346. *The Nitrates of Neodymium and Praseodymium, and their Solubilities in Water.*

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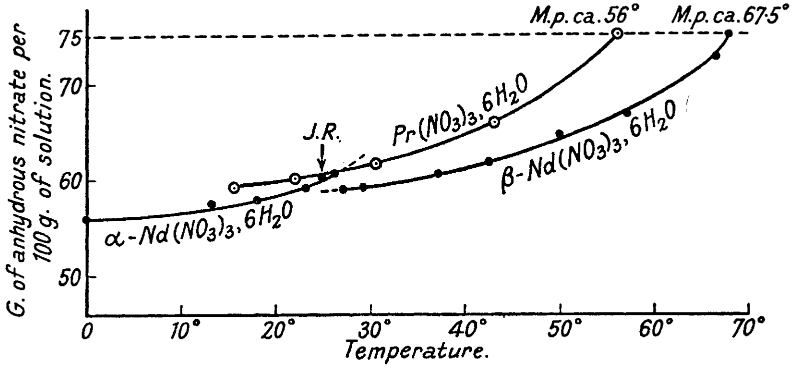
The present research was undertaken in order to ascertain whether or not the differences in the solubilities of the nitrates of the rare-earth elements of the cerium group are sufficiently great to enable the salts to be used for the separation of the elements by fractional crystallisation. The suggestion has been made (Feit and Przibylla, *Z. anorg. Chem.*, 1905, **43**, 205) that lanthanum can be removed from praseodymium in this way, the praseodymium nitrate crystallising in the head fractions, but no data appear to exist as to the solubility of this salt in water.

It has already been shown (Friend, this vol., p. 824) that the lanthanum salt exists in two forms; this appears to be the case for the neodymium salt also, the transition point lying near 22°. Attempts to locate it dilatometrically were not successful. Owing to lack of material, it was not possible to ascertain if praseodymium nitrate can likewise exist in two forms; it was necessary repeatedly to work up the residues and prepare fresh batches of salt. The results for the nitrates of neodymium and praseodymium are shown in the figure. Those for lanthanum (*loc. cit.*) lie intermediately; they are clearly too close to offer a good method of separation in neutral solution.

Neodymium nitrate was prepared by dissolution of the oxide in dilute acid. The filtered solution, after concentration on the water-bath, was seeded on the first occasion with the lanthanum salt. The crystals melted at approx. 67·5°. The apparatus used in determining the solubilities has already been described (Friend, J., 1930, 1633). The solubilities are calculated from the neodymia 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 was diluted to 250 c.c., and the neodymia estimated by precipitation from 50 c.c. with excess oxalic acid and ignition to oxide. As a check, a further 50 c.c. were evaporated to dryness in a platinum dish and ignited to oxide. The latter method gave slightly higher results, as the following data show, possibly on account of the slight solubility of the oxalate but more probably because of traces of soluble impurity which the latter process would fail to remove.



Nd_2O_3 (from oxalate), %	0·4007	0·3582
Nd_2O_3 (direct ignition), %	0·4071	0·3623

The solubilities, *S*, were therefore calculated from the results obtained by precipitation. They are expressed as g. of anhydrous salt per 100 g. of solution, and are shown in the fig. Only a single determination of the solubility of this salt in water appears to have been published, *viz.*, 60·46 g. of $Nd(NO_3)_3$ at 25° (James and Robinson, *J. Amer. Chem. Soc.*, 1913, **35**, 754), a result that agrees with the present data for the α-salt (see fig.).

Solid phase: α-$Nd(NO_3)_3,6H_2O$.

Temp.	0° *	13·2°	18·2° *	23·0° *	25·0° †	26·2° *
S	55·97	57·37	58·03	59·59	60·46	60·69

Solid phase: β-$Nd(NO_3)_3,6H_2O$.

Temp.	27·2°	29·4°	37·2°	42·4°	50·0°	57·2° *	66·2° *	67·5° ‡
S	59·17	59·18	60·95	61·91	64·86	67·00	73·13	75·34

* Analysis of solid phase in saturation bottle showed it to be $Nd(NO_3)_3,6H_2O$.
† James and Robinson, *loc. cit.*
‡ Melting point.

Praseodymium nitrate was prepared by dissolving Hilger's Pr_6O_{11} in diluted acid and seeding the concentrated solution with the *pentahydrate*, $Bi(NO_3)_3,5H_2O$, whereupon a crop of the *hexahydrate*, $Pr(NO_3)_3,6H_2O$, was obtained. If the explanation offered (Friend, this vol., p. 824) for a similar anomalous result with the lanthanum salt is accepted, it would appear that praseodymium nitrate is also isodimorphous with the bismuth salt and thus resembles the nitrates of lanthanum and neodymium (Bodman, *Z. anorg. Chem.*, 1901, **27**, 254). The crystals melted at approximately 56°. The solubilities given below were calculated from the amounts of Pr_6O_{11}

obtained by precipitation of the oxalate and ignition in a platinum crucible. They are expressed as g. of anhydrous salt per 100 g. of solution and are also shown in the figure.

Solid phase: $Pr(NO_3)_3,6H_2O$.

Temp.	15·8°	22·0°	30·4°	43·0°	56° *
S	59·32	60·18	61·94	65·00	75·15

* Melting point.

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