CCXLIII.—*The Selenates of Neodymium and their Solubilities in Water and in Selenic Acid Solutions.*

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A DESCRIPTION has already been given (Friend and Round, J., 1928, 1820) of neodymium selenate and its penta- and octa-hydrates.* Evidence was obtained of the existence of a dodeca-hydrate. The quantity of material at the disposal of the authors was very small, and as larger quantities of neodymia have now been obtained it seemed desirable to check and extend the earlier work, and to determine the solubilities of the salts in water and selenic acid solutions.

The neodymium selenate was prepared by dissolving ignited neodymia in diluted selenic acid and crystallising it on the water-bath. The mother-liquor was poured off and the crystals washed in boiling water, in which they are only slightly soluble.

The neodymia was prepared in a similar manner to that already described (Friend, J., 1930, 1633). It contained traces of praseodymium as indicated by a slight brown tint, but the quantity is believed to have been very much too small to affect the results obtained. The selenic acid was purchased as pure, and was found to be free from sulphuric acid and from halogen derivatives.

Several difficulties have been encountered, not the least of which is the tendency of neodymium selenate to undergo hydrolysis in solution. Even in the cold after several hours of vigorous agitation in the saturation bottle during solubility determinations in neutral solution, the solid residue was invariably slightly basic.

Hot aqueous solutions of neodymium selenate tend to become turbid. This appears to be due in part to formation of a basic salt, the solution becoming slightly acid; but some acid solutions on warming gave an appreciable deposit of insoluble neodymium selenite, as though some catalyst were present accelerating the reduction. One batch of material had to be discarded for this reason, although it appeared to be quite pure. That the deposit consisted essentially of selenite was demonstrated in one case by dissolving it in a little very dilute nitric acid. On passage of sulphur dioxide there was an immediate precipitate of selenium, whereas neodymium selenate gives no precipitate under such conditions. Analysis showed the ratio Nd_2O_3 : Se was 1·3068 [$Nd_2(SeO_3)_3$ requires

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* Meyer and Kittelmann (*Z. anorg. Chem.*, 1931, **195**, 121) have since prepared these two hydrates, apparently in ignorance of the above-mentioned research.

1·4164]. The solid was thus distinctly acid, which suggests the absence of any appreciable amount of basic salt.

The rate of transformation of one hydrate into another is often very slow, and some of the hydrates are very persistent in their metastable regions. Some of the hydrates appear to have very restricted regions of stability, and in some cases it has been found difficult to ensure that the same hydrate will appear in two successive crystallisations under what appear to be identical conditions. This was particularly the case with the acid salts.

Method of Analysis.—One of the most convenient and accurate methods of estimating neodymium consists in precipitation with slight excess of oxalic acid and ignition to oxide, with observance of the precautions already given (Friend, *loc. cit.*). The selenium was usually determined in separate samples by boiling them with concentrated hydrochloric acid to reduce them to selenite, precipitating the element with sulphur dioxide, and collecting it on a sintered glass filter. The selenium was washed with alcohol and dried at 110°.

When the supply of a batch of crystals was small, both neodymia and selenium were estimated in the same sample. It was ascertained that this could be effected with sufficient accuracy in either of two ways. (1) After removal of neodymium as oxalate, the filtrate was taken almost to dryness on the water-bath, washed into a beaker with the minimum quantity of water, and boiled with an equal volume of concentrated hydrochloric acid. Selenium was precipitated with sulphur dioxide; the oxalic acid did not interfere with the reduction, but careful washing of the selenium was essential to remove adsorbed material. Even then the results were invariably very slightly higher than with direct precipitation from the pure selenate solution, as shown by the following results :

	a.	*b*.	*c*.
Direct pptn. from selenate (g. Se)	0·1066	0·1930	0·1616
Pptn. after removal of Nd as oxalate (g. Se)	0·1085	0·1960	0·1649

(2) After precipitation of selenium from the original selenate solution, the filtrate was taken almost to dryness on the water-bath to expel sulphur dioxide. It was then diluted, and neodymium precipitated as oxalate in the usual way. The following results are typical :

	a.	*b*.	*c*.	*d*.
Direct pptn. from selenate (g. Nd_2O_3)	0·1460	0·2483	0·1706	0·2689
Pptn. after removal of Se (g. Nd_2O_3)	0·1479	0·2503	0·1700	0·2690

Either procedure could therefore be used with confidence. The second was usually more convenient. These methods, however, destroy the selenate, and in the case of the solubility determinations it seemed desirable, in view of the high cost of selenic acid, to ascertain whether or not the amount of salt in solution could be estimated with sufficient accuracy either by evaporation on the water-bath to the pentahydrate or by conversion at 180—230° to the anhydrous salt. In neutral solution very satisfactory results could be obtained by the former method when a platinum dish was used, and no free selenic acid was present; but attempts to obtain the anhydrous salt were not satisfactory owing to decomposition of the selenate before complete expulsion of the water.

In the following table are given several series of comparative results obtained by the three methods. As the errors involved in the second method were small, this was occasionally used, in order to conserve material, to gain a general idea of the shapes of the solubility curves. All the data given in Tables II and III, however, were obtained gravimetrically.

TABLE I.

Analyses of Solutions of Neodymium Selenate.

	Result, as g. of $Nd_2(SeO_4)_3$, for three solutions.		
	a.	*b.*	*c.*
1. Gravimetric estimation as oxalate	1·0880	0·5068	0·5933
2. Solution evaporated on water-bath to pentahydrate	1·0945	0·5097	0·5887
3. Pentahydrate heated to 180—230° and weighed as anhydrous salt	1·0968	0·5141	0·5968

Many other analyses were carried out in a similar manner and showed corresponding differences.

When heated to redness, neodymium selenate is gradually converted to neodymia. It was found somewhat difficult to expel the last traces of selenium, but the expulsion was facilitated by alternately heating it to redness and cooling it in air many times until the weight was constant. The process is tedious, but fairly accurate. Thus, in one case, neodymia from oxalate precipitation was 0·1457 g., and by direct ignition 0·1452 g.

Neodymium Sulphate Pentahydrate, $Nd_2(SeO_4)_3,5H_2O$.—The method of preparing the pentahydrate has already been given (Friend and Round, *loc. cit.*), but a slight amplification is necessary. It was stated that, on concentration on the water-bath, a good crop of pink crystals separated from the hot mother-liquor and were dried between filter-paper and stored over sulphuric acid, after which analysis showed them to be the pentahydrate, although in every case the amount of water found was slightly higher than theory demands.

It has now been ascertained, however, that the crystals, so long as they remain in contact with the hot solution, are those of the hexahydrate, but on being dried whilst still warm are more or less converted to the pentahydrate. By evaporating a neutral solution to dryness on the water-bath, a quantitative yield of pentahydrate is obtained. Complete analyses of the salt have not hitherto been published. The following data refer to four different batches prepared by crystallisation on the water-bath, pouring off the mother-liquor, and heating the crystals on the water-bath to constant weight.

	a.	*b.*	*c.*	*d.*	Calc.
Nd_2O_3, %	41·73	41·78	41·32	41·78	41·64
$3SeO_3$, %	46·83	47·14	46·63	47·00	47·22
$5H_2O$ (by diff.), %	11·44	11·08	12·05	11·22	11·14
Ratio Nd_2O_3 : 3Se	1·431	1·423	1·423	1·428	1·416

Hexahydrate, $Nd_2(SeO_4)_3,6H_2O$.—On heating a concentrated solution of the neutral or slightly acid salt above 60°, pink crystals of the hexahydrate separate on the walls of the containing vessel. The whole is rapidly cooled, the mother-liquor poured off, and the crystals thoroughly dried between filter-papers. The following data refer to four different batches prepared in this manner :

	a.	*b.*	*c.*	*d.*	Calc.
Nd_2O_3, %	40·84	40·94	40·38	40·62	40·73
$3SeO_3$, %	45·22	46·05	46·21	45·41	46·19
$6H_2O$ (by diff.), %	13·94	13·01	13·41	13·97	13·08
Ratio Nd_2O_3 : 3Se	1·450	1·428	1·403	1·436	1·416

All the salts except *c* proved to be slightly basic, having undergone hydrolysis during their preparation.

Octahydrate, $Nd_2(SeO_4)_3,8H_2O$.—This salt may be obtained in several ways, *viz.*, (i) by prolonged exposure of the saturated solution or of a higher hydrate over concentrated sulphuric acid (analyses *a* and *b*, below); (ii) by crystallisation from fairly concentrated acid solution (analyses *c*, *d*, and *e*). The salt crystallises as well-defined, rose crystals. The following are typical analyses :

	a.	*b.*	*c.*	*d.*	*e.*	Calc. for $Nd_2(SeO_4)_3,8H_2O$.
Nd_2O_3, %	39·22	38·97	38·64	38·51	39·65	39·03
$3SeO_3$, %	44·12	43·96	45·66	44·36	44·42	44·26
Water (by diff.), %	16·66	17·07	15·70	17·13	15·93	16·71
Ratio Nd_2O_3 : Se	1·428	1·424	1·359	1·394	1·434	1·416

Specimen *c* was crystallised from solution containing 48·2% selenic acid, and probably contained a little acid salt. Salt *e* was obtained as follows : Some neodymia was dissolved in excess of diluted selenic acid and allowed to crystallise in air. Very fine needles were obtained which it was intended ultimately to analyse, as they were believed to be a new acid salt. The mother-liquor was poured off and the crystals set on one side; but in the course of four months the crystals began to disintegrate, yielding an acid liquid and compact rose-coloured crystals.

On addition of alcohol to a concentrated solution of neodymium selenate a viscous liquid is obtained, which on agitation rapidly crystallises. Upon exposure to air the salt rapidly loses in weight and the odour of alcohol gradually vanishes. Analysis, however, invariably agreed more closely with that calculated for an enneahydrate than for the octahydrate. Thus :

	a.	*b.*	Calc. for $Nd_2(SeO_4)_3,9H_2O$.
Nd_2O_3, %	38·57	37·55	38·23
$3SeO_3$, %	43·16	43·52	43·35
Water (by diff.), %	18·27	18·03	18·42
Ratio Nd_2O_3 : 3Se	1·435	1·386	1·416

Whilst the formation of a metastable hydrate of this composition is easily possible, the excess water may be simply due to adsorption. By no other method were crystals of this composition ever obtained.

The *dodecahydrate*, $Nd_2(SeO_4)_3,12H_2O$, is obtained when a solution is allowed to evaporate in the open air at the ordinary temperature until practically constant weight is attained. It is a pale pink powder. Analyses of different batches are as follow :

	a.	*b.*	*c.*	Calc.
Nd_2O_3, %	36·34	35·79	36·14	36·02
$3SeO_3$, %	40·77	40·38	40·66	40·84
$12H_2O$ (by diff.), %	22·89	23·83	23·20	23·14
Ratio Nd_2O_3 : 3Se	1·431	1·423	1·428	1·416

Higher Hydrates.—The higher hydrates do not crystallise easily. The putty-like residues from the saturation bottle, after determination of the solubilities at various temperatures below 60°, were dried between filter-papers and analysed. In general, the analyses agreed with either $Nd_2(SeO_4)_3,18H_2O$ or $22H_2O$. A few typical analyses are as follow :

Temp.	0°	Calc. for $18H_2O$.	8·6°	9·0°	45·6°	Calc. for $22H_2O$.
Nd_2O_3, %	32·77	32·29	30·44	30·52	29·06	30·20
SeO_3, %	37·01	36·61	34·27	34·13	33·58	34·25
H_2O (by diff.), %	30·22	31·10	35·29	35·35	37·36	35·55
Ratio Nd_2O_3 : Se	1·422	1·416	1·426	1·436	1·390	1·416

The salt at 45·6° agrees more closely with $24H_2O$ (Calc. : H_2O, 37·58%), but it was slightly acid and possibly imperfectly dried as selenic acid is hygroscopic. On the other hand several small irregularities have been repeatedly encountered in the solubility determinations below 50° to which reference is made below, and it is possible that two or more hydrates may be co-existent in the solid phase over prolonged periods. The supposed 22-hydrate might conceivably, for example, be a mixture of the 24- and the 18-hydrate. Owing to their putty-like condition, the hydrates do not appear to exhibit any distinctive characteristics.

Anhydrous Neodymium Selenate, $Nd_2(SeO_4)_3$.—It does not appear possible to prepare this salt in a perfectly pure condition by mere heating, as slight decomposition occurs before the whole of the water has been expelled. In this respect it resembles the sulphate. The best result was obtained by maintaining it at 170—190° for 14 hours in an electric oven, whereupon the weight became practically constant. The product still contained 1·36% of water, but dissolved almost completely in water, leaving only a trace of insoluble, brown residue.

Acid Selenates.—Neodymium readily yields acid selenates, $NdH(SeO_4)_2$,aq., in various states of hydration. Upon two occasions different batches of neodymium selenate in acid solution deposited on prolonged standing in air during summer months, rose-red crystals of $2NdH(SeO_4)_2,15H_2O$. They were larger crystals than usual, apparently monoclinic, with the *c* axis measuring 0·5—1 cm. The analyses (below) agreed satisfactorily with the above formula, but all attempts to prepare further crops of such crystals have failed.

	(i).	(ii).	Calc.
Nd_2O_3, %	30·00	29·22	29·69
$4SeO_3$, %	44·91	45·34	44·88
$16H_2O$ (by diff.), %	25·09	25·44	25·43
Ratio $Nd_2O_3 : 4Se$	1·073	1·035	1·062

On another occasion, when it was hoped to prepare the above crystals by concentrating a solution of selenate in diluted selenic acid by prolonged exposure over concentrated sulphuric acid, rose-red crystals separated in the course of a month or two, the composition of which approximated to $2NdH(SeO_4)_2,7H_2O$.

Determination of Solubility.—The apparatus used was similar to that described in connexion with neodymium sulphate (Friend, J., 1930, 1633), a sintered glass filter of the finest grade (No. 4) being employed. In almost every case the amount of selenium in solution was determined as well as of neodymium.

Owing to hydrolysis the saturated solutions were usually slightly acid when crystals of pure neutral salt had been initially taken. The results are given in Table II, in which S represents the solubility as g. of anhydrous neodymium selenate per 100 g. of solution. The theoretical value for the ratio $Nd_2O_3 : 3Se$ is 1·416.

The parentheses indicate that the solubility in neutral solution has been calculated from the curve and not determined directly.

It will be noted that, when the ratio $Nd_2O_3 : Se$ does not quite reach 1·416, the observed solubility is slightly higher than in per-

TABLE II.

(Crystals initially neutral or very slightly basic.)

Temp.	*S.*	Nd_2O_3 : Se.	Temp.	*S.*	Nd_2O_3 : Se.	Temp.	*S.*	Nd_2O_3 : Se.
0°	31·10	1·414	18·4°	27·91	1·437	58·4°	30·67	1·444
0	30·84	1·360	23·6	28·92	1·423	61·6	26·14	1·442
8·6	30·79	1·376	26·2	29·38	1·385	63·2	19·44	—
12·6	30·30	1·394	30·0	29·46	1·391	64·6	17·13	1·319
13·0	29·25	1·371	30·8	28·34	1·428	65·2	16·8	1·383
13·4	28·27	1·417	43·4	27·90	1·426	77·0	8·33	1·411
15·0	29·81	1·394	51·5	29·44	1·430	79·4	6·98	—
17·0	30·85	1·431	54·0	29·30	—	92·4	3·19	1·370
17·6	29·16	1·364	55·4	30·00	1·432			

TABLE III.

(Free selenic acid added to solution.)

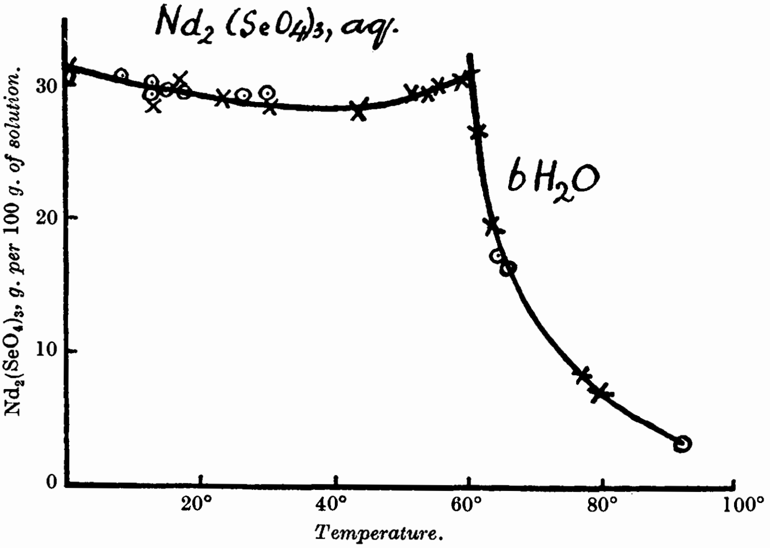
Temp.	H_2SeO_4, %.	*S.*	Temp.	H_2SeO_4, %.	*S.*	Temp.	H_2SeO_4, %.	*S.*
0°	0	31·10	17·6°	12·4	23·72	45·6°	1·34	28·27
0	3·84	29·54	24·0	0	(28·8)	45·6	1·60	28·61
8·6	0	(30·3)	24·0	4·14	26·35	45·6	5·47	27·35
8·6	5·87	26·29	30·0	0	(28·5)	45·6	6·39	27·18
13·0	0	(30·0)	30·0	4·52	25·32	55·4	0	(29·8)
13·0	4·60	27·46	40·0	0	(28·3)	55·4	1·66	27·29
13·0	5·93	24·92	40·0	60	7·9	84·8	0	(5·2)
17·6	0	(29·6)	45·6	0	(28·5)	84·8	44	7·55
17·6	8·6	25·23						

fectly neutral solution, although, as is shown in Table III, a marked increase in acidity due to intentional addition of free selenic acid causes, as usual, a fall in solubility. This suggests that a small amount of acid may tend to raise the solubility, perhaps by retarding hydrolysis, as was found to be the case with neodymium sulphate. As a result of this hydrolysis the residue in the saturation bottle was invariably basic. This probably accounts, in part at any rate, for the slight irregularity of the results to which reference has already been made, and for the difficulty of obtaining accurate " repeat " results, since the extent of hydrolysis depends partly upon the proportion of undissolved residue in the saturation bottle.

The data in Table II are shown in the figure, crosses and circles indicating that the Nd_2O_3 : Se ratio either exceeded or fell below 1·4. The solubility curve indicates the mean values. Between 0° and 60° the solubility varies but slightly : apparently a minimum occurs near 40°. At about 60° a break occurs with the appearance of the hexahydrate, the solubility of which rapidly falls with rise of temperature.

Comparison of Neodymium Selenate and Sulphate.—Although neodymium selenate is much more soluble in water, the solubility curves of the two salts are similar in appearance. The selenate shows a break at 60° and the sulphate at about 80°, although in the latter case the change is polymorphic and not due to a change in hydration; the solubilities above these points fall rapidly with rise of temperature. Free acid in small amounts tends to raise the solubility, but in larger quantity the acid reduces the solubility. Both salts tend to hydrolyse.

FIG. 1.



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