CCXLVII.—*Solubility of Magnesium Neodymium Nitrate in Water, Nitric Acid, and Magnesium Nitrate Solutions.*

By JOHN ALBERT NEWTON FRIEND.

ALTHOUGH the double nitrates of magnesium and the rare-earth metals, of general formula $3Mg(NO_3)_2,2M(NO_3)_3,24H_2O$, are frequently used in the fractional crystallisation of the cerium group (where M represents elements No. 57 to 62) both from acid (Demarçay's method, *Compt. rend.*, 1896, **122**, 728; 1900, **130**, 1019, 1185) and neutral (Drossbach, *Ber.*, 1902, **35**, 2827) solution, it is remarkable that their solubilities have been so little studied. As regards the magnesium neodymium double salt, Jantsch (*Z. anorg. Chem.*, 1912, **76**, 303) has given the solubility at 16° in nitric acid of *d* 1·325. This high acid concentration was used because the supply of material at his disposal was too small to allow of the determination of the solubility in pure water. Unfortunately, the result is expressed as 0·0635 g.-mol. of salt per litre, and as the density of the solution is not given it is impossible to convert the figure into the more usual expression of g. per 100 g. of solution. The only other published data appear to be those of Prandtl and Ducrue (*Z. anorg. Chem.*, 1926, **150**, 105) which comprise four determinations of the solubility in pure water at 15°, 30°, 50°, and 70° (see Fig. 1). It seemed desirable, therefore, to investigate more fully the solubility of the salt in neutral and acid solutions.

EXPERIMENTAL.

Preparation of Material.—An account has already been given of the separation of pure neodymium as the double magnesium nitrate from acid solutions of a mixture of rare-earth residues (Friend, this vol., p. 1633); a batch of the crystals was recrystallised several times from dilute nitric acid, washed with distilled water, and air-dried on filter paper. The double salt does not crystallise so sharply from pure aqueous solution as from dilute acid, and analyses of the crystals from aqueous solution (Table I, *a* and *b*) showed that they contained a slight excess of magnesium as though the neodymium salt had been leached away. Crystals from dilute nitric acid solution, however, usually gave practically normal values for the ratio $Nd_2O_3 : 3MgO$ (Table I, *c* and *d*).

The apparatus used in preparing saturated solutions was the same as that already described (Friend, *loc. cit.*); when the solution density was required, the apparatus figured by Friend and Smirles (J., 1928, 2244) was attached, save that the glass-wool filter was replaced by one of sintered glass. In general, some 10—15 g. of solution were taken, diluted to 250 c.c., and the neodymium precipitated as oxalate from an aliquot portion. The weight of neodymia ranged from 0·3 to 0·6 g., and the equivalent amount of double salt was obtained on multiplying by the factor 4·5702. It was not considered necessary to estimate the magnesium separately, as Prandtl and Ducrue (*loc. cit.*) found that, within the error of experiment, the ratio of neodymium to magnesium in the solution remained constant at approximately the theoretical value, the mean molecular excess of neodymium in solution in their four solubility determinations being only about 0·3%. This amount, although small, is further evidence of the slight leaching action referred to above.

When the solubilities in nitric acid solution were required, owing to the corrosive action of nitrous fumes upon rubber, the saturation bottle was fitted with a ground-in stopper which carried a vertical tube approximately 12 ins. long, down which the stirring rod passed.

Separation of Neodymium from Magnesium.—It has already been pointed out (Friend, *loc. cit.*) that perhaps the most accurate and convenient method of estimating neodymium consists in precipitation as oxalate and ignition to oxide. In the presence of barium salts, however, it was found necessary to take special precautions against adsorption which was liable to affect the result by several units %. Less trouble was to be anticipated with magnesium in view of the generally greater solubility of its salts, although it has long been known that in neutral or ammoniacal solution it is liable to be occluded when calcium has been previously separated as oxalate (see Richards, McCaffrey, and Bisbee, *Z. anorg. Chem.*, 1901, **28**, 71; Korte, J., 1905, **87**, 1503; Lemarchand, *Compt. rend.*, 1925, **180**, 745). Before proceeding with the solubility determinations, therefore, it was necessary to ascertain if the oxalate precipitation would give correct results for neodymium in the presence of magnesium.

(*a*) Approximately 1·6 g. of double nitrate were dissolved in about 350 c.c. of water, raised to boiling point, and neodymium oxalate precipitated by addition of excess hot oxalic acid solution. Next day the precipitate was filtered off, washed with hot, dilute oxalic acid solution, and ignited to oxide, 0·3495 g. being obtained. This was dissolved in nitric acid, reprecipitated as oxalate, and ignited to oxide, yielding 0·3492 g. Any adsorption of magnesium was thus negligibly small.

(*b*) To solutions of neodymium sulphate were added solutions of magnesium nitrate containing respectively 1 and 2 equivs. of magnesium salt. The mixed solutions were diluted to 400 c.c. and treated as in (*a*) above. The weights of neodymia obtained were 0·1422 g. and 0·1421 g. respectively, 0·1416 g. having been taken originally. The data suggest very slight adsorption, but too small appreciably to affect the results of the present research.

In the solubility determinations, therefore, the neodymium, which was the only constituent estimated, was determined as above.

Analysis of the Double Nitrate.—Determination of the neodymia and magnesia was regarded as sufficient. The simplest method consists in melting the crystals in a platinum crucible, gradually raising the temperature to expel combined water and finally decomposing the nitrate. The crucible is cooled, and the friable solid residue crushed with a glass rod and heated over the blowpipe to ensure complete conversion into oxide. After weighing, the residue is dissolved in dilute nitric acid, the neodymia estimated by the oxalate method, and the magnesia by difference. The results of some of the analyses are given in Table I.

TABLE I.

Analyses of different batches of crystals of the double nitrate, $3Mg(NO_3)_2,2Nd(NO_3)_3,24H_2O$.

	a.	*b*.	*c*.	*d*.	Calc.
Nd_2O_3 (%)	21·31	20·84	21·10	21·49	21·88
3MgO (%)	8·01	8·24	7·71	7·81	7·86
Ratio Nd_2O_3 : 3MgO	2·66	2·53	2·74	2·75	2·79

a, *b*. Moist crystals from neutral solution.
c, *d*. Moist crystals from dilute acid solution.

	e.	*f*.	*g*.	*h*.
$2Nd(NO_3)_3$ (%)	40·78	41·37	41·76	41·41
$3Mg(NO_3)_2$ (%)	28·35	28·47	28·77	28·54
H_2O (by diff.) (%)*	30·87	30·16	29·47	30·05
Ratio Nd_2O_3 : 3MgO	2·697	2·725	2·722	2·720

e, *f*. Dried residues from neutral solution in saturation bottle at 0°.
g. Dried residue from *N*-acid solution in saturation bottle at 0°.
h. Dried crystals prepared at −8° (see p. 1907).

* Theory for $27H_2O$, 30·56%.

The solubilities (*S*) given in Table II are expressed as g. of hydrated salt per 100 g. of solution, and are shown in Figs. 1 and 2.

TABLE II.

Neutral solution.

Temp.	0·4°	0·6°	4·4°	14·2°	17·0°	27·2°	40·6°
S	60·42	60·84	61·92	64·00	63·81	67·28	70·72
Temp.	48·8°	65·4°	75·6°	87·0°	90·6°	109°*	
S	72·50	77·64	81·07	84·35	86·89	100·0	

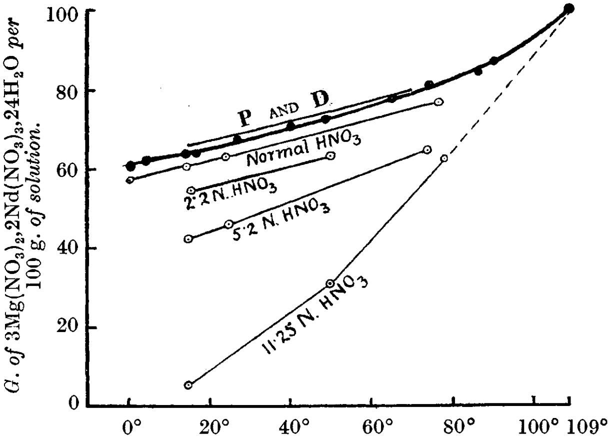
* Congruent melting point (Jantsch, *loc. cit.*).

Nitric acid.	*N.*	*N.*	*N.*	*N.*	2·2*N.*	2·2*N.*
Temp.	0·6°	14·4°	24·2°	77·2°	15·2°	50·2°
S	57·21	60·25	63·06	78·26	54·49	63·14
Density	—	1·499	—	—	—	—

Nitric acid.	5·2*N.*	5·2*N.*	5·2*N.*	11·25*N.*	11·25*N.*	11·25*N.*
Temp.	14·8°	24·8°	74·0°	14·8°	49·0°	78·0°
S	42·01	45·84	64·40	5·64	30·98	62·47
Density	—	—	—	1·357	—	—

Magnesium nitrate.	0·7*N.*	1·77*N.*	Saturated solution.
Temp.	24·8	24·4	24·2
S	59·23	50·31	2·92

FIG. 1.

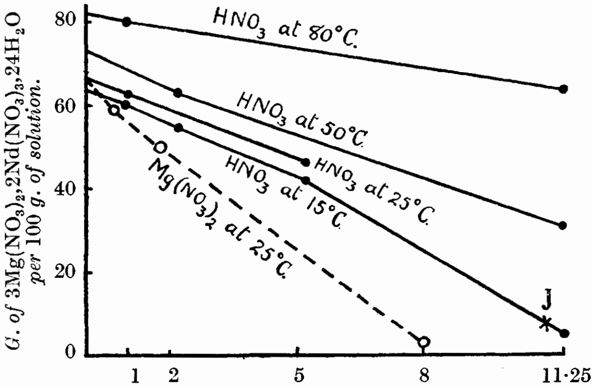


P *and* D = *Prandtl and Ducrue* (loc. cit.).

Consideration of the Results.

Neutral Solution.—The solubility curve (Fig. 1) appears to be continuous from about 5° upwards to the melting point. The results between 15° and 70° are very slightly lower than those of Prandtl and Ducrue, but the difference is relatively small in view of the great solubility of the salt. The results at 0° are slightly lower than one would expect from the general slope of the curve, and analyses of the solid phase in the saturation bottle at 0° (Table I, *e*, *f*, *g*) suggest the existence of a higher hydrate. Attempts were made to prepare it in a pure condition by grinding the tetradodecahydrate in a minimum quantity of dilute nitric acid and stirring vigorously for some 5 hours in a mixture of ice and salt. The solid phase was drained on a sintered-glass funnel, pressed between filter papers, and analysed. The analysis (Table I, *h*) closely resembles analysis *f*. The excess of water above that required for $24H_2O$ appears too great to be due to mere adsorption, but examination of the crystals under the microscope yielded no indication of change of structure. This point is being investigated with allied double salts.

FIG. 2.



Initial normalities of nitric acid and magnesium nitrate.
J = *Jantsch* (loc. cit.).

Nitric Acid Solution.—In these solutions the solubility falls steadily with increase of concentration of acid. No initial increase in solubility on addition of dilute acid was observed similar to that found (Friend, *loc. cit.*) on addition of dilute sulphuric acid to neodymium sulphate. Jantsch (*loc. cit.*) states that 0·0635 g.-mol. of the salt dissolves per litre of solution in nitric acid of *d* 1·325 at 16°. From the "International Critical Tables" (Vol. III, 1928) the normality of the acid is calculated as 10·88. From Table II the density of the solution would be approx. 1·360, from which the solubility of the salt is 7·18 g. per 100 g. of solution at 16°. This result agrees very satisfactorily with the data in Table II (see J, Fig. 2). The rapid rise in solubility with the temperature is mainly due to the large amount of combined water in the crystals, which reduces the normality of the acid in the *solution* until, at the melting point, it has fallen to zero.

Magnesium Nitrate Solution.—Quill, Selwood, and Hopkins (*J. Amer. Chem. Soc.*, 1928, **50**, 2929) have observed that the effect of magnesium nitrate upon the absorption bands of a solution of neodymium nitrate is closely similar to that of free nitric acid; but for equivalent concentrations of the two the band-shift is more pronounced with magnesium nitrate than with free acid.

If the usually accepted explanation is correct, *viz.*, that the shifting of the bands is due largely to increased electrostriction consequent upon a higher concentration of a common ion, one would expect magnesium nitrate to reduce the solubility of the salt to a greater extent than equivalent amounts of nitric acid. Fig. 2 shows that such is the case. The magnesium nitrate was prepared by adding a slight excess of pure magnesia to nitric acid and filtering the solution. The normality of the solution was determined gravimetrically.

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