

NOTE.

The Lower Hydrates of Lanthanum and Praseodymium Nitrates. By J. NEWTON FRIEND and DOUGLAS A. HALL.

SEVERAL supposed hydrates of lanthanum nitrate have been described, but the evidence in favour of their existence is not convincing, being based merely on the loss in weight undergone by the hexahydrated salt when desiccated over sulphuric acid. There has been no attempt to ascertain whether or not there had been a simultaneous loss of nitric anhydride such as occurs with bismuth nitrate under similar conditions (see Friend and Hall, *Trans. Faraday Soc.*,

1938, 34, 777) and also with the rare-earth nitrates themselves at elevated temperatures. It was thought desirable, therefore, to check earlier experiments by exposing the pure salts over concentrated sulphuric acid for prolonged periods and determining, not merely their loss in weight, but also the base and acid contents of their residues.

Method of Analysis.—The dried solid was weighed quickly, dissolved in a known volume of *N*-nitric acid, and made up to 250 c.c. 25 C.c. of this solution were diluted to about 100 c.c. with water, and a measured volume of *N*/2-sodium hydroxide added, so that the latter was in excess. The solution and precipitate were warmed on a hot plate and then kept over-night. The precipitate was collected, washed with hot water, and ignited to constant weight in a platinum crucible. The lanthanum was weighed as La_2O_3 and the praseodymium as Pr_6O_{11} . The whole of the filtrate was titrated with *ca.* *N*/3-nitric acid, thus determining the amount of sodium hydroxide used and hence the nitric acid in the original solution. The N_2O_5 content of the salt was then found by allowing for the nitric acid added in making up the solution.

Lanthanum Nitrate.—The ordinary hexahydrate, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, was stated by Hermann (*J. pr. Chem.*, 1861, 82, 385) to lose $4 \cdot 5\text{H}_2\text{O}$ when exposed over concentrated sulphuric acid. Cleve (*Bull. Soc. chim.*, 1874, 21, 196) found a loss of $2 \cdot 5\text{H}_2\text{O}$, and Löwenstein $5\text{H}_2\text{O}$ (*Z. anorg. Chem.*, 1909, 63, 106). We have confirmed the existence of Löwenstein's monohydrate. The normal hexahydrate lost continuously in weight for about a year and then remained constant; after 3 years, the residue was the monohydrate [Found: La_2O_3 , 47·52; N_2O_5 , 46·99; $\text{La}_2\text{O}_3 : \text{N}_2\text{O}_5 = 1 \cdot 011$ (by wt.). Calc.: La_2O_3 , 47·50; N_2O_5 , 47·24%; $\text{La}_2\text{O}_3 : \text{N}_2\text{O}_5 = 1 \cdot 006$]. When a portion of this salt was dissolved in water it gave a very slightly cloudy solution which (together with the ratio $\text{La}_2\text{O}_3 : \text{N}_2\text{O}_5$ found) suggests the formation of a mere trace of basic salt.

Praseodymium Nitrate.—The ordinary hexahydrate lost weight continuously over concentrated sulphuric acid for about a year; after 3 years, the very pale green residue was proved to be the *dihydrate* [Found: Pr_2O_3 , 45·64; N_2O_5 , 45·01; $\text{Pr}_2\text{O}_3 : \text{N}_2\text{O}_5 = 1 \cdot 014$ (by wt.). $\text{Pr}(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$ requires Pr_2O_3 , 45·44; N_2O_5 , 44·64%; $\text{Pr}_2\text{O}_3 : \text{N}_2\text{O}_5 = 1 \cdot 018$]. There was no detectable formation of basic salt. This hydrate does not appear to have been mentioned hitherto in the literature.

Similar experiments with neodymium nitrate were upset by workmen when near completion, but are again in progress.—CENTRAL TECHNICAL COLLEGE, BIRMINGHAM. [Received, October 1st, 1938.]
