174. *Physicochemical Studies of Complex Acids. Part XV. The Basic Nature of Vanadium Pentoxide.*

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Vanadium pentoxide is shown to be amphoteric, for it dissolves in solutions of acids to an extent depending upon the strength of the acid and the temperature. As a base, the pentoxide is extremely weak, and even in the presence of an excess of acid it is probable that it does not combine much beyond the stage represented by VO_2Cl.

Although vanadium pentoxide is but slightly soluble in water to form a relatively strong polyvanadic acid, it is more so in weak acids and becomes appreciably soluble in strong acids. Fischer (*Trans. Amer. Electrochem. Soc.*, 1916, **30**, 190) determined its solubility in hydrochloric and sulphuric acid solutions of increasing concentration, and Meyer and Aulich (*Z. anorg. Chem.*, 1930, **194**, 278) worked with solutions containing 0—88% of sulphuric acid. Although we have been unable to confirm their results, we have found that the amount of vanadium pentoxide which dissolves increases with increasing acid concentration. This would suggest that vanadium pentoxide assumes basic properties or else that it forms complex acids with hydrochloric and sulphuric acids. The former view is more probable, since Dülberg (*Z. physikal. Chem.*, 1903, **45**, 129) has shown that in acid solutions vanadium migrates to the kathode.

With the exception of sulphuric acid, however, acids fail to produce solid compounds with vanadium pentoxide. Owing to the great ease with which quinquevalent vanadium salts hydrolyse, evaporation of hydrochloric or nitric acid solutions invariably leads to precipitation of the brownish-red hydrated pentoxide. Its basic nature is more apparent towards sulphuric acid, for when it is boiled with an excess of concentrated sulphuric acid very deliquescent golden-yellow, needle-shaped crystals separate, the composition of which has been stated to be $V_2O_5,2SO_3,xH_2O$ and $V_2O_5,3SO_3,3H_2O$ (Gerland, *Ber.*, 1878, **11**, 99; Ditte, *Compt. rend.*, 1886, **102**, 757; Munzing, "Die Verbindungen der Vanadinsäure mit Schwefelsäure," Berlin, 1889).

The work to be described falls into two sections. (1) The extent of precipitation and of redissolution has been studied when various acids are added in increasing amounts to sodium vanadate solutions. From very dilute solutions of alkali vanadate (0·01M and less) no vanadium pentoxide is precipitated. This is to be attributed to the difficulty with which sodium polyvanadate, $Na_2O,2{\cdot}5V_2O_5$ (see Britton and Welford, this vol., p. 764) is decomposed by strong acids, especially when the vanadium pentoxide eventually set free is insufficient to exceed the solubility of the oxide in the acid solutions. A difficulty was encountered in studying the reactions at ordinary temperatures owing to the great tendency of precipitated vanadium pentoxide to become peptised and thus to remain in an unfilterable colloidal suspension, the rate of precipitation being extremely slow. Also, as observed by Biltz (*Ber.*, 1904, **37**, 1098, 1770), precipitates of hydrated vanadium pentoxide produced by adding acids to vanadate solutions are gelatinous and readily become peptised on washing. The solutions were therefore boiled, for then not only is vanadium pentoxide precipitated as brownish-red flakes that are easy to manipulate, but the oxide held in colloidal suspension is thereby coagulated. Only by boiling could reproducible results be obtained.

(2) Direct measurements of the solubility of vanadium pentoxide in various acid solutions were made at 18° and 100°. If the pentoxide behaves as a base towards acids, then considerable differences are to be expected in its solubility in solutions of strong and weak acids. Acids were therefore selected, the strengths of which vary over a wide range. Hydrochloric, nitric, and perchloric acids were chosen as typical examples of strong acids, sodium hydrogen sulphate, *i.e.*, HSO_4', and trichloroacetic acid as moderately strong acids, and sulphuric acid as a dibasic acid containing two stages of ionisation of slightly different strengths. The typical weak acids were di- and mono-chloroacetic and acetic acids.

The investigation of the nature of vanadium pentoxide in acid solutions was also carried a stage further by means of measurements of electrical conductivity, p_H, and freezing points.

EXPERIMENTAL.

1. *The Action of Acids in Excess on Sodium Vanadate in Solution.*—In every case, 50 c.c. of sodium vanadate solution, having the concentrations indicated at the head of Tables I and II, were treated with the volume (*X* c.c.) of acid solutions given in the first column, boiled for about 5 mins., and then allowed to stand at room temperature until the precipitates had completely settled. The amounts of vanadium remaining in the liquid phases were estimated, and thence the percentage amounts of vanadium pentoxide precipitated were calculated. These percentages are recorded in Tables I and II and plotted in the figure, in which the number of equivs. of acid is shown in excess of the amounts required to decompose the sodium vanadate completely (col. 2). As stated above, vanadium pentoxide is not precipitated from dilute solutions of alkali vanadate by any of the three weak acids. Curve *F* and the last column of Table I refer to a series of solutions that had not been boiled. Comparison with curve *C* which refers to the same solutions after boiling shows that less vanadium pentoxide was precipitated than when the solutions had been boiled. If, however, boiling is prolonged, the vanadium pentoxide gradually becomes less soluble in the acids; *e.g.*, curve *K* represents the effect of boiling under a reflux

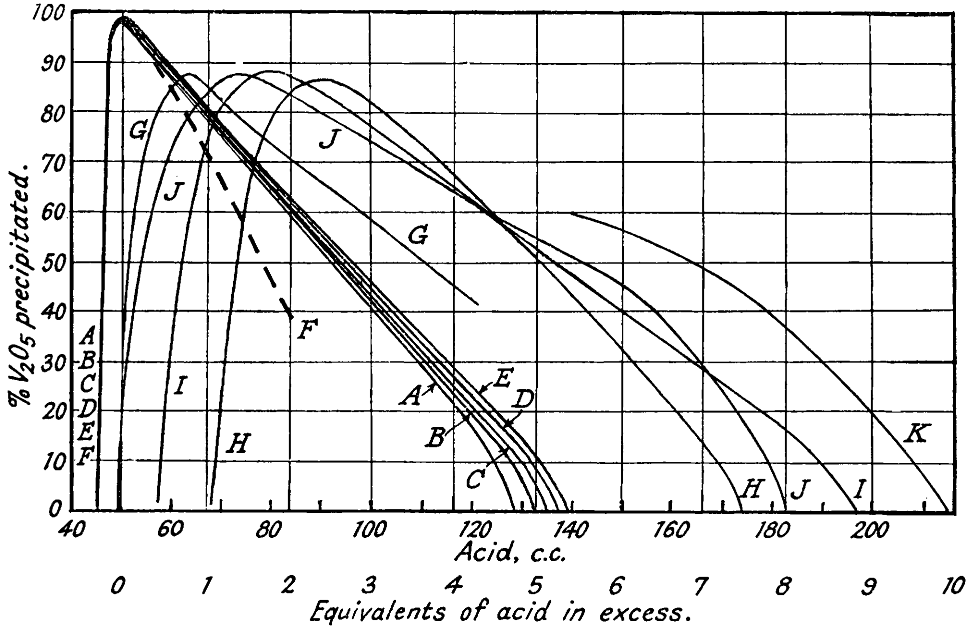

TABLE I.

Percentage Amounts of Vanadium Pentoxide Precipitated.

Acid, c.c. (*X*).	$\frac{HR}{V}$.	Na$_3$VO$_4$. Acid.	0·1M. 0·3N-HCl.	0·2M. 0·6N-HCl.	0·2M. 0·6N-CCl$_3$·CO$_2$H.	0·25M. 0·75N-HClO$_4$.	0·3M. 0·9N-HNO$_3$.	0·4M. 1·2N-HCl.	0·4M. 1·2N-HCl (18°).
45·0	−0·30		1·8	2·5	—	—	16·8	2·3	—
46·0	−0·24		—	—	—	33·8	—	—	—
47·5	−0·15		55·1	74·3	—	—	91·8	93·5	—
48·0	−0·12		—	—	—	83·6	—	—	—
50·0	0·00		96·6	98·9	15·8	98·6	99·1	98·6	99·8
55·0	0·30		92·5	93·5	72·1	94·2	93·8	93·7	92·5
60·0	0·60		86·3	87·2	84·1	88·3	88·0	87·5	84·7
65·0	0·90		—	—	87·9	—	—	—	—
70·0	1·21		75·0	76·2	81·5	77·1	76·8	76·8	65·8
80·0	1·81		62·2	63·4	73·6	65·6	66·2	65·3	47·0
100·0	3·00		40·1	42·7	58·9	44·6	45·1	43·4	0
120·0	4·22		16·3	21·1	42·7	24·3	25·3	22·7	0
130·0	4·82		0	4·8	—	11·6	13·2	10·0	0
Curve			*A*	*B*	*G*	*E*	*D*	*C*	*F*

TABLE II.

Percentage Amounts of Vanadium Pentoxide Precipitated.

H_2SO_4, c.c.	Equivs. H_2SO_4 / V.	Na_3VO_4.	0·125M.	0·25M.	0·50M.
		Acid.	0·375N.	0·75N.	1·5N.
50	0·00		0	0	7·9
60	0·60		0	31·0	72·6
70	1·21		22·9	75·8	86·9
80	1·81		80·0	85·7	85·3
90	2·41		86·7	83·2	—
100	3·01		81·1	75·9	74·6
110	3·61		73·0	70·5	—
120	4·22		63·4	56·2	63·0
140	5·42		43·3	46·8	53·3
160	6·62		21·1	32·2	36·8
170	7·23		8·4	—	—
180	7·83		0	19·7	9·5
200	9·04		0	0	0
210	9·64		0	0	0
Curve			*H*	*I*	*J*

Curve *K* (Fig. 1) represents the percentage precipitation obtained by adding various amounts of 1·5N-H_2SO_4 to 50 c.c. of M-Na_3VO_4, without boiling (cf. curve *J*).

condenser the solutions obtained by adding various amounts of 1·5N-sulphuric acid to 50 c.c. of 0·5M-Na_3VO_4 for 3 hours. When compared with curve *J* it will be seen that greater precipitation resulted from the treatment.

The precipitation data for the moderately strong acid, trichloroacetic acid, are incomplete, owing to errors introduced by decomposition of the acid into chloroform in more concentrated solutions, this being catalysed by the precipitated pentoxide.

2. *The Solubility of Vanadium Pentoxide in Acids.*—The solubility of vanadium pentoxide in acids was determined by shaking the solutions with excess of the pure dry oxide for a month at 18°. The solubilities are recorded in Table III in terms of g. and of g.-mols. of V_2O_5 per l.

TABLE III.

		Solubility of V_2O_5 per l.				HR (g.-mols.) / V (g.-atoms).	
		18°.		100°.			
Acid.	N.	G.	G.-mol.	G.	G.-mol.	18°.	100°.
HCl	2·00	36·40	0·200	32·60	0·179	5·00	5·57
	0·500	12·05	0·0662	10·65	0·0585	3·78	4·28
	0·200	5·40	0·0297	4·30	0·0237	3·37	4·23
HNO_3	0·900	22·80	0·125	14·95	0·0822	3·59	5·47
	0·400	11·60	0·0638	7·05	0·0387	3·13	5·16
	0·100	2·85	0·0157	1·90	0·0104	3·19	4·79
$HClO_4$	0·375	10·10	0·0555	—	—	3·38	—
	0·094	2·85	0·0157	—	—	3·00	—
H_2SO_4	1·800	32·55	0·179	20·60	0·113	5·02	7·94
	0·750	12·25	0·0838	8·70	0·0479	4·48	7·66
	0·180	4·15	0·0228	2·10	0·115	3·95	7·80
$NaHSO_4$	0·450	8·15	0·0448	2·30	0·0127	5·02	17·8
	0·225	4·30	0·0237	1·15	0·0063	4·75	17·8
	0·090	1·95	0·0107	0·55	0·0030	4·20	14·9
$CCl_3{\cdot}CO_2H$	0·888	12·50	0·0687	—	—	6·46	—
	0·222	5·80	0·0318	—	—	3·48	—
	0·089	2·60	0·0143	—	—	3·11	—
$CH_3{\cdot}CO_2H$	2·000	0·40	0·0022	—	—	45·5	—
	0·500	0·55	0·0030	—	—	82·8	—
	0·200	0·80	0·044	—	—	22·8	—

Monochloroacetic and formic acid tended to reduce the oxide to the quadrivalent stage. The data for 100° were obtained by heating the solutions obtained above for 3 hours in a steam-oven.

3. *Physicochemical Measurements on Acid Solutions of Vanadium Pentoxide.*—Solutions of hydrochloric, nitric, and sulphuric acids, 0·05N with respect to the acids and containing increasing

amounts of vanadium pentoxide, were prepared. Their specific conductivities were measured at 25° and are given below.

Specific conductivities at 25° *of* 0·05N-*acids* + *x*M-V_2O_5.

G.-mols. of V_2O_5 per l. = *x*.	0.	0·001.	0·002.	0·003.	0·004.	0·005.
HCl $\kappa \times 10^3$	20·0	19·3	18·7	18·0	17·4	16·8
HNO_3 $\kappa \times 10^3$	19·6	18·9	18·3	17·6	16·9	16·2
H_2SO_4 $\kappa \times 10^3$	13·6	13·1	12·7	12·3	11·8	11·3

The conductivity for each of the acid solutions diminishes as the vanadium pentoxide content is increased, suggesting that the oxide no longer functions as an acid but that it reacts with the strong acids, forming basic ions. Simple calculation reveals that the diminished conductivities may be explained by the formation of a partly ionised salt of the type VO_2R (R = Cl′, NO_3′, or $\frac{1}{2}SO_4''$) if the kation $VO_2^{\bullet}$ is assumed to have a mobility comparable with that of simple metallic kations. This view was confirmed by p_H measurements made by means of the glass electrode. Although this electrode is scarcely capable of accurately giving p_H values of solutions of strong acids, it was found that glass electrodes, which had been carefully calibrated in 0·05N-solutions of the respective acids, indicated slightly higher p_H values when vanadium pentoxide was present; *e.g.*, 0·05N-hydrochloric acid gave a p_H higher by 0·07 unit when 0·005M-pentoxide was added.

The combination which takes place between vanadium pentoxide and strong acids has a small, but definite, effect on the freezing point of the solutions; *e.g.*, 0·1N-hydrochloric acid has f. p. — 0·355°, but in presence of 0·1M-pentoxide the f. p. is −0·345°. The difference of 0·010° is thus to be attributed to the replacement of some hydrogen ions by some other kations, possibly $VO_2^{\bullet}$, the resulting salt not being ionised to the same extent as the hydrochloric acid itself.

DISCUSSION.

The figure shows that hydrochloric, nitric, and perchloric acids, in the particular concentrations used, cause vanadium pentoxide to be precipitated from alkali vanadate solutions before the stoicheiometric amounts of acid have been added. When 2·60 equivs. of a strong acid have been added to a solution of sodium orthovanadate, $Na_2O,2{\cdot}5V_2O_5$ is formed, this being the salt of the comparatively strong acid produced when vanadium pentoxide dissolves in water. The solubility of vanadium pentoxide in water is, however, only small, being slightly less than 0·002 g.-mol./l. Since hydrochloric acid is somewhat stronger than polyvanadic acid, addition of the former to sodium polyvanadate gradually causes replacement of the complex vanadic acid, $Na_2O,2{\cdot}5V_2O_5 + 2HCl = H_2O,2{\cdot}5V_2O_5 + 2NaCl$, and therefore as the equilibrium moves towards the right and the solubility of vanadium pentoxide is exceeded it will be increasingly precipitated. With very dilute solutions no vanadium pentoxide is precipitated even though an excess of mineral acid be added, but as the figure shows, precipitation occurs from 0·1M-vanadate and more concentrated solutions. Redissolution of the vanadium pentoxide takes place when a larger excess of acid is added; the precise amounts of acid required to effect dissolution depend on the strength of the acid and the concentrations of the solutions used (see figure). The three weak acids used cause no precipitation from vanadate solutions. This is attributed to the inability of these acids to replace the much stronger polyvanadic acid from sodium polyvanadate (cf. Britton and Robinson, J., 1932, 1955). The fact that the vanadium pentoxide dissolves in solutions of strong acids when in sufficient concentration reveals that the oxide is amphoteric and behaves as a base in presence of excess of strong acids. This is also brought out by the solubility data in Table III, which show that it is a very weak base, for considerable amounts of the weaker acids are required to effect its dissolution. On the other hand, the amount of vanadium pentoxide is proportionately larger in the dilute solutions than in the more concentrated; *e.g.*, 6·74 mols. of hydrochloric acid are required in 0·2N-solution to dissolve 1 mol. of pentoxide, whereas 10 mols. are required in 2N-acid. With a weak acid, like acetic, the molecular proportions are much greater. This, at first sight, might appear anomalous, for if vanadium pentoxide behaves purely as base, the reverse would be expected. Two influences come into play, however, when vanadium pentoxide dissolves in an aqueous solution of an acid. In addition to that which dissolves in the acid as a base a certain amount dissolves as polyvanadic acid; in dilute acid solutions the latter is appreciable, and consequently the oxide becomes relatively more soluble in dilute than in concentrated acid solutions.

Vanadium pentoxide begins to precipitate with hydrochloric, nitric, and perchloric acids when approximately 2·70 equivs. of acid (per mol. of sodium vanadate) are added. With this amount of acid the sodium polyvanadate is just beginning to suffer replacement by the strong acids, and owing to the sparing solubility of vanadium pentoxide, partial separation of the oxide occurs. Precipitation, however, never becomes complete, but it is significant that with these strong acids it reaches maximum amounts when the added acid is sufficient to convert all the alkali polyvanadate into alkali chloride. With such strong acids, concentration appears to have but a slight effect. With acids, *e.g.*, sulphuric and trichloroacetic, more comparable in strength with polyvanadic acid, the concentration of the reactants has an appreciable effect both on the incidence of precipitation and on the amounts which cause maximum precipitation. This is clearly demonstrated by the curves *H, I, J*, and *G*. In these cases the acids are unable to effect replacement of the polyvanadic acid from its sodium salt.

Redissolution of vanadium pentoxide requires an excess of the strongest acids equal to about 5 equivs. per atom of vanadium, whereas 7·5—9 equivs. of sulphuric acid are required. Here again it will be noticed (curve *A*) that redissolution occurs with less than 5 equivs. of acid when using the most dilute solutions (see below). As a base, vanadium pentoxide is extremely weak, and the fact that about 5 equivs. of a strong acid (per atom of vanadium) dissolve the oxide does not signify that VCl_5 is formed in solution, for both the p_H value and electrical conductivity indicate considerable hydrolysis, so much so that the acid does not combine appreciably beyond the stage $V(OH)_4Cl$ or VO_2Cl. Both the conductivity and the small change in freezing point suggest that the basic salt is partly ionised. The excess of acid required to promote the dissolution of the pentoxide would thus appear to be necessary to prevent the basic salt from hydrolysis. Similar reasoning applies to the combination with nitric and perchloric acids and also to sulphuric acid, but since the last acid is weaker than the other two, greater concentrations of it are required to stabilise the basic sulphate $(VO_2)_2SO_4$ by repressing the hydrolysis.

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