

629. Condensed Ions in Aqueous Solutions. Part II.*
Compounds of Quinquevalent Vanadium with Orthophosphate.

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Phase studies of the system vanadium(v) oxide-phosphoric oxide-water at 25° with from 5% to 65% phosphoric oxide have shown the presence of two sparingly soluble yellow compounds $V_2O_5 \cdot P_2O_5 \cdot 6H_2O$ and $V_2O_5 \cdot 1.5P_2O_5 \cdot 6.5H_2O$ as stable solid phases.

Ion-exchange and potentiometric titration studies of the red solutions obtained by adding phosphoric acid to solutions of vanadates have indicated a decavanadophosphate ion to be the only heteropolyanion formed.

EARLY studies¹⁻³ revealed two types of compounds containing quinquevalent vanadium and orthophosphate. In one series the ratio of vanadium to phosphate was low and the compounds were yellow, while in the other the ratio was high and the colour red. Modern views accord with those of Friedheim³ who regarded the yellow compounds as containing basic (*i.e.*, cationic) vanadium and the red ones as containing acidic (anionic) vanadium (vanadophosphates).

Various yellow vanadyl(v) phosphates have been described and the ratios of vanadium to phosphate found have been 2 : 1, 3 : 2, 1 : 1, 2 : 3, and 1 : 2, of which the value 1 : 1 has been most frequently recorded.^{4,5} In a study of the system vanadium(v) oxide-phosphoric oxide-water at 25°, Tietze⁶ had difficulties in that metastable solid phases were found to separate, but he found evidence for compounds with vanadium to phosphate ratios of 1 : 1, 2 : 3, and 1 : 3. Of these the first two appear to be stable and the third metastable.

Solid vanadophosphates have been reported with the ratios of vanadium to phosphorus of 4 : 1,¹ 8 : 1,⁷ 10 : 1,⁸ 12 : 1,^{3,5} and 20 : 1.² Jander and Jahr⁷ observed that when phosphoric acid was added to vanadic acid the ion formed had approximately the same diffusion coefficient as the ion present in vanadic acid solutions. It was evident, however, that most of the knowledge of the nature of both the vanadyl phosphates and the phosphovanadates was based on the analytical data for solid materials precipitated under a wide

* Part I, *J.*, 1958, 4708.

¹ Ditte, *Compt. rend.*, 1886, **102**, 757, 1019, 1105.

² Gibbs, *Amer. Chem. J.*, 1885, **7**, 209.

³ Friedheim and Szamatolsky, *Ber.*, 1890, **23**, 1530.

⁴ Rosenheim and Yang, *Z. anorg. Chem.*, 1923, **129**, 181; Rosenheim, Brauer, and Materne, *ibid.*, 1934, **220**, 73; Jander, Jahr, and Witzmann, *ibid.*, 1934, **217**, 65.

⁵ Souchay and Dubois, *Ann. Chim. (France)*, 1948, **3**, 88.

⁶ H. R. Tietze, M.Sc. Thesis, London, 1952.

⁷ Jander and Jahr, *Kolloid-Beih.*, 1934, **41**, 1, 297.

⁸ Rosenheim and Pieck, *Z. anorg. Chem.*, 1916, **98**, 223.

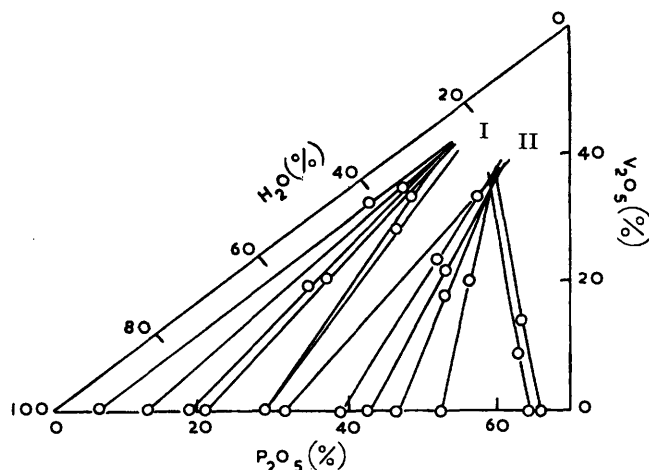
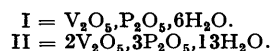
variety of conditions. The present studies had as their object a more systematic study of both systems.

EXPERIMENTAL

Phase-diagram Studies.—Vanadic oxide was added in small portions to solutions of phosphoric acid with stirring until an undissolved residue remained. The solutions and solids were left in contact with intermittent stirring in stoppered tubes immersed in a thermostat-bath at 25° for three months, by which time no further changes in the compositions of the aqueous phases could be detected. The liquids and the moist solid phases were then separated by

TABLE I. *The system V₂O₅-P₂O₅-H₂O at 25°*

Solution		Moist solid phase		Solution		Moist solid phase	
V ₂ O ₅ (%)	P ₂ O ₅ (%)	V ₂ O ₅ (%)	P ₂ O ₅ (%)	V ₂ O ₅ (%)	P ₂ O ₅ (%)	V ₂ O ₅ (%)	P ₂ O ₅ (%)
0.6	5.7	32.4	26.9	0.05	38.4	25.8	39.0
0.5	12.6	35.2	30.5	0.07	39.8	22.6	41.6
0.2	18.2	20.0	24.8	0.07	45.8	17.9	43.9
0.4	19.0	21.7	25.3	0.07	52.0	20.5	46.4
0.35	28.6	23.4	32.1	0.17	64.6	8.0	59.0
0.25	28.7	16.7	15.8	0.12	64.6	14.2	56.3
0.3	30.9	33.9	40.4				

FIG. 1. *The system V₂O₅-P₂O₅-H₂O at 25°.*

filtration and aliquot parts or samples of each were analysed. The analytical data are given in Table 1 and in Fig. 1.

Ion-exchange Experiments.—(a) *Batch experiments.* Solutions (150 ml.) of known composition were left in contact with 0.5-g. portions of anion-exchanger (DeAcidite FF, Cl-form, water regain 1.82) for 150–200 hr. The solution was then separated from the resin, and aliquot portions were analysed. From the analytical data the R_v values^{9,10} were calculated (see Table 2), namely:

$$R_v = \frac{\text{G.-atoms of V in solution initially} - \text{g.-atoms of V in solution finally}}{\text{G.-atoms of Cl in solution finally}}$$

$$\text{and } R_p = \frac{\text{G.-atoms of P in solution initially} - \text{g. atoms of P in solution finally}}{\text{G.-atoms of Cl in solution finally}}$$

(b) *Column experiments.* Solutions (500 ml.) of known composition were passed during 3 days through a small column of anion exchanger (0.5 g. of DeAcidite FF, Cl-form, water regain 1.82), aliquot portions of the effluent were analysed, and R_v and R_p calculated (Table 2). The choice of a resin of water regain 1.82 was governed by the inference (drawn from Jander's

⁹ Russell and Salmon, *J.*, 1958, 4708.

¹⁰ Everest and Salmon, *J.*, 1954, 2348.

observation ⁷) that the vanadophosphate ion was comparable in size with the decavanadate ion (see ref. 9).

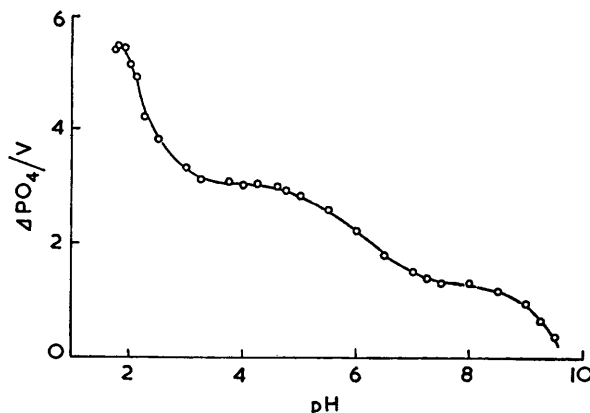
Potentiometric Titration.—An aqueous solution of ammonium vanadate (0.068 g.-atom of V; pH 9.5) and one of ammonia (pH 9.5) were each titrated with phosphoric acid (0.5 mole), and the changes in pH during the titration followed by use of a glass electrode–calomel electrode system with a commercial pH-meter. If, at a given pH, P_x g.-atoms of phosphorus (as H_3PO_4) had been added to the ammonium vanadate solution and P_y g.-atoms of phosphorus to the ammonia

TABLE 2. *Anion-exchange experiments with vanadophosphate solution using DeAcidite FF (0.5 g. of Cl-form, water regain 1.82).*

Experiment	Initial solution			Vol. used (ml.)	R_v	R_p
	10 ² g.-atoms/l. V	P ^c	pH			
Column	6.5 ^a	6.5	1.8	500	3.17 ^e	0.33 ^e
Batch	6.5 ^a	6.5	1.8	150	3.29 (±0.03)	0.37 (±0.03)
"	6.6 ^b	d	1.8 ^d	150	3.3	g
"	6.6 ^b	d	2.6 ^d	150	3.4	g
"	6.6 ^b	d	2.9 ^d	150	3.3	g
"	6.6 ^b	d	3.5 ^d	150	3.0	g
"	6.6 ^b	d	4.0 ^d	150	3.0	g
"	6.6 ^b	d	4.4 ^d	150	2.9	g
"	6.6 ^b	d	4.9 ^d	150	2.6	g
"	6.6 ^b	d	5.6 ^d	150	2.6	g
"	6.6 ^b	d	5.9 ^d	150	2.6	g
"	7.4 ^b	3.2	5.0—5.4	150	2.55 (±0.05) ^e	0.27 (±0.06) ^e
"	7.4 ^b	3.3	5.6—5.9	150	2.55 (±0.10) ^e	0.24 (±0.06) ^e

^a As vanadic acid prepared from ammonium vanadate solution by passage through ZeoKarb 225 (H-form) column. ^b As ammonium vanadate. ^c Added as orthophosphoric acid. ^d pH varied by addition of varying amounts of phosphoric acid. ^e Mean of 4 experiments. Mean of 3 experiments. ^g Not determined.

FIG. 2. *Titration of ammonium vanadate with phosphoric acid.*



solution, then it was found that $P_x \gg P_y$. It was assumed that P_x represented phosphoric acid used to neutralise the free ammonia arising by hydrolysis of the ammonium vanadate solution (P_z) and additional phosphoric acid to provide hydrogen ions used in a condensation reaction. A further assumption made was that $P_y = P_z$ and hence that $\Delta P = P_x - P_y$ represented the phosphoric acid used in the latter reaction. A plot of $\Delta PO_4/V$ (where $V = 0.068$ g.-atom of vanadium) against pH is given in Fig. 2.

Analysis.—Vanadium and chloride were determined as previously described,⁹ and phosphate gravimetrically as ammonium phosphomolybdate after removal of vanadium by reduction to vanadium(IV) and sorption of the latter on a column of ZeoKarb 225 cation-exchanger.¹¹

RESULTS AND DISCUSSION

Vanadyl Phosphates.—Because of the very low solubility of the yellow vanadyl phosphates in phosphoric acid solution (Fig. 1, Table 1) it was impossible to discuss the break in

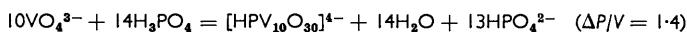
¹¹ Salmon and Tietze, *J.*, 1952, 2324.

the solubility isotherm corresponding to the change in solid phase, but from the tie lines (Fig. 1) it is evident that a compound of composition $V_2O_5 \cdot P_2O_5 \cdot 6H_2O$ (I) is the stable solid phase for solutions containing from 5% to ~30% phosphoric oxide and that from these to at least 65% phosphoric oxide the stable solid phase is $2V_2O_5 \cdot 3P_2O_5 \cdot 13H_2O$ (II). Compound (I) corresponds to $(VO)PO_4 \cdot 3H_2O$ or to $(VO_2)H_2PO_4 \cdot 2H_2O$, and compound (II) to $(VO)_2(HPO_4)_3 \cdot 5H_2O$ or to $[(VO_2)H_2PO_4]_2 \cdot H_3PO_4 \cdot 3H_2O$. The vanadyl(v) cation in solution appears to be $[VO_2]^+$ (ref. 12), and this is in accord with its very low relative affinity (as compared with hydrogen ions) for a cation-exchanger. Nevertheless, formulation of the solid compounds as derivatives of the VO^{3+} cation is preferred for three reasons: (i) the low solubility of the compounds in phosphoric acid is typical of trivalent phosphates [*e.g.*, Fe(III), Bi(III)] rather than of univalent ones; (ii) in no case so far studied (see, *e.g.*, ref. 13) has a primary (*i.e.*, dihydrogen) phosphate appeared as solid phase in contact with solutions containing less than 30% phosphoric oxide; and (iii) all compounds containing "phosphoric acid of crystallisation," such as $[(VO_2)H_2PO_4]_2 \cdot H_3PO_4 \cdot H_2O$ are readily soluble, deliquescent compounds (see, *e.g.*, ref. 13*a*) whereas compound II is highly insoluble.

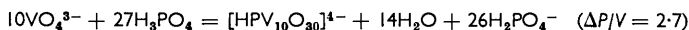
In view of the very low solubility of the compounds no attempt was made to study their state in solution.

Vanadophosphates.—The results of the ion-exchange experiments with the red vanadophosphate solutions (Table 2) are consistent with the sorption of $[HPV_{10}O_{30}]^{4-}$ ions ($R_v = 2.5$, $R_p = 0.25$) over the pH range 4.9—5.9, of $[H_2PV_{10}O_{30}]^{3-}$ ions ($R_v = 3.3$, $R_p = 0.33$) over the pH range 1.8—2.9, and of a mixture of these between pH 2.9 and 4.9. There seems to be little competition from isopolyvanadic ions or from phosphate ions. Since in all the solutions studied the amount of phosphate present exceeds by at least four-fold that required to form decavanadophosphate ions the concentration of isopolyvanadate is probably low. Although some bivalent HPO_4^{2-} ions must be present in the solution of $pH > 5$ the proportion of these is probably insufficient to complete effectively with the decavanadophosphate which presumably is like the decavanadate ion in being very strongly sorbed. Results for solutions of $pH > 6$ were variable and inconsistent.

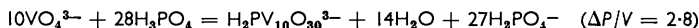
The plot of $\Delta P/V$ against pH (Fig. 2) shows two inflexions, at about $\Delta P/V = 1.3$ and 3.0, which would correspond respectively to the reactions:



and



It may be noted that the first inflexion occurs at $pH 7-8$, at which the phosphate ions are present mainly as HPO_4^{2-} ions, and the second at $pH 4.6$ at which the phosphate ions will be present mainly as $H_2PO_4^-$ ions. The fact that the experimental value of $\Delta P/V$ (3.0) is slightly greater than that calculated (2.7) may arise from incomplete dissociation of the phosphoric acid to $H_2PO_4^-$. If this is accepted then the value of $\Delta P/V = 3.3$ at $pH 3$ is in reasonable accord with the reaction:



since at this pH the first dissociation of the phosphoric acid will be still less complete. Thus the results of both ion-exchange and potentiometric studies can be explained in terms of a decavanadophosphate ion which is $[H_2PV_{10}O_{30}]^{3-}$ at $pH 1.8$ and $[HPV_{10}O_{30}]^{4-}$ at $pH \sim 6$ (and this possibly present in diminishing amount up to $pH 8$).

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¹² Carpenter, *J. Amer. Chem. Soc.*, 1934, **56**, 1847.

¹³ (a) Salmon and Terrey, *J.*, 1950, 2813; (b) Jameson and Salmon, *J.*, 1954, **28**, 4013; 1955, 360; (c) Redfern and Salmon, *J.*, 1961, 291.