesium or

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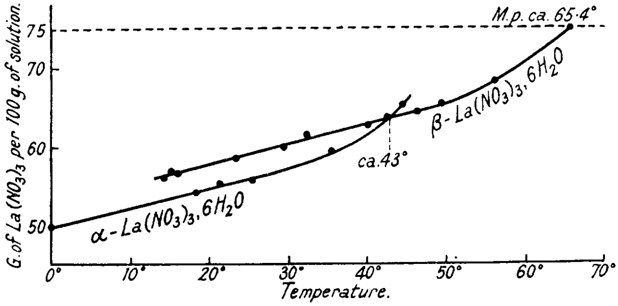
* The assumption of different apparent sizes for isotopic molecules is strengthened by the difference of 11% in the molecular volumes of liquid D_2 and liquid H_2 recently reported (Clusius and Bartholomé, *Naturwiss.*, 1934, **22**, 526). Similarly, the molecular volume of solid LiH has been found to be 1·5% greater than that of LiD (Zintl and Harder, *Z. physikal. Chem.*, 1935, **28***B*, 478).—The results for water itself are more difficult to interpret owing to the complex structure of both solid and liquid, but the difference in the molecular volumes of the two kinds of ice may be due to the same effect.

Further investigation of the problem (Bell, *Trans. Faraday Soc.*, in the press) shows that the dipole moment of D_2O may be expected to be slightly greater than that of H_2O. This would provide an additional reason for the greater osmotic abnormality of the former.

ammonium nitrates being employed in general. Feit and Przibylla (*Z. anorg. Chem.*, 1905, **43**, 205) recommend the removal of lanthanum from praseodymium by crystallisation from the simple nitrates, the praseodymium salt crystallising in the head fractions. There appear to be only two published data for the solubilities of the salts in water, *viz.*, that at 25°, 100 g. of solution contain 60·18 g. of $La(NO_3)_3$ (James and Whittemore, *J. Amer. Chem. Soc.*, 1912, **34**, 1168), and 60·46 g. of $Nd(NO_3)_3$ (James and Robinson, *ibid.*, 1913, **35**, 754). Preliminary experiments by the present author did not confirm these figures, and attempts to separate the cerium earths by fractional crystallisation of the simple nitrates have not yielded satisfactory results.

It seemed of interest, therefore, to ascertain the reason for this; it was soon found that the problem is complicated by the existence of two forms of the hexahydrated salt.

Lanthanum nitrate was prepared by dissolution of the oxide in diluted nitric acid. The filtered solution, after concentration on the water-bath, may remain supersaturated for many days. To induce crystallisation, it was seeded with $Bi(NO_3)_3,5H_2O$, and immediately yielded a crop of the β-hexahydrate, $La(NO_3)_3,6H_2O$. This somewhat anomalous result may be explained as follows. Although $La(NO_3)_3,5H_2O$ is too unstable to exist alone other than momentarily, it can exist in dilute solid solution in crystals of the corresponding stable bismuth salt (Bodman, *Z. anorg. Chem.*, 1901, **27**, 254). Similarly $Bi(NO_3)_3,6H_2O$ can only exist in solid solution in the corresponding lanthanum salt. On inoculation with $Bi(NO_3)_3,5H_2O$ it is presumed that crystals of the isomorphous $La(NO_3)_3,5H_2O$ are first formed; these immediately change into those of the more stable β-hexahydrate, which now form nuclei for the separation of the remainder of the salt. That the change is extremely rapid was shown by immediate separation of the crystals and analysis, by determination of their lanthana content by precipitation as oxalate, and subsequent ignition in the usual way. The results always corresponded to the hexahydrate.



Upon prolonged standing at room temperature, the β-salt is transformed into α-$La(NO_3)_3,6H_2O$, which is stable at the lower temperature and has the lower solubility (see fig.). This salt is also formed from the supersaturated solution by appropriate seeding.

The apparatus used in determining the solubilities has already been described (Friend, J., 1930, **1633**); the solubilities are calculated from the lanthana contents of the solutions, this being deemed most accurate as the pure crystals used in preparing the solutions do not undergo perceptible hydrolysis. The saturated solution from the saturation bottle was diluted to 250 c.c. The lanthana was estimated by precipitation from 50 c.c. with excess oxalic acid solution and ignition to oxide. The precipitated oxalate was less granular than that obtained with neodymium and praseodymium, and it was found advisable to digest it on the water-bath for several hours and keep it over-night; finally, it was filtered off in the cold and washed with hot, dilute oxalic acid solution. As a check, a further 50 c.c. were evaporated to dryness in a platinum dish and ignited to oxide. The two methods gave closely similar results, as the following data show:

La_2O_3 (from oxalate), %	0·5317	0·4230	0·5497	0·9467	0·7564
La_2O_3 (direct ignition), %	0·5333	0·4236	0·5491	0·9504	0·7587

The latter method invariably yielded a slightly larger amount of lanthana, possibly on account of slight solubility of the oxalate, but more probably because of traces of soluble impurity which the second process would fail to remove. The differences are too small, however, perceptibly to influence the calculated solubilities, *S*, given below. These are expressed as g. of anhydrous salt per 100 g. of solution, and are shown in the fig.

Solid phase, α-$La(NO_3)_3,6H_2O$.

Temp.	0°	18·4°	21·2°	25·4°	35·4°	42·4°	44·2°
S	50·03	54·16	55·03	55·80	59·12	63·84	65·13

Solid phase, β-$La(NO_3)_3,6H_2O$.

Temp.	14·4°	15·2°	15·8°	16·0°	23·2°	29·6°	32·2°	40·0°	46·4°	49·4°	56·0°	65·4° *
S	56·27	56·94	56·85	56·74	58·70	60·08	61·34	62·71	64·55	65·17	68·30	75·04

* Melting point.

The transition temperature, α ⟶ β, as read from the solubility curves is approx. 43°.

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