

XXXVI.—*The Ortho-Vanadates of Sodium and their Analogues.*

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MENDELÉEFF in his *Periodic System* states his opinion that the true analogues of vanadium are chromium and titanium on the one hand, and on the other niobium and tantalum, to which it exhibits a greater resemblance than to phosphorus. Again, Rammelsberg (*Sitzungsber. d. K. Akad. d. Wissensch.*, Berlin, 1883) after describing a great number of alkaline vanadates, comes to the conclusion that "the phosphates cannot be directly compared with the vanadates, although $R''_3P_2O_8$ and $R''_3V_2O_8$, and also $R''_4P_2O_9$ and $R''_4V_2O_4$ are isomorphous," *i.e.*, the minerals of the apatite-group and vanadinite, and the minerals of the liebethenite-group and descloisite. Recently Ditte (*Compt. rend.*, **96**, 575—577) has described the preparation of some new members of the apatite and wagnerite-groups of minerals, amongst them being $3(Ca_3V_2O_8)CaBr_2$ and $Ca_3V_2O_8, CaBr_2$, which exactly resemble in form the corresponding phosphorus and arsenic compounds. After the replacement of phosphorus by vanadium in the apatite series had been recognised, it was next discovered in the case of a double fluoride and phosphate of sodium formed during the manufacture of caustic soda. No other cases of crystalline compounds in which phosphorus or arsenic is partially or wholly replaced by vanadium are known.

In order to trace the resemblance between the vanadates and phosphates and arsenates, it is evidently necessary to confine one's attention to the tribasic ortho-salts, since acid ortho-salts of vanadium, it would appear, cannot be prepared, and on the other hand, the pyro- and meta-arsenates are not known in the crystalline state. The only tribasic ortho-vanadates soluble in water are those of the two alkali-metals sodium and potassium; and of these only the sodium salt is available, since the potassium salts crystallise with great difficulty.

The tribasic phosphate and arsenate of sodium crystallise each with 12 mols. of water, in the form of hexagonal prisms, whilst the only known tribasic vanadate of sodium is described (Roscoe, *Phil. Trans.*, 1870) as separating with 16 mols. of water, in the form of needle-shaped crystals. It was, however, soon found that a vanadate containing the same quantity of water as the phosphate and the arsenate, and having the same form, could be obtained without any difficulty. Furthermore, less hydrated forms of the vanadate exist, and the phosphate and arsenate corresponding with two of these forms are shown to be formed under the same circumstances; and finally the

pure vanadium compound, corresponding with the double phosphate and fluoride of sodium, already mentioned, is described.

I. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4 \cdot 12\text{H}_2\text{O}$.—This salt is readily obtained by adding an excess of caustic soda to a solution of sodium pyrophosphate, and also by igniting vanadic acid with sodium carbonate, and crystallising the product from water or caustic soda solution. The salt is very soluble in water, but much less so in caustic soda solutions.

It crystallises in longer or shorter hexagonal prisms, terminated with the basal plane; occasionally traces of a rhombohedron are present. The optical behaviour is that of a hexagonal crystal; sections parallel to the base show a normal uniaxial interference figure; it is positive. The following refractive indices were determined on crystals with ground and glazed faces:—

	o.			e.		
	Li.	Na.	Tl.	Li.	Na.	Tl.
Crystal No. 1	1·5044	1·5099	1·5151	1·5177	1·5238	1·5296
„ 2	1·5035	1·5092	1·5148	1·5170	1·5228	1·5290
Mean	1·5040	1·5095	1·5150	1·5173	1·5232	1·5293

The analyses of this and the following salts were effected as follows:—The water was determined by simple ignition and loss of weight; in the residue, or in the original substance, the vanadium could be determined by titration with potassium permanganate. The vanadic, phosphoric, or arsenic acids were removed from another portion by precipitation generally as silver salts; the washed precipitates were dissolved in nitric acid, the silver precipitated by hydrochloric acid, and in the filtrate the vanadic acid determined by simple evaporation and ignition, or the phosphoric or arsenic acids by precipitation with magnesia mixture; the weight of silver chloride was also used to calculate the amount of these acids. The filtrate from the silver vanadate, &c., after removal of excess of the reagent by means of ammonium chloride, or sulphide, was used for estimating either the sodium by evaporation with sulphuric acid and ignition, or the fluorine by precipitation with calcium chloride.

For analysis, moderately large crystals were employed, and were freed from solution either by washing with dilute alcohol or by means of filter-paper, by which they were also dried. The analytical data are—

Preparation 1.—0·6280 gram substance lost 0·3296 gram water =

52.48 per cent., and 0.6908 gram substance required 20.3 c.c. permanganate (1 c.c. = 0.007772) = 22.83 per cent. vanadic oxide.

Preparation 2.—1.1438 gram substance gave 1.2416 gram AgCl = 23.04 per cent. vanadic oxide, and 0.6419 gram sodium sulphate = 24.51 per cent. sodium oxide.

Preparation 3.—0.9680 gram substance gave 0.5415 gram sodium sulphate = 24.43 per cent. sodium oxide, and 0.2206 gram vanadic oxide, requiring 110.6 c.c. permanganate (1 c.c. = 0.002002) and 1.0540 gram silver chloride = 22.79, 22.89, and 23.11 per cent. vanadic oxide respectively.

0.5290 gram substance left 0.2531 gram residue = 52.16 per cent. water.

1.1157 gram substance left 0.5323 gram residue = 52.20 per cent. water.

0.6963 gram substance required 78.9 c.c. permanganate = 22.70 per cent. vanadic oxide.

	Na ₃ VO ₄ .12H ₂ O.	Found.						Mean.
		22.83	23.04	22.79	22.89	23.11	22.70	
V ₂ O ₅	22.81	—	24.51	24.43	—	—	—	22.89
Na ₂ O	23.25	52.48	—	52.16	52.20	—	—	24.47
H ₂ O	53.94	—	—	—	—	—	—	52.24
	100.00							

Although these data are sufficient to show the composition of the body, it is to be noted that the mean sodium per cent. is 1.22 too high, and the water 1.66 per cent. too low. This is due to the salt containing mechanically admixed caustic soda, and the amount of the error may be determined by precipitating the solution of the salt with barium chloride, and determining the alkalinity of the filtrate, which is quite free from vanadium. The sample No. 3, although it had been washed thoroughly with dilute alcohol, was found to contain caustic soda equivalent to 1.14 per cent. sodium oxide; after recrystallisation it contained 1.56—1.60 per cent.

The corresponding phosphate and arsenate being well known, it only remains to compare the determinations of the refractive indices and to remark that in their analysis the same difficulty is encountered as with the vanadate, although to a less extent. The crystalline form of both compounds is exactly that of the vanadate, but the arsenate generally forms much longer and thinner crystals. A crystal of the vanadate continues its growth in a solution of the phosphate, and a minute crystal of any one of the three salts will immediately cause a

supersaturated solution of either of the other salts to commence crystallising. The optical character is positive—

	Li.	Na.	Tl.
$\text{Na}_3\text{PO}_4, 12\text{H}_2\text{O}$..	$\left\{ \begin{array}{l} o \dots \\ e \dots \end{array} \right.$	$\left\{ \begin{array}{l} — \\ — \end{array} \right.$	$\left\{ \begin{array}{l} 1.4486 \\ 1.4539 \\ — \end{array} \right.$
$\text{Na}_3\text{AsO}_4, 12\text{H}_2\text{O}$..	$\left\{ \begin{array}{l} o \dots \\ e \dots \end{array} \right.$	$\left\{ \begin{array}{l} 1.4553 \\ 1.4630 \end{array} \right.$	$\left\{ \begin{array}{l} 1.4589 \\ 1.4669 \\ 1.4704 \end{array} \right.$

While making the preceding vanadate, the formation of other crystals was frequently noticed, and since the solutions employed in such cases were either very concentrated or contained much caustic soda, it appeared probable that they were forms of the tribasic vanadate containing less water of crystallisation. This is borne out by the subsequent observations.

The following three salts are all prepared from solutions of sodium ortho-vanadate by concentration and cooling, or by the addition of caustic soda, which acts as a dehydrating agent, and also renders the salts more insoluble. The solubility of these salts being considerable and greatly influenced by slight changes of temperature, no detailed directions for obtaining them can be given, and although their formation may be easily watched under the microscope—the different hydrates being at once recognised by their crystalline forms—their preparation in quantity remains a matter of trial and experience. A great difficulty is the removal of the mother-liquor, which, as regards the most stable salt, $\text{Na}_3\text{VO}_4, 12\text{H}_2\text{O}$, is always in a state of supersaturation, and thus ready to solidify on the slightest provocation; in the preparation of the lowest hydrate, $\text{Na}_3\text{VO}_4, 8\text{H}_2\text{O}$, this difficulty is almost insurmountable.

The salt, $\text{Na}_3\text{VO}_4, 10\text{H}_2\text{O}$, exists in two distinct modifications, differing in their crystalline form, one appearing as rhombic dodecahedrons and being easily obtained, the other appearing as hexagonal plates, and not so often observed.

II. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4, 10\text{H}_2\text{O}$. *Regular*.—The crystals are limpid, well-formed rhombic dodecahedrons with occasional faces of the octahedron. They are isotropic. The refractive index was determined on ground and glazed crystals—

Li.	Na.	Tl.
1.5244	1.5305	1.5366

The sample for analysis was dried by pressure between papers. 0.9972 gram substance lost on ignition 0.4929 gram = 49.43 per cent. water, and gave 0.2582 gram vanadic oxide = 25.89 per cent., and 0.5899 gram sodium sulphate = 25.83 per cent. sodium oxide—

	$\text{Na}_3\text{VO}_4, 10\text{H}_2\text{O}$.	Found.
V_2O_5	25·07	25·89
Na_2O	25·53	25·83
H_2O	49·41	49·43
	100·01	

III. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4, 10\text{H}_2\text{O}$. *Hexagonal*.—This salt, having almost the same form as the pyrovanadate, $\text{Na}_4\text{V}_2\text{O}_7, 18\text{H}_2\text{O}$, was at first mistaken for the latter; the crystals of the ortho-vanadate are, however, thicker than the pyrovanadate. The forms are simply $\infty\text{P} \cdot 0\text{P}$, and the habitus thin tabular; the crystals exhibit a uniaxial interference figure; they are positive. The refractive index was determined upon ground and glazed crystals—

	o.			e.		
	Li.	Na.	Tl.	Li.	Na.	Tl.
Crystal No. 1	1·5327	1·5396	1·5461	1·5403	1·5473	1·5536
" 2	1·5336	1·5399	1·5460	1·5413	1·5478	1·5538
Mean	1·5332	1·5398	1·5460	1·5408	1·5475	1·5537

For analysis the crystals were dried between papers.

0·4810 gram substance lost 0·2378 gram water = 49·44 per cent., and required 31·9 c.c. permanganate (1 c.c. = 0·003858) = 25·59 per cent. vanadic oxide. A portion of the same sample was analysed after exposure to the air. 0·5590 gram substance required 36·1 c.c. permanganate = 24·91 per cent. vanadic oxide; 0·7642 gram substance lost 0·3785 gram water = 49·53 per cent., and required 50·3 c.c. permanganate = 25·39 per cent. vanadic oxide. Again, 0·7500 gram substance gave 0·4402 gram sodium sulphate = 25·63 per cent. sodium oxide, 0·8738 gram silver chloride, and 0·1921 gram vanadic oxide = 24·73 and 25·61 per cent. vanadic oxide respectively—

	$\text{Na}_3\text{VO}_4, 10\text{H}_2\text{O}$.	Found.				
V_2O_5	25·07	25·59	24·91	25·39	24·73	25·61
Na_2O	25·53	—	—	—	25·63	—
H_2O	49·41	49·44	--	49·53	—	—
	100·01					

IV. *Sodium Ortho-vanadate*, $\text{Na}_3\text{VO}_4, 8\text{H}_2\text{O}$ (?).—This salt separates in apparently rhombic plates, sometimes rectangular in outline, some-

times octangular through the presence of an obtuse prism whose obtuse angle measures 122—128°. The crystals are frequently very minute, but at other times rather large; they do not show any axial interference figure, but depolarise parallel light like a rhombic crystal.

The isolation of the thin flat plates from the mother-liquor is extremely difficult; placed on paper to drain, the whole at once begins to solidify; the only method is to pour off the liquid carefully and replace it by dilute alcohol of such strength that no precipitation can take place, to pour off this liquid, and replace it by fresh alcohol of suitable strength, and so on, but the crystals must not be stirred or broken until all the mother-liquor is removed.

After many attempts, only two approximate analyses could be made; the numbers show clearly that the salt contains much less water of crystallisation than the preceding salts, but the exact amount remains doubtful:—

	$\text{Na}_3\text{VO}_4, 8\text{H}_2\text{O}$.	Found.	
V_2O_5	27·81	28·79	27·50
Na_2O	28·35	—	27·69
H_2O	43·84	41·86	44·81
	100·00		

The phosphates and arsenates corresponding with the last three vanadates do not appear to have been previously obtained; the existence of two of them, viz., $\text{Na}_3\text{PO}_4, 10\text{H}_2\text{O}$ regular, and $\text{Na}_2\text{AsO}_4, 10\text{H}_2\text{O}$ regular, and $\text{Na}_3\text{PO}_4, 8\text{H}_2\text{O}$ (?), and $\text{Na}_3\text{AsO}_4, 8\text{H}_2\text{O}$ (?) are easily demonstrated by the use of the microscope, their forms being exactly those of the corresponding vanadates. They have not been prepared in quantity.

V. *Sodium Vanadofluoride*, $2\text{Na}_3\text{VO}_4, \text{NaF}, 19\text{H}_2\text{O}$, is formed by fusing together the requisite quantities of vanadic acid, sodium carbonate, and sodium fluoride, and crystallising the product from warm water, or by adding sodium fluoride in calculated quantity to a solution of trisodic orthovanadate, or to one of sodium pyrovanadate mixed with excess of caustic soda. From any of these solutions, the salt crystallises in limpid octohedrons, which may be recrystallised without change from a very dilute caustic soda solution. The crystals do not act on polarised light; they belong to the regular system; their form is that of the octohedron, or the same modified by the rhombic dodecahedron; crystallised rapidly it forms skeletons derived from

the preceding two forms. The refractive indices were determined on ground and glazed crystals:—

	Li.	Na.	Tl.
Crystal No. 1.....	1·5176	1·5235	1·5290
„ 2.....	1·5165	1·5224	1·5277
Mean	1·5171	1·5230	1·5284

For analysis the crystals were dried between papers.

Preparation 1.—0·9443 gram substance gave 0·6208 gram sodium sulphate = 28·72 per cent. sodium oxide, and 1·0701 gram silver chloride and 0·2312 gram vanadic oxide = 24·06 and 24·48 per cent. vanadic oxide respectively; 1·2625 gram substance lost 0·5704 gram water = 45·17 per cent.; 1·3429 gram substance gave 0·072 gram calcium fluoride = 2·61 per cent. fluorine.

Preparation 2.—Analyses made by Mr. A. Siebold. 1·6893 gram substance gave 0·081 gram calcium fluoride and 1·8370 gram substance gave 0·0868 gram calcium fluoride = 2·34 and 2·30 per cent. fluoride; 1·0090 gram substance gave 1·1454 gram silver chloride = 24·12 per cent. vanadic oxide; 1·1685 gram substance gave 0·7700 gram sodium sulphate = 28·77 per cent. sodium oxide and 0·2860 gram vanadic oxide = 24·47 per cent.; 0·6960 gram substance required 47·5 c.c. permanganate (1 c.c. = 0·003555) = 24·26 per cent. vanadic oxide; 1·2932 gram substance lost 0·5852 gram water = 45·25 per cent.

	$2\text{Na}_3\text{VO}_4, \text{NaF}, 19\text{H}_2\text{O}$.	Found.				
V_2O_5 ...	24·27	24·06	24·48	24·12	24·47	24·26
Na	21·42 = Na_2O 28·87	28·72	—	28·77	—	—
O	6·37	—	—	—	—	—
F	2·52	2·61	—	2·34	2·30	—
H_2O ...	45·42	45·17	—	45·17	—	—
	100·00					

A salt could not be obtained containing a larger quantity of fluorine. The crystals of the corresponding phosphate obtained during the manufacture of caustic soda contained up to 1·28 per cent. vanadic oxide, and the artificial salt, prepared by Rammelsberg—and to which 18 mols. of water only are ascribed—3·39 per cent.

The corresponding phosphofluoride and arsenofluoride were first prepared by Briegleb (*Annalen*, 1856, 95), but he ascribed to them the incorrect formulæ $\text{Na}_3\text{PO}_4, \text{NaF}, 12\text{H}_2\text{O}$ and $\text{Na}_3\text{AsO}_4, \text{NaF}, 12\text{H}_2\text{O}$. In 1864 Rammelsberg (*J. pr. Chem.*, 94, 237) first examined the small red crystals obtained in the soda manufacture, and supposed them to be a double phosphate and silicate of sodium, which by recrystallisation is decomposed and converted into a new hydrate of

sodium phosphate, viz., $\text{Na}_3\text{PO}_4, 10\text{H}_2\text{O}$. That this last salt contains fluorine and is a fluorphosphate was admitted in 1880 (*Monatsh. Akad. Berl.*, 1880, 777); but it is then described as containing only 18 instead of 19 mols. of water, i.e., $2\text{Na}_3\text{PO}_4, \text{NaF}, 18\text{H}_2\text{O}$. In 1865 Baumgarten (*Zeit. f. Chem.*, N.S., **1**, 605) re-examined the octohedrons from the soda manufacture, ascribing to them the formula $4\text{Na}_3\text{PO}_4, \text{Na}_2\text{SiO}_3, 2\text{NaF}, 40\text{H}_2\text{O}$; by recrystallisation they lost their silica and were converted into $2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$; this last salt, as well as another, $2\text{Na}_3\text{PO}_4, \text{NaF}, 22\text{H}_2\text{O}$, he also obtained by synthesis, but was unable to obtain a compound having the composition described by Briegleb. The crystals from the soda liquors were again examined in 1872 by Thorpe (this Journal [2], **10**, 660) who found them to have a composition expressed exactly by Baumgarten's formula $2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$.

I have confirmed the preparation of the salt with 19 mols. of water by Baumgarten's method, but the salt with 22 mols. of water could not be obtained; a water determination gave 48·10 per cent., which agrees exactly with the calculated quantity for the 19 mol. hydrate, viz., 48·01 per cent.

Thus no less than six different formulæ have been proposed for the sodium phosphofluoride, and *in every case* the crystals analysed were regular octohedrons. Coupling this with the contrary statements and the analyses here given, it follows that only one fluorphosphate is known, viz., $2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$; for neither Briegleb's salt nor Baumgarten's $2\text{Na}_3\text{PO}_4, \text{NaF}, 22\text{H}_2\text{O}$ can be obtained by the methods given for their preparation, and that the crystals from the soda liquors have the composition $2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$ has been shown by Thorpe.

Further, it follows from the correction of Briegleb's formula for the phosphorus salt, that the isomorphous arsenic compound must have the composition $2\text{Na}_3\text{AsO}_4, \text{NaF}, 19\text{H}_2\text{O}$, and not $\text{Na}_3\text{AsO}_4, \text{NaF}, 12\text{H}_2\text{O}$; this is confirmed by the annexed analysis.

Sodium arsenofluoride was prepared from a solution containing sodium arsenate, sodium fluoride, and caustic soda. The crystals are brilliant octohedrons, and are isotropic.

	$2\text{Na}_3\text{AsO}_4, \text{NaF}, 19\text{H}_2\text{O}$.	Found.			
As_2O_5	28·77	28·97	29·22	28·82	28·97
Na	20·15	20·26	—	—	—
O	5·99	—	—	—	—
F	2·37	2·26	—	—	—
H_2O	42·72	42·68	42·74	42·80	—
	100·00				

That the phospho-, arseno-, and vanado-fluorides of sodium form an isomorphous series is seen from their composition, their form, and from the observation that a crystal of the vanadate continues its growth unimpeded in solutions of either the phosphate or of the arsenate, and also a mixture of equal parts of the phosphate and vanadate deposited crystals containing both phosphoric and vanadic acids, viz., 11.42 and 11.68 per cent. of the latter, 24.27 per cent. being contained in the pure vanadate.

A comparison of the refractive indices of the phosphofluoride and arsenofluoride with those of the vanadofluoride show that in this series of salts, as in the series $\text{Na}_3\text{XO}_4, 12\text{H}_2\text{O}$, the vanadium compound has a greater refractive and dispersive power than either the phosphorus or arsenic compounds :—

	Li.	Na.	Tl.
$2\text{Na}_3\text{PO}_4, \text{NaF}, 19\text{H}_2\text{O}$	1.4489	1.4519	1.4545
$2\text{Na}_3\text{AsO}_4, \text{NaF}, 19\text{H}_2\text{O}$	1.4657	1.4693	1.4726

The annexed series of crystalline ortho-phosphates, vanadates, and arsenates are thus known, and the conclusion follows that the crystalline ortho-vanadates, so far as they are known, do correspond exactly in composition and in form with the ortho-phosphates and arsenates :—

Hexagonal.	$\text{Na}_3(\text{P or V or As})\text{O}_4, 12\text{H}_2\text{O}$.
Regular.	$\text{Na}_3(\text{P or V or As})\text{O}_4, 10\text{H}_2\text{O}$.
Hexagonal.	$\text{Na}_3\text{V}(? \text{P or As})\text{O}_4, 10\text{H}_2\text{O}$.
Rhombic	$\text{Na}_3(\text{P or V or As})\text{O}_4, (?)8\text{H}_2\text{O}$.
Regular.	$2\text{Na}_3(\text{P or V or As})\text{O}_4, \text{NaF}, 19\text{H}_2\text{O}$.
