XVIII. *Researches on Vanadium.*—Part III.

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I. METALLIC VANADIUM.

In the second Part of my "Researches on Vanadium," communicated to the Royal Society (Phil. Trans. 1869, p. 691), I stated that metallic vanadium absorbs hydrogen. This conclusion has been fully borne out by subsequent experiment; and it appears that the amount of absorbed or combined hydrogen taken up by the metal varies according to the state of division, first, of the chloride (VCl_2) from which the metal is prepared, and secondly, and especially, of the metallic powder itself. The metal containing absorbed hydrogen on exposure to dry air slowly takes up oxygen, water being formed and the metal undergoing oxidation to a substance which resembles the metal in its appearance, but possesses a darker grey colour, and has a less brilliant metallic lustre than vanadium itself. At this point the oxidation stops, although in moist air it proceeds still further. Thus a portion of pure dichloride was reduced in hydrogen; of the reduced substance, free from chlorine, 0·2666 grm. yielded on complete oxidation 0·4441 of V_2O_5, corresponding to a percentage of 93·6 of pure metal. On exposure to the air for some days this substance absorbed oxygen, losing its brilliant metallic lustre; and when burnt in a current of dry oxygen, water was given off, thus:—

(1) 0·4232 grm. gave 0·0502 grm. of water and 0·6615 grm. V_2O_5,
(2) 0·2695 „ „ 0·0315 „ „ 0·414 „ „

or

(1) gives 87·8 p. c. vanadium; 1·3 p. c. hydrogen; 10·9 p. c. oxygen.
(2) „ 86·7 p. c. vanadium; 1·3 p. c. hydrogen; 12·0 p. c. oxygen.

The difficulty of obtaining metallic vanadium perfectly free from admixture of oxide was again rendered evident. Pure tetrachloride was prepared in quantity, and from this the dichloride was made. On heating this dichloride to whiteness for forty-eight hours a substance was obtained which gained on oxidation 70·7 per cent., and therefore still contained a slight admixture of oxide. The reducing action of sodium on the solid chlorides was next examined; in this case the reduction takes place rapidly but quietly in an atmosphere of hydrogen at a red heat, and may be best conducted in strong iron tubes proved air-tight under hydraulic pressure of 200 lbs. on the square inch. Explosions occur when the tetrachloride is heated with sodium. The substance thus obtained by the action of sodium was found on lixiviation to be free from chlorine, and on washing it was found to separate into two parts—(1) a light and finely divided black powder

(trioxide), soluble in hydrochloric acid, which remains in suspension, and (2) a heavier grey powder (insoluble in hydrochloric acid), which is deposited, and which by repeated washing may be entirely freed from the lighter trioxide. This bright grey powder consists of metallic vanadium mixed with more or less oxide. If the finely divided metallic powder, after drying *in vacuo*, be reduced at a low red heat in a current of pure hydrogen, it takes fire spontaneously, when cold, on exposure to air or oxygen, a distinct flame being seen playing on the surface whilst water is formed. In one experiment a product thus prepared contained 91·1 per cent. of metallic vanadium (0·354 substance gave 0·574 grm. V_2O_5). This substance, exposed for some weeks to dry air, slowly absorbed oxygen, and on roasting gave a percentage increase of 53·75 (0·453 grm. yielded 0·6965 V_2O_5), whilst 0·034 grm. or 7·5 per cent. of water was at the same time formed. This shows that the point of oxidation at which the metal containing hydrogen becomes stable in dry air nearly corresponds to the oxide V_2O.

A similar slow change in the appearance of the metal has been noticed in some of the portions of the metallic powder placed on microscopic slides.

II. VANADIUM AND BROMINE.

1. *Vanadium Oxytribromide or Vanadyl Tribromide*, $VOBr_3$, molec. wt.=307·3.—When the vapour of perfectly dry and pure bromine is passed over vanadium trioxide (V_2O_3) heated to redness, dense yellowish-white fumes of the oxytribromide are formed in the heated portion of the tube, and these condense together with the excess of bromine to form a dark red transparent liquid. In order to free the oxytribromide from excess of bromine, the mixed liquids must be rectified *in vacuo*, as the temperature of decomposition of the oxybromide lies (under the ordinary atmospheric pressure) below its boiling-point. By distilling under a pressure of 106 millims. of mercury in a current of perfectly dry air the whole of the bromine was got rid of before the thermometer rose to 45° C. The transparent liquid remaining in the retort had a dark red colour, gave off white fumes on exposure to moist air, and when thrown into water produced a light yellow-coloured solution of a vanadic salt. It is possible to distil the oxybromide under diminished pressure with but slight decomposition occurring, although when heated under the atmospheric pressure it suddenly solidifies at 180° C., splitting up into the oxydibromide and bromine. Under a pressure of 100 millims. of mercury the oxytribromide volatilizes without decomposition between 130° to 136° C.

The following analytical results were obtained:—Analysis No. 1 was made from a portion of oxytribromide which had not been distilled, No. 2 from a portion of the same substance, after further treatment with dry air at 63°, No. 3 from another preparation which had been distilled *in vacuo*, and in which the bromine determination is too high owing to traces of free bromine.

	Oxybromide taken.	Silver bromide found.	Vanadium pentoxide found.	Percentages of bromine.	Percentages of vanadium.
1.	0·7173	——	0·2110	——	16·52
	0·8022	1·5013	——	79·62	——
2.	0·9150	——	0·2748	——	16·87
	0·5580	1·038	——	79·10	——
3.	0·4850	——	0·1435	——	16·62
	0·3745	0·7085	——	80·48	——

Hence we have as the composition of the oxytribromide:

	Calculated.		Found. I.	Found. II.	Found. III.	Mean.
V =	51·3	16·69	16·52	16·87	16·62	16·67
Br_3 =	240·0	78·10	79·62	79·10	80·48	79·36
O =	16·0	5·21	——	——	——	——
	307·3	100·00				

The colour of the oxytribromide is somewhat redder than that of bromine, and it is more transparent in thin films, and much more translucent than bromine.

The oxytribromide slowly decomposes at the ordinary atmospheric temperature into bromine and oxydibromide; it is very deliquescent and hydroscopic, and cannot be formed in presence of moisture. The specific gravity of the oxytribromide at 0° is 2·9673, and at 14°·5 it is 2·9325.

2. *Vanadium Oxydibromide or Vanadyl Bromide*, $VO Br_2$, molec. wt. =227·3.—This substance forms suddenly when the oxytribromide is heated to temperatures above 180°, and it is slowly produced by the same decomposition at lower temperatures. The oxydibromide is a yellowish-brown solid body, in appearance resembling ochre; it is very deliquescent, and on heating in the air it loses all its bromine and is converted into the pentoxide. Thrown into water it dissolves, furnishing a blue solution of hypo-vanadic ($V_2 O_4$) salt.

The following analyses were made from oxydibromide prepared on different occasions.

	Oxydibromide taken.	Vanadium pentoxide found.	Silver bromide found.	Percentages of vanadium.	Percentages of bromine.
(1)	0·7260	0·3025	1·2245	23·40	71·75
(2)	0·5910	——	0·9738	——	70·11
	1·1259	0·4308	——	21·50	——

Hence we have

	Calculated.		Found. (1).	Found. (2).	Mean.
V . .	51·3	22·57	23·40	21·50	22·45
Br_2 . .	160·0	70·39	71·75	70·11	70·93
O . .	16·0	7·04	——	——	——
	227·3	100·00			

3. *Vanadium Tribromide*, VBr_3, molec. wt. $=291{\cdot}3$.—This body condenses as a greyish-black opake amorphous sublimate, when dry bromine vapour is passed in excess over vanadium nitride heated to redness. Brown vapours are given off, which soon condense in the cooler portions of the tube. The tribromide is a very unstable compound, losing bromine even at the ordinary temperature in dry air, and being converted into V_2O_3 when gently heated. It deliquesces rapidly on exposure to moist air, giving rise to a brown-coloured liquid, in this respect resembling the trichloride, but on addition of a few drops of hydrochloric acid the brown liquid changes to the green colour characteristic of a solution of a vanadous salt (V_2O_3). No free bromine is evolved when the tribromide dissolves in water. In order to prepare the tribromide, pure nitride of vanadium, contained in a porcelain boat, was introduced into a combustion-tube, and after all the air had been displaced by dry carbonic acid, the part of the tube containing the nitride was heated to redness, the other part of the tube being kept at such a temperature as to volatilize any excess of bromine which might pass over. After all the nitride had burnt away, the bulb containing the bromine was sealed off, and a current of dry carbonic acid passed over the solid bromide to displace all traces of free bromine. A second method of preparing the tribromide is to pass bromine vapour over a mixture of vanadium trioxide and charcoal; in this reaction the oxytribromide is first formed, then the oxydibromide, and lastly, the tribromide, VBr_3; but this plan is not to be recommended, as the tube soon becomes stopped up by the formation of these solid compounds. The bromide thus prepared was not analyzed, but it presented exactly the same appearance and properties as the tribromide obtained by the first method.

No higher compound of bromine and vanadium than the tribromide could be obtained. The volatile liquid passing into the bulb in the first preparation was carefully rectified, and it was all found to distil over at the boiling-point of bromine, leaving only a small quantity of the tribromide in the bulb. Some difficulty was experienced in obtaining satisfactory analytical results with the tribromide, owing to the fact, already observed by Stas*, that bromide of silver, when boiled with excess of nitrate of silver, carries down with it some of this latter salt inclosed in the bromide, and that this impurity cannot be got rid of by washing. Owing to this admixture of nitrate of silver the bromine determinations usually come out about two per cent. too high, whilst the vanadium determinations gave constant numbers, agreeing much more nearly with the calculated results. Thus in four analyses of the tribromide prepared on different occasions the mean percentage of bromine was found to be $84{\cdot}15$, the calculated percentage being $82{\cdot}4$; whilst the vanadium determinations of the same portions gave $18{\cdot}57$ per cent. instead of $17{\cdot}6$ per cent. In order to lessen as much as possible this error, the precipitated bromide of silver was reduced in hydrogen until no further diminution of weight occurred, and the percentage of bromine calculated from this loss.

* Stas, Recherches sur les Lois des Proportions chimiques, p. 156.

	Weight of tribromide taken.	Vanadium pentoxide found.	Loss of bromine.	Percentages of vanadium.	Percentages of bromine.
(1)	0·8004	0·2630	0·6500	18·46	81·21
(2)	0·3462	0·1160	0·2790	18·80	80·58
(3)	0·5960	0·1965	0·4815	18·52	80·85

Hence we have:—

	Calculated.		Found. (1).	(2).	(3).	Mean.
V = . .	51·3	17·6	18·46	18·80	18·52	18·59
Br_3= . .	240·0	82·4	81·21	80·58	80·78	80·86
	291·3	100·0	99·67	99·38	99·30	99·45

Experiments made with the bromine employed, which had been rectified over potassium bromide, and was carefully tested for chlorine and iodine and showed to be pure, proved that a similar excess of weight occurred on precipitation with nitrate of silver. In one experiment the percentage of bromine thus found was 100·96, and in a second experiment 101·41. It will also be seen that the bromine determinations of the oxybromides are similarly all too high from the same cause.

III. VANADIUM AND IODINE.

When the vapour of iodine is passed over the red-hot nitride of vanadium contained in a tube no action whatever takes place, the nitride after the operation remaining perfectly unchanged. Vanadium trioxide is likewise unacted upon by iodine at all temperatures.

IV. METALLIC VANADATES.

In the first Part of these researches* I pointed out (1) that the vanadates analyzed by BERZELIUS, prepared by boiling vanadic acid with the alkaline hydroxides and by double decomposition, must be considered as meta- or monobasic vanadates, (2) that the so-called bi-vanadates analyzed by Von HAUER†, and prepared by acting on the metavanadates with acids are anhydro-salts, and (3) that the naturally occurring vanadates are tribasic salts, and that sodium ortho-vanadate is formed when one molecule of vanadium pentoxide is fused with three molecules of carbonate of soda, three molecules of carbon dioxide being expelled. I have now to describe the preparation and properties of some characteristic members of these three classes of vanadates, as well as those of a fourth new class, viz. the tetrabasic or pyro-vanadates.

Determination of vanadium in the soluble vanadates.—The separation of vanadic acid from the metals of the alkalies by means of chloride of ammonium, as proposed by Von HAUER, is apt to give too low results, both as regards the vanadium and the alkali. It

* Philosophical Transactions, 1868 (Bakerian Lecture).

† Journ. Prac. Chem. Bd. lxix. p. 388, 1856.

is almost impossible to prevent traces of ammonium metavanadate from dissolving, and on ignition, even with the greatest care, some portions of the finely divided vanadium pentoxide are invariably carried off when the ammonia escapes. On the other hand, the volatilization of the comparatively large quantities of sal-ammoniac which must be employed in order to ensure the complete precipitation of the vanadium, almost always entails a considerable loss of the fixed alkaline chlorides. A far more accurate plan for the separation of vanadium is the precipitation of the soluble vanadate by acetate of lead, when basic lead vanadate is precipitated, which is so insoluble that a portion when finely powdered and boiled in water did not dissolve in sufficient quantity to enable the lead reaction with sulphuretted hydrogen to be detected in the filtrate. This salt is also insoluble in acetic, but it dissolves readily in nitric acid, liberating vanadic acid, which separates out, but dissolves completely when the liquid is warmed. In the analysis of a soluble vanadate this insoluble lead salt is collected on a filter, dried at 100° C. and weighed; a given quantity of the dried salt is then dissolved in nitric acid, the lead precipitated by pure sulphuric acid, and the lead sulphate determined with the usual precautions of evaporation with addition of alcohol, &c. The lead sulphate thus obtained is (contrary to BERZELIUS'S statement) quite free from vanadium, whilst the vanadic acid in the filtrate is obtained perfectly pure, and well crystallized on evaporation and ignition. The filtrate from the lead vanadate, freed from excess of lead by means of sulphuric acid and evaporated, yields the alkaline sulphate not containing a trace of vanadium.

Sodium Vanadates.

1. *Sodium Orthovanadate*, $Na_3VO_4 + 16H_2O$.—When a mixture of three molecules of sodium carbonate and one molecule of vanadium pentoxide is fused until no further evolution of carbon dioxide is observed, three molecules of CO_2 have been expelled and a tribasic vanadate remains as a white crystalline mass.

In one experiment in which a slight excess of sodium carbonate was taken 0·5785 grm. V_2O_5 liberated on fusion 0·4185 grm. CO_2. According to the equation

$$V_2O_5 + 3Na_2CO_3 = 2Na_3VO_4 + 3CO_2,$$

the weight of CO_2 liberated by this quantity of vanadium pentoxide is 0·4182 grm.

The mixture is easily fusible at first, but becomes less so as the reaction proceeds; whilst to begin with the heat of a Bunsen's burner is sufficient to melt the mass, it is necessary to apply the heat of a blowpipe-flame to keep up the fusion when the decomposition becomes more nearly complete. On cooling, the solidified mass acquires first a dark green colour, and then passes through yellow, until when cold it becomes perfectly white, and is found to possess a crystalline appearance. It dissolves easily in cold water, but is insoluble in alcohol. Hot water must *not* be employed for dissolving the fused mass, and as little cold water as possible. The cold strong aqueous solution must be instantly mixed with excess of strong alcohol; two layers of liquid are then formed, the upper one consisting of dilute alcohol, the lower one of the saline solution. After

standing for a few hours the lower layer of liquid solidifies, forming an aggregate of colourless needle-shaped crystals. These crystals, which possess a strong alkaline reaction, are washed with small quantities of alcohol, then placed on a porous plate over sulphuric acid *in vacuo*, and after remaining for a short time they may be taken out for analysis. The following analytical results were obtained:—

Water determination.—0·8077 grm. of the crystals which first fuse in their water of crystallization lost on careful ignition in platinum 0·4882 grm. H_2O; corresponding to 60·44 per cent.

Vanadium determination.—The residual anhydrous salt left in the crucible after the previous experiment, gave, on precipitation with lead acetate, a precipitate (dried at 100° C.) weighing 0·7472 grm.; 0·7245 grm. of this precipitate was dissolved in nitric acid, and the lead precipitated with slight excess of sulphuric acid, the usual precautions being taken. The filtrate from the lead sulphate yielded on evaporation 0·1515 grm. of finely crystallized V_2O_5. Consequently the whole lead precipitate contained 0·1565 grm. V_2O_5, corresponding to 19·34 per cent., or to 10·86 per cent. of vanadium, on the sodium salt taken.

Sodium determination.—The liquid filtered off from the lead precipitate, and freed from excess of lead, left on evaporation and ignition 0·3440 grm. of Na_2SO_4, corresponding to 0·1502 Na_2O, or 13·8 per cent. of sodium in the salt.

These numbers correspond to the formula

$$Na_3VO_4 + 16H_2O.$$

	Calculated.		Found.
Na_3 . . .	69·0	14·61	13·80 per cent.
V	51·3	10·86	10·86 „ „
O_4	64·0	13·56	——
$16H_2O$ . .	288·0	60·97	60·44 „ „
	472·3	100·00	

Sodium orthovanadate is an extremely unstable compound. Its aqueous solution slowly undergoes decomposition on standing at the ordinary temperature of the air out of contact with atmospheric carbonic acid, whilst at higher temperatures the same change takes place quickly. This decomposition consists in the formation of a new salt, sodium tetravanadate, the liquid becomes strongly alkaline, whilst caustic soda is liberated, according to the equation

$$2(Na_3VO_4) + H_2O = Na_4V_2O_7 + 2NaHO.$$

This remarkable reaction was carefully investigated, as is seen in the sequel.

I have not been successful in several attempts to prepare a tribasic sodium vanadate containing basic hydrogen. All the reactions which with the corresponding phosphate yield hydrogen-sodium salts give with the vanadate the tetrabasic compound above mentioned. The orthovanadates of most of the metals are insoluble compounds obtained

by precipitating neutral solutions of the soluble metallic salts with a solution of orthovanadate of sodium. The reactions of the more important metals are as follows:—

Reactions of the Orthovanadates.

1. Ferric salt . . . Gelatinous precipitate of a light brownish-yellow colour, soluble in hydrochloric, insoluble in acetic acid.
2. Ferrous salt . . Dark grey precipitate.
3. Manganous salt . Brownish-yellow crystalline precipitate.
4. Zinc salt . . . White gelatinous precipitate.
5. Cobalt salt . . . Brown-grey gelatinous precipitate.
6. Nickel salt . . . Canary-yellow crystalline precipitate.
7. Aluminium salt . Bright yellow gelatinous precipitate, soluble in excess of both reagents; on boiling a white precipitate is again thrown down.
8. Copper salt . . . Apple-green coloured precipitate.
9. Mercuric salt . . Orange-yellow precipitate.

The reaction which serves best to distinguish the ortho- from the metavanadates is that of the corresponding copper salts. Orthovanadate of copper possesses a bright apple-green colour, whilst the metavanadate falls down a light yellow crystalline powder.

2. *Tetrasodium Vanadate, or Pyrovanadate*, $Na_4V_2O_7+18H_2O$.—This salt crystallizes in beautiful six-sided tables. It is easily soluble in water, insoluble in alcohol, and is precipitated from aqueous solutions by the latter liquid in the form of white scales of a pearly lustre. The pyrovanadate can be readily obtained by fusing one molecule of vanadium pentoxide (V_2O_5) with two molecules of sodium carbonate (Na_2CO_3), dissolving and crystallizing. It can also be obtained by the decomposition of the orthovanadate in aqueous solutions. As long as the tetrabasic salt contains free alkali, from the decomposition of the orthovanadate, the precipitate with alcohol forms oily drops, which only solidify after some time, whilst the pure salt is at once thrown down in the form of silky scales. If the fusion of vanadium pentoxide with three molecules of carbonate of soda be not completed at a very high temperature, the carbonate is not fully decomposed, and the fused mass when dissolved in water crystallizes at once in six-sided tables, or, if the solution be very concentrated, in nodular groups of needle-shaped crystals. The tetrabasic salt is more easily fusible than the tribasic salt, and on cooling from fusion it also forms a crystalline mass.

Decomposition of Tribasic into Tetrabasic Vanadates by boiling the aqueous solution.—That a decomposition of the above nature takes place is seen by the analyses of the different samples of 4 basic sodium salt which follow, not one of which was prepared by fusing two molecules of the carbonate with only one of vanadic acid, but by repeatedly recrystallizing the tribasic salt. The decomposition is not brought about by atmospheric carbonic acid; for in the following experiments the solution of the salts and the filtration of their solutions were effected in an apparatus from which all access of carbonic acid

was so completely excluded that the alkaline mother liquor from the tetrabasic salt did not effervesce on the addition of excess of acid.

This apparatus consisted of two flasks connected with each other in such a way that the liquid contained in one of them could be passed into the other by compressing an india-rubber ball, and before the liquid entered the second flask it passed through a wide piece of glass-tubing in which a small filter was placed. The apertures were then closed by tubes containing solid caustic soda, and the salt could thus be dissolved in alcohol or water without any fear of entrance of carbonic acid.

2·0393 grms. pure V_2O_5 and 3·7 grms. pure carbonate of soda were mixed and fused until no further effervescence occurred. The loss of weight amounted to 1·441 grm., whilst the theoretical loss for three molecules of CO_2 is 1·474 grm. The fused mass was dissolved in water and boiled for some time in an atmosphere free from carbonic acid, and finally precipitated with an excess of strong alcohol. After filtration the clear solution containing the caustic soda formed by the decomposition was neutralized by standard hydrochloric acid; it required 4 cub. centims. for saturation (1 cub. centim. $=0·0366$ grm. H Cl), corresponding to 0·124 grm. Na_2O. The precipitate was again dissolved in a small quantity of water and reprecipitated by alcohol; this second solution needed 4·6 cub. centims. of acid for saturation, corresponding to 0·1429 grm. Na_2O. A third repetition of the process showed that 2 cub. centims. of acid was needed, or 0·062 grm. Na_2O. Thus altogether 0·3289 grm. of Na_2O was obtained, or nearly half the amount required by the formula $2Na_3VO_4=Na_4V_2O_7+Na_2O$, namely 0·692 grm. The alcoholic solutions were free from carbonic acid, and they yielded, on addition of silver nitrate, a brown precipitate of silver oxide. They were likewise proved, by evaporation and treatment with oxalic acid, to be free from any trace of vanadic acid.

From the above experiment it is seen that the decomposition of the tetrasodium salt goes on by degrees, a fresh portion of free soda being found in solution each time the salt is dissolved and precipitated; it is even possible that the precipitation with alcohol causes a partial recombination of the caustic soda with the tribasic salt.

Analyses of Tetrasodium Vanadate. Vanadium determinations:—

(1) 1·0325 grm. of crystallized pyro-salt was dissolved in a small quantity of water and mixed with pure chloride of ammonium. After standing for twelve hours the insoluble metavanadate of ammonium* filtered off, washed first with a mixture of a saturated aqueous solution of sal-ammoniac and alcohol, and lastly with pure alcohol. On ignition 0·2995 grm. V_2O_5 was left, corresponding to 29·00 per cent. of V_2O_5, or 16·29 per cent. of vanadium.

(2) 1·3155 grm. of crystallized salt from another preparation, precipitated as above with sal-ammoniac, gave 0·3680 V_2O_5, corresponding to 27·97 per cent. of V_2O_5, or to 15·71 per cent. of vanadium.

* This reaction shows that the pyrovanadate of ammonium is not formed by double decomposition, but that the meta-salt is precipitated whilst the solution becomes alkaline. Thus:—

$$Na_4V_2O_7+4NH_4Cl=4NaCl+2(NH_4VO_3)+2NH_3+H_2O.$$

(3) 0·5227 grm. of substance was dissolved in water and reduced by means of zinc and sulphuric acid until the liquid acquired the permanent lavender tint of hypovanadous salt. A standard permanganate solution (1 cub. centim.=0·00066 grm. oxygen) was then added until the oxidation was complete; cub. centims. needed, 57·8=0·03815 grm. oxygen, corresponding to 0·1451 V_2O_5, or 15·60 per cent. of vanadium.

(4) 0·5858 grm. substance was precipitated with lead acetate, and yielded 0·6845 grm. of $2(Pb_2V_2O_7)+PbO$ (see lead salts) dried at 100°. Hence the pyro-salt contained 0·09487 grm. of vanadium, or 16·19 per cent.

(5) 0·5285 grm. of a third preparation yielded on precipitation with sal-ammoniac 0·1506 V_2O_5, corresponding to 16·06 per cent. of vanadium.

Sodium determinations:—

(1) 0·5858 grm. substance (Analysis No. 4) yielded in the filtrate from the lead precipitate 0·2655 grm. Na_2SO_4, corresponding to 14·67 per cent. of sodium.

(2) 0·5415 substance of another preparation yielded in a similar way, on evaporation and ignition, 0·2470 grm. Na_2SO_4, corresponding to 14·79 per cent. of sodium in the crystallized salt.

(3) 0·5285 grm. of the crystals (Analysis No. 5) gave 0·1925 grm. NaCl, corresponding to 14·57 per cent. of sodium.

Water Determinations.—The crystals lose at 100° C. seventeen molecules of water; at 140° C. eighteen molecules are driven off:—

(1) 0·572 grm. crystals dried at 140° lost 0·290 grm., or 50·69 per cent. of water.
(2) 0·5415 grm. lost on ignition 0·2893, or 53·4 per cent. of water.
(3) 0·5285 grm. lost on ignition 0·2719, or 51·44 per cent. of water.

In vacuo over sulphuric acid or at 100° C.:—

(1) 0·6535 grm. *in vacuo* lost 0·3185=48·73 per cent.
(2) 0·499 grm. of another preparation lost *in vacuo* 0·234=46·89 per cent.
(3) 1·0755 grm. dried at 100° lost 0·5205=48·39 per cent.
(4) 0·572 grm. dried at 100° lost 0·279 =48·77 per cent.

The numbers obtained from the foregoing analyses agree with those calculated from the formula

$$Na_4V_2O_7+18H_2O.$$

	Calculated.		Found.					Mean.
Na_4 . . .	92·0	14·58	14·67	14·79	14·57	——	——	14·68
V_2 . . .	102·6	16·27	16·29	15·71	[15·60]	16·19	16·06	16·06
O_7 . . .	112·0	17·77	——	——	——	——	——	——
$18H_2O$ . .	324·0	51·38	50·69	53·40	51·44	——	——	51·84
	630·6	100·00						

When a solution of tetrasodium vanadate is treated with carbonic acid the salt is

decomposed into sodium carbonate, which crystallizes out, and sodium metavanadate, which, being the more soluble salt, remains in solution; thus:—

$$Na_4V_2O_7+CO_2=2NaVO_3+Na_2CO_3.$$

The insoluble pyrovanadates precipitated in solutions of the various metals possess properties generally similar to those of the corresponding tribasic vanadates.

Calcium Vanadates.

If to a freshly prepared solution of trisodium vanadate a solution of chloride of calcium be added, a white precipitate falls down, whilst the liquid possesses a strongly alkaline reaction and absorbs carbonic acid from the air. The precipitate is a mixture of calcium pyrovanadate and calcium hydroxide; the tribasic calcium salt, therefore, cannot thus be obtained, as it at once decomposes as follows:—

$$Ca_3V_2O_8+H_2O=Ca_2V_2O_7+CaH_2O_2.$$

Calcium Pyrovanadate, $Ca_2V_2O_7+2\frac{1}{2}H_2O$.—This compound is precipitated as a white amorphous powder when a solution of chloride of calcium is added to one of the tetrabasic sodium salt. The salt was dried at 100° C., and of this dry salt 0·132 grm. lost on ignition 0·0270 grm., corresponding to 12·63 per cent. of water. For the calcium determination 0·3366 grm. was dissolved in acetic acid and precipitated by oxalic acid, the liquid being warmed until all the vanadic acid was reduced; the precipitation of the oxalate had to be twice repeated in order to free the precipitate completely from vanadium. 0·1956 grm. $CaCO_3$ was thus obtained, corresponding to 23·23 per cent. of calcium, and the filtrate yielded on evaporation 0·1802 grm. V_2O_5, or the salt contained 30·16 per cent. of vanadium.

These numbers correspond to the formula

$$Ca_2V_2O_7+2\tfrac{1}{2}H_2O.$$

	Calculated.		Found.
Ca_2	80·0	23·56	23·23
V_2	102·6	30·21	30·16
O_7	112·0	32·98	——
$2\frac{1}{2}H_2O$ . . .	45·0	13·25	12·63
	339·6	100·00	

Barium Pyrovanadate, $Ba_2V_2O_7$.—The dibasic barium salt is anhydrous, but otherwise it closely resembles the corresponding calcium compound. It is slightly soluble in water. For analysis it was dried at 100° C. 0·438 grm. dissolved in hydrochloric acid and precipitated with sulphuric acid yielded 0·4097 grm. $BaSO_4$, corresponding to 54·69 per cent. of barium. The filtrate from the barium precipitate left on evaporation 0·1678 grm. V_2O_5, corresponding to 21·5 per cent. of vanadium.

	Calculated.		Found.
Ba_2	274·0	56·08	54·69
V_2	102·6	20·99	21·50
O_7	112·0	22·93	——
	488·6	100·00	

Lead Vanadates.

Three native lead vanadates are known.

(*a*) Lead metavanadate, $Pb(VO_3)_2$, occurs as Dechenite.

(*b*) Lead pyrovanadate, $Pb_2V_2O_7$, occurs as Descloizite.

(*c*) Lead orthovanadate and lead chloride, $3(Pb_3(VO_4)_2)+PbCl_2$, occurs as vanadinite.

1. *Basic Pyrovanadate of Lead*, $2(Pb_2V_2O_7)+PbO$.—When a solution of the tetrasodium vanadate is mixed with a solution of lead acetate, a pale yellow precipitate is thrown down, and the liquid acquires an acid reaction.

The properties of this salt have already been described.

For analysis the salt was dissolved in nitric acid, and (with the exception of No. 1) the lead precipitated by sulphuric acid. The sulphate of lead was found to be quite free from vanadium, and the vanadic acid contained no lead provided care had been taken to remove all nitric acid by evaporation, and if the liquid was mixed with alcohol before the lead sulphate was filtered.

(1) From a tetrasodium salt which had been only once recrystallized, substance taken 0·3935 grm.; fused with bisulphate of potash, weight of $PbSO_4$=0·4084 grm., corresponding to 70·92 per cent. of lead.

(2) 0·373 grm. of the same salt gave 0·0902 V_2O_5, or 13·55 per cent. of vanadium.

(3) 0·365 grm. substance gave 0·3732 grm. $PbSO_4$, or 69·85 per cent. of lead and 0·086 V_2O_5, or 12·98 per cent. of vanadium.

(4) 0·5195 substance gave 0·5311 $PbSO_4$ or 69·83 per cent. of lead, and 0·125 V_2O_5, or 13·52 per cent. of vanadium.

(5) 0·681 substance gave 0·7036 $PbSO_4$ or 70·57 per cent. of lead, and 0·158 V_2O_5, or 13·03 per cent. of vanadium.

These numbers correspond to the formula $2(Pb_2V_2O_7)+PbO$.

	Calculated.		Found.				Mean.
Pb_5 .	1035·0	69·92	70·92	69·85	69·83	70·57	70·29
V_4 .	205·2	13·86	13·55	12·98	13·52	13·03	13·27
O_{15} .	240·0	16·22	——	——	——	——	——
	1480·2	100·00					

2. *Lead Orthovanadate*, $Pb_3(VO_4)_2$.—The tribasic vanadate of lead falls as an insoluble nearly white powder when tribasic sodium salt is precipitated by lead acetate. 0·7245 of the substance, when decomposed by nitric acid and precipitated by sulphuric

acid, yielded 0·1515 of V_2O_5, or contained 11·75 per cent. of vanadium, the percentage required by the formula being 12·04.

3. *Lead Orthovanadate and Lead Chloride, artificial Vanadinite*, $3(Pb_3(VO_4)_2)PbCl_2$, or lead trivanado-chlorhydine, $\left.\begin{matrix}3VO''' \\ Pb_5 \\ Cl\end{matrix}\right\}O_9$.

If oxide of lead, vanadic acid, and chloride of lead be fused together for a few hours in the proportions in which they are contained in the above formula, the mass after slowly cooling is found to consist of a greyish-yellow crystalline substance, in the interstices of which groups of needle-shaped crystals occur. The fused mass on boiling in water is soon reduced to a powder entirely consisting of fine crystals. This crystalline powder is boiled with water until no further trace of chlorine can be detected in the washings when it is dried ready for analysis. The crystals obtained were too small for measurement; they were, however, seen to consist of hexagonal prisms; the faces of the hexagonal pyramid could not be identified. The crystals have a yellow colour, and possess the waxy lustre characteristic of the natural mineral.

(1) 0·738 substance fused with Na_2CO_3 gave 0·0525 Ag Cl and 0·0122 Ag, or 2·33 per cent. of chlorine.

(2) 0·4135 substance dissolved in nitric acid and precipitated with silver nitrate, gave 0·0347 Ag Cl and 0·0003 Ag, or 2·17 per cent. of chlorine.

(3) 0·5582 substance dissolved in nitric acid and precipitated with sulphuric acid, gave 0·5881 $PbSO_4$, or 71·96 per cent. of lead, and 0·1104 of V_2O_5, corresponding to 11·11 per cent. of vanadium.

(4) 0·5443 substance of another preparation, dissolved in nitric acid and precipitated with silver nitrate, gave 0·045 Ag Cl and 0·0035 Ag, corresponding to 2·17 per cent. chlorine, and 0·5705 $PbSO_4$, or 71·57 per cent. of lead.

The following gives the composition of various specimens of natural vanadinites compared with that of the artificial mineral:—

		Natural vanadinites.				Artificial vanadinites.	
	Calculated $3(Pb_3(VO_4)_2)PbCl_2$.	Zimapan (Berzelius).	Windischkappel (Rammelsberg).	Wieklow.	Beresesowsk (Struve).	(1)	(2)
Lead . .	73·08	70·40	71·20	68·72	73·76	71·96	71·57
Vanadium .	10·86	——	9·77	13·15	9·54	11·11	——
Phosphorus	——	——	——	——	——	1·34	——	——
Chlorine .	2·56	2·54	2·23	2·44	2·46	2·33	2·17
Oxygen. .	13·55	——	——	——	——	——	——

The specific gravity of the artificial vanadinite at 12° C. is 6·707, that of the natural mineral varies from 6·66 to 7·2*.

* Pyromorphite and apatite were prepared artificially for the first time in 1852 by Manross (Ann. Ch. Pharm. lxxxii. p. 348), and afterwards by Deville and Caron, and Debray. Mimetesite has also been recently artificially prepared by Lechartier (Comptes Rendus, 1867, lxv. p. 172).

Silver Vanadates.

1. *Silver Orthovanadate, or Tribasic Silver Vanadate*, Ag_3VO_4, is precipitated as a deep orange-coloured powder when a freshly prepared solution of tribasic sodium salt is mixed with a perfectly neutral solution of silver nitrate. If the precaution of neutralizing the silver solution with carbonate of soda, filtering, and boiling be not adopted, a salt is precipitated which consists of a mixture of tribasic and tetrabasic silver salt. The colour of this mixed salt is lighter than that of the tribasic compound, and it gives on analysis a percentage of silver and vanadium intermediate between the two salts.

Silver orthovanadate is easily soluble in nitric acid and ammonia. For analysis it was dissolved in nitric acid, the silver being precipitated as chloride, and the vanadium estimated in the filtrate.

(1) 0·385 substance gave 0·369 Ag Cl and 0·0076 Ag, or 74·12 per cent. of silver, and 0·0795 V_2O_5, or 11·59 per cent. of vanadium.

(2) 0·522 substance, of another preparation, gave 0·508 Ag Cl and 0·0016 Ag, or 73·54 per cent. of silver, and 0·111 V_2O_5, or 11·94 per cent. of vanadium.

Hence we have:—

	Calculated.		Found.		
			(1)	(2)	Mean.
Ag_3 . .	324·0	73·75	74·12	73·54	73·83
V . .	51·3	11·67	11·59	11·94	11·86
O_4 . .	64·0	14·58	——	——	
	439·3	100·00			

2. *Tetrabasic Silver Vanadate*$=Ag_4V_2O_7$.—This salt is prepared by precipitating a solution of pure tetrasodium salt with a neutral solution of silver nitrate. It is a dense yellow precipitate, settling very easily when the liquid is warmed, and resembling in its appearance ordinary tribasic phosphate of silver.

(1) 0·4725 substance gave 0·4105 Ag Cl and 0·0051 Ag, or 66·45 per cent. of silver, and 0·1345 V_2O_5, corresponding to 15·99 per cent. vanadium.

Hence we have:—

	Calculated.		Found.
Ag_4 . .	432·0	66·81	66·45
V_2 . .	102·6	15·87	15·99
O_7 . .	112·0	17·32	——
	646·6	100·00	

From the foregoing experiments on the vanadates it appears:

(1) That the soluble tribasic salts are less stable at the ordinary temperature than the tetrabasic compounds, Na_3VO_4, splitting up in solution into free caustic soda and the pyro-salt.

(2) That at a high temperature, on the other hand, the tribasic form is the most

stable, V_2O_5 liberating three molecules of CO_2 when fused with carbonate of soda, but forming a monobasic (meta)salt when boiled with a solution of alkaline carbonate.

(3) That as the majority of the naturally occurring vanadates are tribasic compounds, we may assume that these have been produced at a high temperature.

(4) That in aqueous solutions the soluble pyrovanadates are easily decomposed by carbonic acid into an alkaline carbonate and a monobasic or metavanadate.

Hence the order of stability of the different vanadates at the ordinary temperatures is as follows:—

(1) Monobasic or metavanadates.
(2) Tetrabasic or pyrovanadates.
(3) Tribasic or orthovanadates.

In the phosphorus series the order of stability is (as is well known) exactly the reverse of this, the tribasic phosphoric acid and soluble orthophosphates being most stable, and being formed from the other two classes of acids and soluble salts, either by ebullition alone or in presence of weak acids.

I have much pleasure in acknowledging the able assistance which I have received from Messrs. ŒLHOFER and FINKELSTEIN in carrying out the above investigation.