

### 78. Solubilities of the Double Magnesium Nitrates of the Cerium Group.

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THE double nitrates of magnesium and the metals of the cerium group are frequently used in the separation of the latter by fractional crystallisation either from acid (Demarçay's method, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019) or neutral (Drossbach, *Ber.*, 1902, **35**, 3827) solution. Their general "ideal" formula is  $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{M}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ , where M represents elements No. 57 to 62. Appreciable variation in composition occurs, however, if the mother-liquor does not contain the theoretical proportions of the constituent salts. All are hygroscopic and yield supersaturated solutions with ease. As the data concerning their relative solubilities in water are scanty, it seemed desirable to study them more closely.

Jantsch (*Z. anorg. Chem.*, 1912, **76**, 303) has given their solubilities (except for II, No. 61) at 16° in nitric acid of *d* 1.325 and their congruent melting points. This high acid concentration was used because his supply of material was too small to admit of the determination of the solubility in pure water or dilute acid. Prandtl and Ducrue (*ibid.*, 1926, **150**, 105) determined the solubilities of the praseodymium and neodymium double salts in water at 15°, 30°, 50°, and 70°, and Friend (J., 1930, 1903) determined the solubility of the latter in water and in nitric acid solutions over the range 0° to 90°. Apart from these, no systematic data appear to have been published.

In the present research, the solubilities of the lanthanum and cerium salts have been determined for the first time, and further data have been obtained for the praseodymium salt.

The apparatus used has already been described (Friend, J., 1930, 1633).

At first, considerable difficulty was experienced in obtaining reproducible results. This was particularly so at the lower temperatures, and the solubility appeared to vary with the relative proportions of solution and undissolved salt in the saturation bottle. It was thought that this might be due to an initial selective dissolution of the components of the double salt so that true equilibrium between solution and crystals might not be easily attained, although the solutions in the saturation bottle were agitated at constant temperature for some 4—6 hours. An attempt was made to overcome this difficulty by preparing a more or less saturated solution at 90—100° and quickly cooling it to the required temperature in a thermostat; stirring for several hours after this was essential to remove supersaturation, to which these salts are prone. As obtained in this way, the results were more concordant but still not quite as good as one usually obtains with single salts.

*Lanthanum Magnesium Nitrate*,  $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{La}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$ .—The initial supply of lanthana was purchased from Messrs. Hilger; it was very free from other rare earths and contained only the merest trace of  $\text{Pr}_6\text{O}_{11}$ , which imparted a barely perceptible brown tint to it. The double salt was prepared by dissolving the requisite amounts of lanthana and B.P. magnesium oxide in dilute nitric acid, crystallising, and recrystallising from dilute acid.

*Method of analysis.* Determination of the two oxides was regarded as sufficient. Usually the crystals were dissolved in water and diluted to 250 c.c. The lanthana was estimated by precipitation from 50 c.c. with excess oxalic acid from hot solution and ignition to oxide; the precipitate was less granular than that of neodymium or praseodymium, and it was found

advisable to digest it on the water-bath for several hours and keep it over-night before attempting to filter it off. A further 50 c.c. were taken to dryness in a platinum dish, ignited to the mixed oxides, and magnesium oxide calculated by difference. A few analyses are as follow :

	1.	2.	3.	4.	5.	Calc.
La <sub>2</sub> O <sub>3</sub> (%) .....	21.05	18.67	20.20	20.23	21.05	21.33
MgO (%) .....	8.03	7.34	7.77	8.07	7.66	7.92
Ratio La <sub>2</sub> O <sub>3</sub> /MgO .....	2.62	2.54	2.60	2.51	2.75	2.69

Even when well-developed crystals were chosen, their compositions showed considerable variation in the La<sub>2</sub>O<sub>3</sub> : MgO ratio according to the composition of the mother-liquor. It was important, therefore, to check the composition of every batch of crystals; this complicated the work, for, owing to the relatively limited supply of material and the high solubility of the salt, the residues had to be repeatedly worked up.

When only small batches of salt were available, the two oxides were estimated in the same sample by first igniting it to mixed oxides; these were subsequently dissolved in acid and the lanthana determined as before. The results were equally satisfactory, as the following data indicate :

La <sub>2</sub> O <sub>3</sub> (direct), g. ....	0.2007	0.3189	0.3298	0.3791
La <sub>2</sub> O <sub>3</sub> (after ignition), g. ....	0.2008	0.3184	0.3294	0.3801

This shows that if any compound is formed during ignition it is completely decomposed by subsequent treatment. As explained later, this method could not be adopted with the praseodymium and cerium salts.

*Solubility.* The solubilities, S, given below are expressed as g. of hydrated salt per 100 g. of solution; they are also shown in the fig.

Temp. ....	18.6°	31.6°	46.8°	50.8°	61.4°	74.8°	113.5° *
S .....	62.19	63.96	68.57	70.17	73.05	77.43	100
Ratio La <sub>2</sub> O <sub>3</sub> /MgO .....	2.68	2.61	2.68	2.60	2.63	2.59	—

\* Melting point (Jantsch, *loc. cit.*).

*Praseodymium Magnesium Nitrate, 3Mg(NO<sub>3</sub>)<sub>2</sub>.2Pr(NO<sub>3</sub>)<sub>3</sub>.24H<sub>2</sub>O.*—This salt was prepared by dissolving the calculated quantities of Pr<sub>6</sub>O<sub>11</sub> and magnesium oxide in dilute nitric acid and crystallising. The original supply of Pr<sub>6</sub>O<sub>11</sub> was purchased from Messrs. Hilger and was very free from other rare earths. The oxide was dissolved in nitric acid, and the oxalate precipitated and ignited in order to remove traces of halide found to be present. The supply of crystals of double salt was seldom sufficient for more than one solubility determination; it was necessary, therefore, repeatedly to work up the residues and prepare fresh batches. Moreover, it was necessary to analyse each batch, since the crystals showed analogous variations to those of the lanthanum salt (see analyses below).

*Method of analysis.* Determination of the two oxides was regarded as sufficient. The former was estimated by precipitation as oxalate, ignition in a platinum crucible and weighing as Pr<sub>6</sub>O<sub>11</sub> (Brinton and Pagel, *J. Amer. Chem. Soc.*, 1923, 45, 1460), the precautions already detailed (Friend, J., 1932, 2410) being observed. Duplicate experiments showed satisfactory concordance, as the following pairs indicate: Pr<sub>6</sub>O<sub>11</sub>, g. : 0.2548, 0.2538; 0.2668, 0.2676; 0.3220, 0.3226.

When heated with certain oxides, such as lanthana and ferric oxide, the state of oxidation of the praseodymium varies between the limits Pr<sub>2</sub>O<sub>3</sub> and PrO<sub>2</sub> according to circumstances (Prandtl and Huttner, *Z. anorg. Chem.*, 1925, 149, 235); but the presence of magnesium oxide is stated to have no influence, the oxide being Pr<sub>6</sub>O<sub>11</sub>. It was thought, therefore, that the method of determining magnesium oxide by difference, as before, would prove satisfactory; but the observed ratio Pr<sub>6</sub>O<sub>11</sub> : MgO was always lower than expected; this, coupled with the fact that there was usually a difficulty in obtaining a constant weight on ignition, suggested that Pr<sub>6</sub>O<sub>11</sub> is not so inert towards magnesium oxide as Prandtl believed.

To test this, solutions of the two nitrates of known concentration were mixed, evaporated and ignited, with the following results :

Pr <sub>6</sub> O <sub>11</sub> taken, g.	MgO taken, g.	Total taken, g.	Ratio Pr <sub>6</sub> O <sub>11</sub> : MgO.	Obs. wt. of mixed oxides, g.	Increase in wt. of Pr <sub>6</sub> O <sub>11</sub> , %.
0.4030	0.1492	0.5522	2.70 : 1	0.5573	1.29
0.2538	0.1315	0.3853	1.93 : 1	0.3886	1.30
0.2548	0.1687	0.4235	1.51 : 1	0.4268	1.30

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For complete oxidation of  $\text{Pr}_6\text{O}_{11}$  to  $\text{PrO}_2$  the percentage increase in weight is 1.57; under the conditions of the experiments, therefore, more than 80% of the  $\text{Pr}_6\text{O}_{11}$  had been converted into  $\text{PrO}_2$ . In calculating the weight of magnesium oxide by difference from the mixed oxides this correction must be applied. The result is sufficiently accurate for present purposes, as the solubility data are based on the quantity of praseodymium present in solution. Typical analyses of different batches of the double salt are as follow :

	1.	2.	3.	4.	Calc.
$\text{Pr}_6\text{O}_{11}$ (%) .....	21.57	21.24	21.02	21.35	22.24
$\text{MgO}$ (%) (corr.) .....	7.81	7.97	7.37	7.48	7.90
Ratio (corrected) .....	2.76	2.67	2.85	2.86	2.82

*Solubility.* The following solubilities,  $S$ , are expressed as before; they are also shown in the fig. The data in parentheses are those of Prandtl and Ducrue (*loc. cit.*); the agreement is good.

Temp. ....	15.0°	17.8°	30.0°	37.4°	50.0°	61.8°	70.0°	74.6°	111.2° *
$S$ .....	(63.0)	63.1	(66.4)	67.74	(71.0)	74.25	(77.5)	78.39	100

\* Melting point (Jantsch, *loc. cit.*).

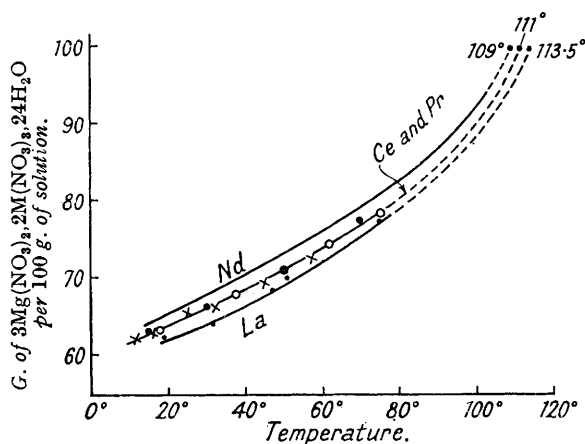
*Cerium Magnesium Nitrate,  $3\text{Mg}(\text{NO}_3)_2 \cdot 2\text{Ce}(\text{NO}_3)_3 \cdot 24\text{H}_2\text{O}$*  (with W. N. WHEAT).—In the preparation of this salt, Kahlbaum's cerous nitrate was used.

*Method of analysis.* Determination of  $\text{CeO}_2$  and magnesium oxide was regarded as sufficient. The former was estimated by precipitation as oxalate and ignition; the latter was determined by difference from the mixed oxides from a second aliquot portion. That this method yields fairly accurate results was proved by separate determinations of the magnesium as phosphate. The following results are typical :

$\text{MgO}$ (by difference) ...	0.0744	0.0823
$\text{MgO}$ (as phosphate) ...	0.0753	0.0814

It is evident that the presence of magnesium oxide does not appreciably alter the state of oxidation of the cerium. It was not practicable to determine the ceric oxide and magnesium oxide from the same sample by difference, owing to the difficulty of dissolving the former after the first ignition to mixed oxides.

The compositions of the crystals of different batches of double salt showed variations similar to those of the



- Pr double salt (Prandtl and Ducrue, *loc. cit.*).
- Pr double salt, present research.
- × Ce double salt, present research.

preceding double salts. The following analyses are illustrative :

	1.	2.	3.	Calc.
$\text{CeO}_2$ (%) .....	21.45	21.39	22.44	22.51
$\text{MgO}$ (%) .....	8.24	8.61	7.90	7.91
Ratio $\text{CeO}_2/\text{MgO}$ .....	2.604	2.485	2.841	2.846

*Solubility.* The following solubilities,  $S$ , are expressed as before and are also shown in the fig.

Temp. ....	11°	16°	24.6°	31.8°	42.2°	57.0°	111.5° *
$S$ .....	61.98	62.89	65.63	66.20	69.26	72.78	100
Ratio $\text{CeO}_2/\text{MgO}$ .....	2.84	2.78	2.87	—	—	2.77	—

\* Melting point (Jantsch, *loc. cit.*).

The solubility curves of the praseodymium and the cerium salt are very similar, and lie between those of the lanthanum and the neodymium salt. In concentrated acid solution, however, Jantsch found the cerium salt to be less soluble than the lanthanum salt. Possibly for this reason, it appears to be customary to remove cerium chemically from rare-earth mixtures prior to fractional crystallisation of the double nitrates. The results of the present research explain the observation of Feit and Przibylla (*Z. anorg. Chem.*, 1905, **43**, 205) that it may be an ad-

vantage to retain the cerium, or even to add more of it, in order to facilitate the separation of praseodymium along with it. A preliminary set of fractionations based on this principle gave encouraging results. To 250 g. of a mixture of praseodymium and neodymium double magnesium nitrates, at which the ratio Pr : Nd was about 15 : 85, approx. 50 g. of the cerium double salt were added. On fractionation the praseodymium salt rapidly collected along with the cerium salt in the head fractions.

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