CCXIII.—*The Solubility of Neodymium Sulphate in Water and in Sulphuric Acid Solutions at Various Temperatures. A New Hydrate.*

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FRACTIONAL crystallisation of salts of the rare-earth metals from pure aqueous or dilute acid solutions constitutes one of the most convenient methods of separating the contiguous metals from each other. Nevertheless, comparatively few trustworthy data are on record concerning the effect of change of temperature upon the solubilities of the salts. It appeared probable that an extended study of this phase of the subject might enable more rapid methods of fractionation to be devised; a series of researches on the solubilities of lanthanum and neodymium salts has accordingly been instituted in this laboratory. The present paper deals exclusively with neodymium sulphate.

The only available data on the solubility of this salt in water appear to be those of Muthmann and Rölig (*Ber.*, 1898, **31**, 1718). The oft-quoted figure for 25° given by Wirth (*Z. anorg. Chem.*, 1912, **76**, 174) is not an original one, but was calculated from the results of the previous authors. The salt used by them was admittedly impure; it was estimated to contain some 3% of praseodymium, in addition to small, undetermined quantities of some metal or metals of the erbium group, as shown by the absorption spectrum. These impurities were not removed, as the quantity of material at the disposal of the authors was too small to admit of useful fractionation. It was evident, therefore, that the data required revision.

EXPERIMENTAL.

Preparation of Material.—Some rare-earth residues from monazite sand, from which the thorium had been almost completely removed, were dissolved in nitric acid, and cerium was removed by the permanganate method. Upon filtration, the oxalates of the rare-earth metals were precipitated from acid solution, washed thoroughly, dried, and ignited to oxides.

The product, which was contaminated with traces of metallic oxides other than the rare earths proper, was dissolved in nitric acid, magnesia added, and the rare-earth metals fractionally crystallised as the double magnesium nitrates. The original crystals were separated into about 12 fractions, and when this series had been systematically fractionated about 10 times the central fraction was treated with permanganate to remove any remaining traces of cerium, again converted into the double magnesium nitrate, and expanded into 12 or 14 fractions. These were fractionated more than 100 times each, the praseodymium head and samarium tail concentrates being periodically removed. Ultimately a fraction was obtained, the absorption spectrum of which showed only neodymium bands. Upon precipitation as oxalate and ignition to oxide, the pale blue colour of neodymia appeared. This oxide was dissolved in nitric acid, reprecipitated as oxalate, and ignited to oxide in order to remove traces of adsorbed magnesium and manganese. The last traces of thorium were removed by the hydrogen peroxide method, the neodymia was recovered, dissolved in dilute sulphuric acid, and the sulphate recrystallised on the water-bath from faintly acidulated solution. The salt thus obtained is believed to possess a high degree of purity.

Method of Analysis.—(1) Probably the most accurate method of estimating neodymium consists in precipitating the oxalate in acid solution and igniting it to oxide. The precipitation is best accomplished by addition of an excess of hot oxalic acid solution to a hot solution of the neodymium salt, rendered slightly acid to prevent hydrolysis to a basic salt. The whole is allowed to stand over-night, filtered cold, and washed with hot dilute oxalic acid solution. Obtained in this way the precipitate is granular, easily filtered, and rapidly washed free from adsorbed ions.

If the solution is filtered immediately after precipitation, the results may prove a little low; *e.g.*, a solution containing 0·9857 g. of neodymium sulphate crystals was precipitated with excess oxalic acid solution and filtered whilst still hot within $\frac{1}{2}$ hour, yielding 0·4862 g. of Nd_2O_3, whereas a similar solution, which was allowed to stand for 24 hours, and filtered cold, as above, yielded 0·4879 g. of Nd_2O_3. The filtrate from the former experiment was kept and, upon shaking after 24 hours, showed traces of oxalate which had either been in solution or in sol form and so had passed through the filter paper.

In view of the tendency of the oxalate to scatter suddenly when first heated, the filter paper was, after drying, folded to enclose the precipitate and pushed into the platinum crucible. The latter was slowly heated over the Bunsen burner with the lid on; the flame was applied first at the lid, and ultimately the crucible was heated in the blow-pipe with the lid raised at intervals to effect the complete decomposition of any carbonate. The charred filter paper effectively prevented loss by scattering before its conversion to ash (compare Brauner and Pavlíček, J., 1902, **81**, 1265). In addition to its accuracy, this process has the advantage of purifying the neodymia at each precipitation from any accidental contamination.

(2) Good results were also obtained by collecting the precipitated

oxalate on an asbestos filter and titrating with permanganate; but this method was not proceeded with, since contamination of the neodymium residues by manganese salts made the recovery of pure neodymia less easy.

It was thought that possibly the neodymium sulphate might be estimated more rapidly and directly by (3) evaporation of the saturated solution on the water-bath to the octahydrate, or by (4) conversion to the anhydrous salt at a higher temperature. The third method was found unsatisfactory as the salt continuously lost slightly in weight on continued heating owing to gradual decomposition of the octahydrate. The fourth method was adopted by Muthmann and Rölig, who heated their salt on a sulphur bath, but the salt tends to decompose before losing the whole of its moisture (compare Bailey, J., 1887, **51**, 676) and the results may be too high or too low according to circumstances.

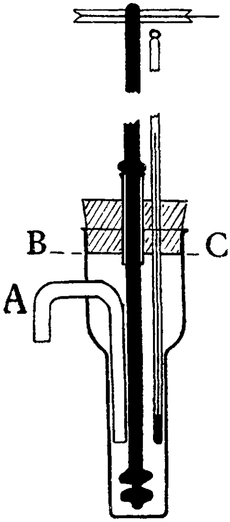
In the present research, therefore, the neodymium was estimated exclusively by the first process.

When the percentage of sulphur trioxide was required in addition to that of neodymia, as in the analysis of crystals (see Table II), it was found expedient to use two separate portions of material. The neodymia was determined as above in one portion and the sulphur trioxide by precipitation with barium chloride in only very slight excess and in almost neutral solution in the other. In every case the solutions were almost boiling when mixed, and were allowed to stand over-night before being filtered. Good results were not obtained when barium sulphate was precipitated from solution after removal of the neodymium as oxalate; and it was found difficult to avoid adsorption of barium when neodymium was precipitated as oxalate after removal of the sulphate ion with barium chloride, although Smith and James (*J. Amer. Chem. Soc.*, 1913, **35**, 563) claim to have obtained good separations from mixed solutions of the chlorides in that way. Redissolution of the neodymia, separation of the adsorbed barium as sulphate, and reprecipitation as oxalate reduced the percentage error, but invariably gave too low a result, possibly due to adsorption in the barium sulphate.

By the method of separate precipitation mentioned above, the neodymium was certainly estimated with fair accuracy; the barium sulphate was white and appeared to be free from adsorbed neodymium. The agreement between successive analyses from the same batch of material (analyses *d* and *e*, Table II) appears to confirm the general trustworthiness of the method, for approximately 0·4 g. of crystals was used in each precipitation in *d* and 0·25 g. in *e*, thus giving an opportunity for adsorption effects to manifest themselves.

Determination of Solubility.—The method already described for other salts (Friend and Smirles, J., 1928, 2242) was adopted, a sintered-glass filter being used. The thermometers, which were graduated to 0·2°, had been compared with the standard instrument at the National Physical Laboratory. Owing to the limited supply of neodymium sulphate, the saturation bottle was smaller than usual, and of the shape shown in Fig. 1. The delivery tube A was sealed through the side of the bottle, so that it was only necessary to immerse the apparatus in the thermostat to the level BC. This greatly prolonged the life of the rubber bung at the higher temperatures. Owing to the formation of a cloud of insoluble basic salt, particular care was necessary during filtration to avoid obtaining an opalescent solution from the saturation bottle.

FIG. 1.



At first considerable difficulty was experienced in obtaining reproducible results, and this was ultimately traced to three causes, *viz.*, (1) the unusually slow rate of solution of the salt, particularly below about 50°, (2) the presence of free acid, and (3) that of basic salt. To avoid the first error, the solution in contact with excess of salt was kept over-night in the saturation bottle after several hours of vigorous stirring, and during the following day it was vigorously stirred for 6—8 hours at the desired temperature prior to removal of a portion for analysis. The excess of free acid was removed by crushing the crystals to small grains with a glass rod in the saturation bottle and repeatedly rinsing with warm water. The washings were always slightly acid owing to hydrolysis. The presence of basic salt invariably caused the solubility results to be too low, and it was necessary to use a fresh batch of material for each solubility determination.

As the supply of material was limited, the solid phase left in the saturation bottle after each experiment was washed out, dissolved in water containing sufficient acid to yield a clear solution, and the pure normal salt crystallised out on the water-bath, to be used again.

The results are given in Table I, *S* representing the solubility as g. of anhydrous neodymium sulphate per 100 g. of solution.

TABLE I.

Neutral solution.

Solid phase.	$Nd_2(SO_4)_3,15H_2O$.	α-$Nd_2(SO_4)_3,8H_2O$.			
Temp.	0·4°	13·8°	14·4°	14·8°	19·8°
S	11·38	7·88	7·64	7·50	6·58

Solid phase.	α-$Nd_2(SO_4)_3,8H_2O$.						
Temp.	30·4°	39·8°	46·4°	49·8°	61·6°	71·2°	74·2°
S	5·00	4·03	3·42	3·33	2·71	2·36	2·37

Solid phase.	α-$Nd_2(SO_4)_3,8H_2O$.		β-$Nd_2(SO_4)_3,8H_2O$.		
Temp.	77·6°	79·6°	87·2°	95·0°	97·2°
S	2·18	2·12	1·28	1·13	1·23

Sulphuric acid solution.

H_2SO_4	*N*/3	*N*/3	*N*/3	*N*/3	*N*/3	*N*	*N*
Temp.	0°*	30·4°	46·4°	81·0°	89·6°	0·2°	15·4°
S	10·04	5·71	4·79	3·54	2·15	9·89	7·00
H_2SO_4	*N*	*N*	*N*	*N*	*N*	4*N*	4*N*
Temp.	30·4°	46·4°	79·2°	90·0°*	96·8°	0·2°	14·8°
S	6·10	5·35	4·41	3·41	2·69	4·56	3·92
H_2SO_4	4*N*	4*N*	4*N*	4*N*	8*N*	8*N*	8*N*
Temp.	30·4°	46·4°	59·0°	81·0°*	11·0°	30·4°	46·4°
S	3·61	3·78	3·62	3·64	1·62	2·04	2·19

* For analysis of solid phase, see Table II.

TABLE II.

Analyses of neodymium sulphate.

	(*a*).	(*b*).	(*c*).	(*d*).	(*e*).	(*f*).
Nd_2O_3, %	46·64	47·07	43·88	40·62	40·68	40·69
$3SO_3$, %	33·17	32·80	31·49	27·58	27·72	27·46
H_2O (by diff.), %	20·19	20·13	24·63	31·80*	31·60*	31·85*
Ratio $Nd_2O_3/3SO_3$......	1·406	1·425	1·393	1·473	1·467	1·482

	(*g*).	(*h*).	(*k*).	$Nd_2(SO_4)_3,8H_2O$ requires
Nd_2O_3, %	47·30	46·68	46·20	46·68
$3SO_3$, %	32·54	32·93	33·78	33·32
H_2O (by diff.), %	20·16	20·39	20·02	20·00
Ratio $Nd_2O_3/3SO_3$......	1·454	1·417	1·368	1·401

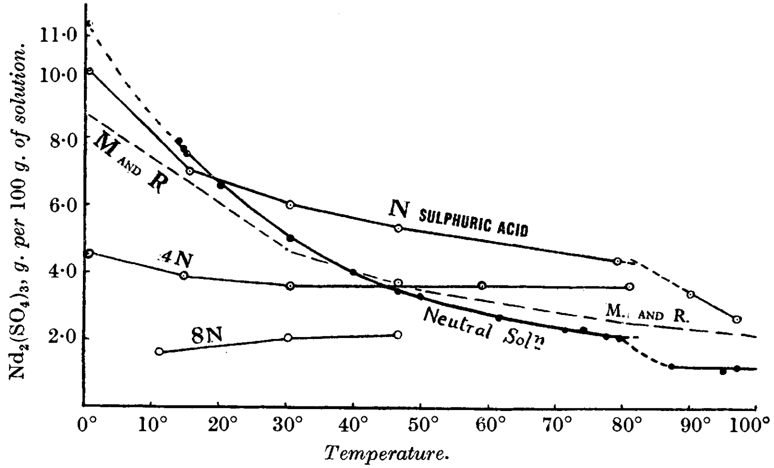
* $Nd_2(SO_4)_3,14H_2O$ requires H_2O, 30·43; $Nd_2(SO_4)_3,15H_2O$ requires H_2O, 31·97%.

(*a*) Crystals grown at room temperature from faintly acid solution.
(*b*) Precipitated from saturated aqueous solution at 18° on addition of absolute alcohol.
(*c*) Solid phase in saturation bottle in *N*/3-H_2SO_4 at 0°.
(*d*) and (*e*) Crystals stirred vigorously for 12 hours at 0° in approximately 0·02*N*-H_2SO_4.
(*f*) Crystals stirred vigorously for 16 hours at 0° in approximately 0·02*N*-H_2SO_4.
(*g*) Solid phase in saturation bottle in neutral solution at 97·2°.
(*h*) ,, ,, ,, ,, in *N*-H_2SO_4 at 90°.
(*k*) ,, ,, ,, ,, in 4*N*-H_2SO_4 at 81°.

Consideration of Results.

Results in Neutral Solution.—The solubility curve (Fig. 2) appears to fall steadily from 0° to about 80° and crosses that of Muthmann and Rölig near 40°. The break above 80° is of special interest; it was not observed by Muthmann and Rölig. The possibility that it was due to basic salt formation might be regarded as receiving support from analysis *g* (Table II), in which the $Nd_2O_3 : SO_3$ ratio is a trifle high; but it appears to be negatived by the appearance of similar breaks in *N*/3- and *N*-acid solutions, which cannot be attributed to the formation of an acid salt since even the *N*-acid is scarcely sufficiently concentrated to inhibit completely hydrolysis in the solid phase at that temperature (analysis *h*).

FIG. 2.



M. and R. = Muthmann and Rölig's results (loc. cit.).

Muthmann and Rölig found a break in the solubility curve of praseodymium sulphate octahydrate between 75° and 85° due to the appearance of the pentahydrate. It seemed probable, therefore, that the breaks in Fig. 2 might be due to a similar cause, especially as Matignon (*Ann. Chim. Phys.*, 1907, **10**, 104) postulated the existence of neodymium sulphate pentahydrate, although he did not indicate how it might be obtained, and no other investigator has succeeded in isolating it. Analyses *g* and *h* lend no support to this view, but they do not definitely disprove it, since the author's experience fully confirms that of earlier investigators that the rates of change of hydration of certain salts of rare-earth metals, like those of thorium and zirconium, are excessively slow (see Koppel, *Z. anorg. Chem.*, 1904, **41**, 405; Hauser, *ibid.*, 1907, **54**, 199; 1908, **58**, 218;

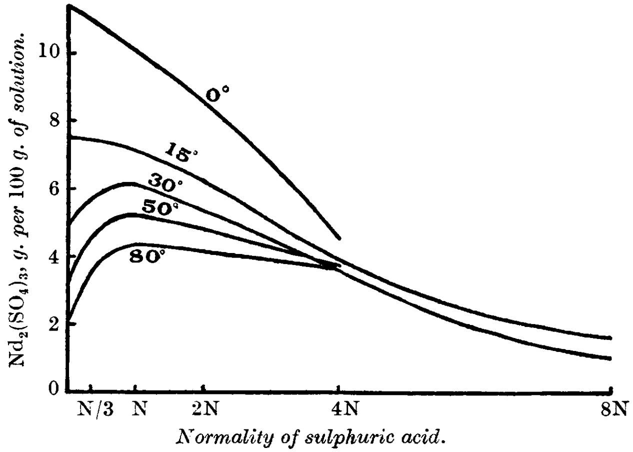
also Roozeboom, *Z. physikal. Chem.*, 1890, **5**, 158). Many attempts were therefore made to prepare a pentahydrate by heating solutions of such concentration that no deposition of crystals occurred below 90°, and then maintaining the solutions and crystals at the boiling point for several hours under vigorous stirring. The crystals were then drained in a sintered-glass funnel, pressed between filter papers, and analysed. Two batches contained H_2O, 21·13 and 20·99% respectively, and were thus the octahydrate. No evidence was obtained of the existence of a lower hydrate.

There remains, therefore, the probability that the break in the curve is due to some polymorphic change. This receives support from the fact that crystals deposited from the boiling solution, when examined under the microscope, were seen to consist of needle-like prisms, apparently still monoclinic, but differing from those deposited at room temperature in the great length of their vertical axis relatively to their horizontal axes.

A new hydrate, $Nd_2(SO_4)_3,15H_2O$. The composition of the solid phase in the saturation bottle in *N*/3-sulphuric acid at 0° (analysis *c*) indicated that a higher hydrate than the octahydrate might exist at low temperatures. Attempts were made to prepare it by finely grinding octahydrate crystals in a saturated solution in very dilute acid and then stirring vigorously for 12 hours at —3° to 0°. The solid phase was drained on a sintered-glass filter, dried between filter paper, and analysed. Analyses *d* and *e* from the same batch of crystals correspond closely to that required for the pentadecahydrate. The crystals readily lost water at the ordinary temperature, and possibly slight loss occurred during drying. Owing to the slow rate at which changes in hydration are effected (see p. 1638) it was thought advisable to keep the crystals in contact with solution at 0° for a longer time, in order to ascertain whether or not hydration was complete. The experiment was therefore repeated, the finely divided crystals being stirred with solution for 12 hours at 0°, kept over-night in an ice-chest, and again stirred for 6 hours in an ice-chest. The composition of the solid phase (analysis *f*) agrees very closely with analyses *d* and *e*, and hydration may therefore be presumed to be complete at that temperature. This new *hydrate* is analogous to $La_2(SO_4)_3,16H_2O$, described by Brauner and Pavlíček (*loc. cit.*), and to the supposed $Pr_2(SO_4)_3,15\frac{1}{2}H_2O$ (von Scheele, *Z. anorg. Chem.*, 1898, **17**, 310; 1898, **18**, 352). A break in the solubility curve between 0° and 14° is to be expected, corresponding to the appearance of this new phase. This range of temperature, however, is a very difficult one to investigate with ordinary apparatus during the summer months and the data obtained are insufficient. It is hoped to investigate this region during the winter.

Results in Acid Solution.—At 0° both *N*/3- and *N*-sulphuric acid have relatively little influence upon the solubility; above 20° they progressively increase the relative solubilities until, at 80°, the solubility in *N*-acid is twice as great as in pure water (see Fig. 3). The more concentrated acids greatly reduce the solubility of the salt in the cold; the temperature coefficient in 4*N*-acid between 20° and 80° (see Fig. 2) is practically nil. The isothermal curves in Fig. 3 show the effect of the addition of acid on the solubility of the salt at five different temperatures. The shape of the curve at 30° closely resembles that given by Wirth (*Z. anorg. Chem.*, 1912, **76**, 174) for lanthanum sulphate at 25°—the only temperature he investigated. The initial rise in solubility on addition of the acid was explained by him as due to step-wise dissociation. But at least two other explanations appeared possible, *viz.*, complex ion formation, and hydrolysis with formation of basic salt.

FIG. 3.



Since scandium sulphate tends to yield complex ions in solution, the possibility that neodymium sulphate might behave similarly in the presence of acid deserved consideration. The freezing points of dilute solutions of neodymium sulphate in water and in *N*/3-sulphuric acid were therefore determined, with the following results :

$Nd_2(SO_4)_3,8H_2O$, %	0·0	0·25	1·0	2·0
δT (in water)	0·0°	0·024°	0·070°	0·130°
δT (in $N/3$-H_2SO_4)	0·0°	0·015°	0·060°	0·100°

In both cases the depression of the freezing point, δT, increases with the concentration; but for corresponding concentrations the depression is less in acid than in pure aqueous solution, which is to be expected since the excess of SO_4'' ions tends to increase electrostriction. There is thus no indication of appreciable complex-ion formation such as occurs under analogous conditions with mercuric chloride and hydrochloric acid solutions (Le Blanc and Noyes, *Z. physikal. Chem.*, 1890, **6**, 395). Nevertheless, it is still possible that in saturated solution some complex-ion formation may take place.

The suggestion may now be considered that the initial rise in solubility is due to prevention by the acid of hydrolysis and hence of basic salt formation. Hydrolysis takes place to a slight extent in hot saturated solutions, and unless special care is taken during filtration of these from the saturation bottle, the filtrate is liable to be opalescent. A few drops of acid, however, rapidly render the solution clear. Analysis *g* (Table II) shows that the solid phase left in the saturation bottle after agitation with pure water at 97° contained some basic salt. At ordinary temperatures, hydrolysis is but slight in concentrated solution, as with lanthanum salts of strong acids (Ley, *Z. physikal. Chem.*, 1899, **30**, 236). Crystals prepared by slow evaporation in air from a faintly acid solution possess a normal composition (analysis *a*).

From Fig. 3, it is evident that at 0° and 15° addition of *N*-acid has somewhat *reduced* the solubility of the salt; at 30° it has increased it appreciably, and at 80° the solubility is more than doubled. At every temperature, once the maximum solubility has been attained, further addition of acid reduces the solubility, but at 90° even the *N*-acid is barely able to retard hydrolysis (analysis *h*). It is not until 4*N*-acid is used at 81° that a possible indication is given of the formation of an acid salt (analysis *k*) by reduction of the $Nd_2O_3 : 3SO_3$ ratio, and even here it might be due to traces of adsorbed acid on the crystal grains. Matignon (*Compt. rend.*, 1902, **134**, 657) used *boiling* solutions of diluted sulphuric acid to prepare the pure acid salt.

The facts support the suggestion that the initial rise in solubility on addition of acid is due, in part at least, to repression of hydrolysis. Further evidence lies in the observation referred to above, *viz.*, that if solubility determinations were made with the solid phase that had previously been used in the saturation bottle in neutral solution without thorough washing, the results were invariably too low. On the other hand, it is curious that the three analyses *d*, *e*, and *f* (Table II) of crystals which had been stirred vigorously at 0° are the most basic of all the analyses in Table II, although one would expect hydrolysis to be less than at higher temperatures. As the crystals were those of the pentadecahydrate, it is possible that they were more easily hydrolysed than the octahydrate. If so, addition of dilute acid would be expected to *increase* the solubility at 0°, which, however, is not the case (Fig. 3). That might be accounted for, on the other hand, by the tendency of the acid to convert the pentadecahydrate into the octahydrate.

From the foregoing it is evident that several explanations are possible for the effect of dilute acid on the solubility of the salt and it may be that more than one of them are partially true.

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