352. *The Solubility of Praseodymium Selenate in Water.*

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THE sulphates of lanthanum, praseodymium, and neodymium exhibit considerable differences in their solubilities in water, a fact that has occasionally been utilised in their separation by fractional crystallisation. The method has not proved popular, however, on account of the slight solubility of the salts, which renders the process more tedious than the usual double nitrate methods. Owing to the much greater solubilities of the selenates of these rare-earth metals, it was thought that, if they showed similar percentage differences in their solubilities, a convenient and rapid method of separation might be evolved. The selenates of neodymium and lanthanum have accordingly been studied (Friend, J., 1931, 1802; this vol., p. 1597), and that of praseodymium is now described, thus completing the research.

The Pr_2O_3 was purchased from Messrs. Hilger; spectroscopic examination by Dr. S. Judd Lewis showed that it contained only the merest traces of other rare-earth metals. In order to ensure the removal of any other impurities not readily detected spectroscopically, the oxide was dissolved in dil. HNO_3 aq. and the perfectly clear solution was boiled, praseodymium oxalate being pptd. with hot $H_2C_2O_4$ aq. After being filtered, washed, and dried, the oxalate was ignited to oxide.

The selenate was prep. by dissolving the oxide in dil. H_2SeO_4 aq. and crystallising it on the water-bath. The salt is only slightly sol. in hot H_2O, so the mother-liquor was poured off and used in preparing further batches.

The H_2SeO_4 was purchased as pure and found to be free from H_2SO_4 and halogen.

Method of Analysis.—The Pr was estimated by pptn. with excess of $H_2C_2O_4$ and ignition to oxide, with observance of the precautions already given in connexion with Nd salts (Friend, J., 1930, 1633). The ppt. of $Pr_2(C_2O_4)_3$ was granular and more easy to filter than that of $La_2(C_2O_4)_3$, closely resembling in this respect the Nd salt. The Se was determined in separate samples in the manner already indicated (Friend, this vol., p. 1598).

As with $Nd_2(SeO_4)_3$, both the metal and the acid radical could be determined with considerable accuracy by successive treatment of the same samples. The following results are typical :

(i) Direct pptn. from selenate (Pr_6O_{11}, g.)	0·2478	0·2861	0·2534	0·1933	0·2184
Pptn. after removal of Se (Pr_6O_{11}, g.)	0·2486	0·2860	0·2548	0·1938	0·2176
(ii) Direct pptn. from selenate (Se, g.)	0·2262	0·2148	0·1142	0·0936	
Pptn. after removal of Pr (Se, g.)	0·2260	0·2134	0·1148	0·0944	

The results with Se are more satisfactory than those obtained from $La_2(SeO_4)_3$ (Friend, this vol., p. 1599), probably because of the greater adsorptive character of the latter ppt.

The oxalate was always ignited in a Pt crucible, and weighed as the oxide Pr_6O_{11} (Brinton and Pagel, *J. Amer. Chem. Soc.*, 1923, **45**, 1460). The crucible lid was adjusted to allow access of air, otherwise the weight of oxide fluctuated slightly, presumably owing to partial reduction to Pr_2O_3. After thorough ignition, the *maximum* wt. of oxide was taken as the true one. On account of this uncertainty, the results are probably slightly less accurate than the corresponding data for La and Nd.

Anhydrous $Pr_2(SeO_4)_3$ was obtained by Scheele (*Z. anorg. Chem.*, 1898, **18**, 352) by heating the octahydrate to 250°. It does not appear possible, however, by mere heating to remove the last traces of H_2O without causing partial decomp. of the salt, as was found to be the case with the corresponding La and Nd salts (Friend, *locc. cit.*). A slight residue is obtained, insol. in H_2O, suggesting reduction to selenite.

The existence of the penta- and octa-hydrates, described by Scheele, has been confirmed.

Dodecahydrate, $Pr_2(SeO_4)_3,12H_2O$. Crystals separating when a cold, conc. solution was heated above the transition point were dried between filter-paper. They rapidly lost wt. in the balance case, ultimately yielding the octahydrate. The latter salt, when exposed to air satd. with H_2O vapour, gradually absorbs H_2O, the powdery product ultimately containing approx. 22·9—23·7% H_2O [$Pr_2(SeO_4)_3,12H_2O$ requires H_2O, 23·31%]. Presumably, therefore, the crystals in contact with hot H_2O are those of the *dodecahydrate*.

The putty-like residues in the saturation bottle below the transition temp. closely resembled those obtained with La and Nd selenates and were not analysed. Their separation for analysis involves considerable loss of very expensive material without yielding any precise results.

Determination of Solubility.—The apparatus used was similar to that described for $Nd_2(SO_4)_3$ (Friend, J., 1930, 1633), the procedure adopted being precisely similar to that for La (*idem*, this vol., p. 1601). Owing to hydrolysis,

the sat. solutions were usually slightly acid and, as before, difficulty was experienced in obtaining accurately reproducible results. At the higher temps. hydrolysis was very pronounced. In the following tables, S represents the solubility as g. of anhyd. $Pr_2(SeO_4)_3$ per 100 g. of solution, calc. from the wts. of Pr_6O_{11} found. In every case the Se was also determined separately. The theor. value for the ratio Pr_6O_{11} : 9Se is 1·4330.

FIG. 1.

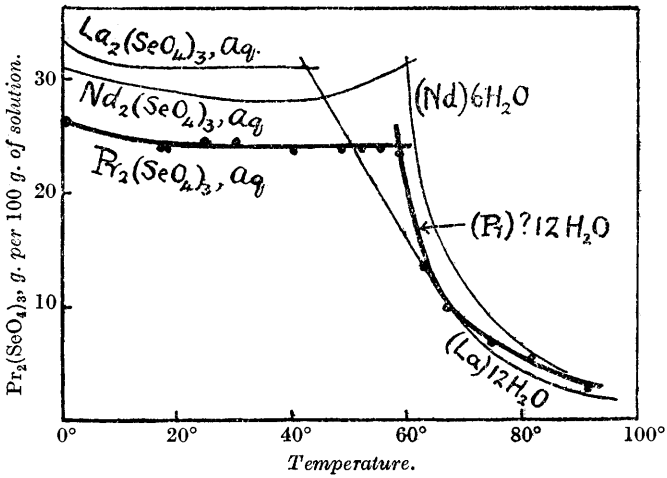

TABLE I.

(*Approximately neutral solution initially.*)

Solid phase $Pr_2(SeO_4)_3$, Aq.			Solid phase $Pr_2(SeO_4)_3,12H_2O$.		
Temp.	S.	Pr_6O_{11} : 9Se.	Temp.	S.	Pr_6O_{11} : 9Se.
0·5°	26·59	1·419	59·5°	23·33	1·291
17·4	23·88	1·403	63·6	14·00	1·275
17·8	23·79	1·393	67·0	9·96	1·364
24·6	24·29	1·403	75·0	6·89	1·024
30·0	24·50	1·431	81·0	5·64	1·150
40·2	23·67	1·395	92·0	2·99	0·952
48·6	24·00	1·444			
52·0	23·89	1·395			
55·5	23·99	1·320			

TABLE II.

(*Free selenic acid added to solution.*)

Temp.	14·6°	14·6°	15·8°	15·8°	16·4°	16·4°	28·6°
Free H_2SeO_4, %	0	4·7	0	0·7	0	0·86	0
S	25·0*	20·97	24·7*	25·33	24·5*	25·01	24·2*
Temp.	28·6°	40·2°	40·2°	43·1°	43·1°	49·6°	49·6°
Free H_2SeO_4, %	5·12	0	0·84	0	1·84	0	4·85
S	19·34	24·0*	23·85	24·0*	22·86	24·0*	20·41

* Calculated.

The foregoing results are shown in the figure, together with the solubility curves for $Nd_2(SeO_4)_3$ and $La_2(SeO_4)_3$. The three curves have the same

general shape, the solubilities falling rapidly with rise of temp. above the transition points. For the Pr salt the transition temp. is approx. 60°. Between 20° and 55°, S is practically independent of the temp.

The data in Table II indicate that, as with $Nd_2(SO_4)_3$, a slight increase in acidity at the lower temps. tends to increase S, probably for the reasons already given (Friend, J., 1930, 1640). Increase of acidity beyond 1% reduces S at temps. below the transition point.

Separation of La, Pr, *and* Nd.—The solubilities of the double nitrates usually employed in separating these elements follow the serial order, those of Nd being most sol. It is comparatively easy, therefore, to separate La from Nd, but the elimination of Pr is difficult. Below their transition temps., on the other hand, $Pr_2(SeO_4)_3$ is the least sol. selenate and, by warming a cool, satd. solution on the water-bath, the Nd and La salts tend to concentrate in the cryst. deposit and the Pr in the mother-liquor. This has been confirmed by experiment. The difference in their solubilities is not as great as was expected and the separation is slow. This fact, coupled with the high cost of H_2SeO_4 and the tendency for reduction to take place to insol. selenite renders the method of doubtful practical value.

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