

124.—*Solubilities of the Chlorides of Lanthanum, Praseodymium, and Neodymium.*

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Between 0° and 80° the solubilities of the heptahydrated chlorides of praseodymium and lanthanum are almost identical. Above 55°, $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ is appreciably less soluble than either of these salts.

THESE salts are readily soluble in water and it was thought that a more extended use might be made of them in separating the elements by fractional crystallisation, as has been done successfully with members of the terbium group (see James and Bissel, *J. Amer. Chem. Soc.*, 1914, **36**, 2060). Apart from the determination of the solubilities of neodymium chloride at five different temperatures by Williams, Fogg, and James (*ibid.*, 1925, **47**, 297) and three scattered data by Matignon (*Ann. Chim. Phys.*, 1906, **8**, 249, 386), there appears to be no published information on the subject. A systematic study of the solubilities of

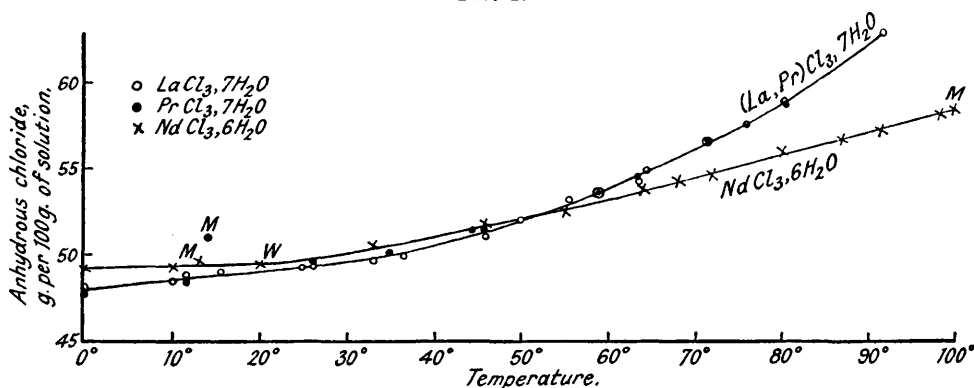
these salts was therefore undertaken, and although the results proved disappointing, they are placed on record.

EXPERIMENTAL.

The chlorides were prepared by dissolution of the pure oxides (for sources, see earlier papers) in diluted acid and concentration on the water-bath. The crystals were thoroughly drained on a sintered glass funnel. Perfect neutrality of these salts is well known to be difficult to attain. This was found to be particularly so with neodymium chloride. Analyses of the different batches of salts used in this research yielded the following atomic ratios: La : Cl = 2.965, 3.047; Pr : Cl = 2.925, 2.991, 3.062; Nd : Cl = 2.978, 2.966, 2.956, 2.920. The apparatus used for determining the solubilities has already been detailed (Friend, J., 1930, 1633). At the higher temperatures attempts were made to use the synthetic method, which was found to work well with lithium chloride up to 160° (Friend, Hale, and Ryder, J., 1937, 970), but above 80° the results were somewhat irregular, possibly owing to slight basic salt formation. The solubilities have been calculated from the oxide contents of the solutions, this being regarded as most accurate since the salts undergo but little hydrolysis. In the worst cases, the diluted solutions were faintly opalescent, although the concentrated solutions in the saturation bottle were perfectly clear.

The saturated solution was diluted to 200 c.c. and the oxide estimated by precipitation from an aliquot portion with oxalic acid and ignition to oxide, the precautions already outlined for each element (Friend, J., 1930, 1633; 1932, 2410; 1935, 824) being observed. The chlorine

FIG. 1.



M = Maignon, loc. cit. W = Williams, Fogg, and James, loc. cit.

was determined gravimetrically as silver chloride, and the free acid in acidulated solutions was estimated by titration with alkali, methyl-orange being used as indicator.

Throughout the research difficulty has been experienced in obtaining reproducible results.

Data obtained at different times either agreed closely, like those for the praseodymium and neodymium salts at 0°, or they differed by several units %, the error then being much greater than the ordinary experimental error. A similar difficulty was experienced with the nitrates of these elements and with certain bismuth salts and is possibly caused by the presence of some metastable salt.

In the tables, S represents the solubility as g. of anhydrous salt (MCl_3) per 100 g. of solution.

Lanthanum Chloride.—The solid phase was found by analysis to be $LaCl_3 \cdot 7H_2O$. The results are shown in Fig. 1.

Temp. ...	0°	10.0°	11.4°	15.4°	25.0°	26.2°	33.0°	36.4°	45.8°	50.2°
S	48.12	48.46	48.83	48.99	49.27	49.40	49.69	49.87	51.16	52.00
Temp. ...	55.4°	59°	63.6°	64.6°	64.6°	71.5°	76.0°	80.4°	92.1°	
S	53.15	53.65	54.30	54.96	54.84	56.70 *	57.59	58.87	63.02 *	

* Synthetic method.

The addition of small amounts of sulphuric acid to lanthanum sulphate was shown by Wirth (*Z. anorg. Chem.*, 1912, 76, 174) to enhance the solubility of the salt at 25°. The same is true for neodymium sulphate at 30°, a maximum solubility being attained in n-acid solution, and the solubility falling again with higher acid concentrations; on the other hand, at 15°,

addition of acid continuously reduced the solubility (Friend, J., 1930, 1640). It was of interest, therefore, to ascertain the effect of free acid on the solubility of lanthanum chloride. The following data indicate that both at 25° and at 50° the addition of acid reduces the solubility almost linearly (Fig. 2).

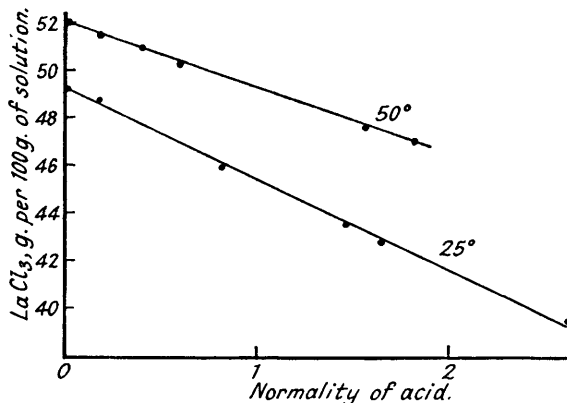
Solubility of lanthanum chloride at 25°.

Normality of acid	0	0.174	0.817	1.471	1.644	2.611
S	49.27	48.79	45.87	43.55	42.78	39.47

Solubility of lanthanum chloride at 50°.

Normality of acid	0	0.171	0.400	0.597	1.568	1.831
S	52.00	51.46	50.88	50.28	47.66	46.95

FIG. 2.



Praseodymium Chloride.—The solid phase was found by analysis to be $\text{PrCl}_3 \cdot 7\text{H}_2\text{O}$. These results are shown in Fig. 1. Matignon's figure is too high. Between 0° and 80° the solubilities of lanthanum and praseodymium chlorides are too similar to offer a useful method of separation by fractionation.

Temp.	0°	0°	11.4°	13.0°	26.2°	35.0°	44.6°
S	47.64	47.87	48.39	50.96 *	49.65	50.15	51.46
Temp.	45.8°	55.4°	59.0°	63.6°	71.5°	80.2°	
S	51.47	53.04	53.60	54.51	56.62	58.62	

* Matignon, *loc. cit.*

Neodymium Chloride.—The solid phase was proved by analysis to be $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ and the occurrence of a hexa- instead of a hepta-hydrate might be expected to cause an appreciable difference in the solubility from the preceding two salts. This was the case only at temperatures above 55°. Some of these results are shown in Fig. 1.

Temp.	0°	0°	10.0°	10.0°	13.0°	15.4°	20.0°	26.2°
S	49.18	49.20	49.33	49.16 †	49.67 *	49.34	49.49 †	49.61
Temp.	30.0°	33.0°	45.8°	54.8°	55.4°	59.0°	64.0°	68.0°
S	49.91 ‡	50.69	51.88	52.51	52.90	53.33	53.88	54.39
Temp.	72.0°	80.0°	87.0°	91.7°	93.5°	97.6°	98.3°	100°
S	54.61	56.04	56.75	57.19 †	57.41	58.29 †	58.15 †	58.4 *

* Matignon, *loc. cit.*

† Synthetic method.

‡ Williams, Fogg, and James, *loc. cit.*

Matignon's result at 13° is slightly high, but his figure at 100° appears to agree with ours. The data given by Williams, Fogg, and James for 40° and 50° are slightly lower than ours. From 30° upwards the solubility rises linearly with the temperature. Attempts to concentrate neodymium by fractional crystallisation were not successful.

When kept in desiccators over excess sulphuric acid for prolonged periods, the several chlorides lost steadily in weight, becoming constant in about a year. The coloured salts became paler and all lost some chlorine, the residues being slightly basic.