406. *Physicochemical Studies of Complex Acids. Part XIII. The Constitution of Quinquevalent and Quadrivalent Vanadium Solutions; with a Note on their Respective Reduction and Oxidation.*

By H. T. S. BRITTON.

IN Part II (J., 1930, 1261), Britton and Robinson tentatively explained in the light of their approximate p_H curves, why Rosenheim and Yang (*Z. anorg. Chem.*, 1923, **129**, 181) were able to titrate boiling alkali vanadate solutions with sulphuric acid to phenolphthalein and more accurately to α-naphtholphthalein. The glass electro-titration curve (Part VII, J., 1932, 1956) representing the changes in p_H of solutions of sodium vanadate after successive additions of hydrochloric acid, boiling, and cooling to 18°, reveals that a sharp diminution in p_H occurs when the vanadate formed has the composition Na_2O,V_2O_5, the p_H then being 7·5. As the normal colour change of α-naphtholphthalein occurs at about p_H 8·5 such an explanation is not sufficiently quantitative, and this led to the suspicion that the reactions of vanadic acid towards alkali at elevated temperatures might differ from those at lower temperatures. Glass electro-titrations of alkali vanadate solutions with sulphuric acid, and also of a very dilute solution of vanadium pentoxide and of more concentrated solutions in sulphuric acid with alkali, have therefore been performed at various temperatures. At 85° well-defined inflexions are obtained corresponding to the formation of alkali metavanadate, Na_2O,V_2O_5, whereas at lower temperatures the inflexions are indefinite and depend upon both the time allowed and the temperature.

In sulphuric acid solutions vanadium pentoxide is readily reduced to the blue quadrivalent state. In the presence of excess acid these solutions are remarkably stable (cf.

Furman, *J. Amer. Chem. Soc.*, 1928, **50**, 1675; Stout and Whittaker, *Ind. Eng. Chem.*, 1928, **20**, 210), and owing to the fact that on crystallisation they often yield salts having the composition, $V_2O_4,2SO_3,xH_2O$, they are usually considered to contain " vanadyl " sulphate, $VOSO_4$. The following work supports this view and indicates, moreover, that vanadium tetroxide is incapable of reacting in dilute solution with larger proportions of sulphuric acid; contrary to the general belief (see, *e.g.*, Mellor, " A Comprehensive Treatise, etc.," 1929, Vol. IX, p. 745), the tetroxide is not amphoteric in dilute solution for it is neither attacked by, nor dissolves in, alkali solutions.

Unless the utmost care is taken to prevent oxidation by air, both precipitated vanadium tetroxide and vanadyl sulphate solutions containing no excess of acid rapidly become oxidised and then on treatment with alkali give yellow vanadate solutions. That acidity has an important influence on the oxidation of quadrivalent vanadium solutions was observed by Gustavson and Knudson (*J. Amer. Chem. Soc.*, 1922, **44**, 2756); temperature also was found to have an important effect by E. Müller and his co-workers (*Z. anorg. Chem.*, 1922, **125**, 155; *Z. Elektrochem.*, 1923, **29**, 500).

EXPERIMENTAL.

1. *Glass Electro-titrations of Vanadate and Vanadic Acid Solutions.*—Preliminary titrations of the universal buffer solution (Prideaux, *Proc. Roy. Soc.*, 1916, **92**, *A*, 463; Britton and Robinson, J., 1931, 1456) at various temperatures by means of the glass electrode showed that the *P.D.*'s which are immediately established across the glass membrane are a function of the p_H values of the solutions of the opposite sides. For titrimetric work, this electrode therefore provides an excellent indicator, and as no attempt was made to employ it for the measurement of p_H at elevated temperatures, a problem which in itself necessitates the careful calibration of buffer solutions at a series of such temperatures, the ordinary electrode system was used, *viz.*,

Pt | 0·1*N*-HCl, Quinhydrone | Glass | Test solution | Satd. KCl | *N*-Calomel

and everything, save the junction liquid and the calomel electrode, which was kept at room temperature, was heated to the desired temperature. The *E.M.F.*'s of the cell, measured by means of an Osram electrometer valve and a galvanometer (Harrison, J., 1930, 1528), were plotted against the amount of titrant added. On titrating 100 c.c. of 0·0167*M*-sodium orthovanadate with 0·1*N*-sulphuric acid at 85°, the curve obtained was similar to that at 18° (see Part VII) with the exception that when the acid was sufficient to form the 1 : 1 vanadate there occurred a sharp inflexion, and immediately afterwards the solution became acidic. There was a little unsteadiness in the *E.M.F.*'s in the vicinity of the inflexion. Back-titration with sodium hydroxide yielded an inflexion at the same stage.

An aqueous solution of vanadium pentoxide was next titrated with alkali. It was prepared by shaking the oxide, obtained by careful ignition of pure ammonium metavanadate, with water for a fortnight at room temperature. The resulting solution contained 0·304 g. of vanadium pentoxide per litre, *i.e.*, 0·00167*M*-V_2O_5. Meyer and Aulich (*Z. anorg. Chem.*, 1930, **194**, 278) obtained an aqueous solution containing 0·7 g. per litre by using a " specially reactive " sample of vanadium pentoxide. On titration at 18° with alkali, a curve of which the mid-point of the inflexion corresponded to the production of $Na_2O,2V_2O_5$, was obtained, identical with those given in Fig. 2 of Part VII. Throughout the titration the solution remained yellow. The p_H of the vanadic acid solution was 3·0 and indicates that ionisation, considered as $H_3VO_4 \rightleftharpoons H^{\bullet} + H_2VO_4'$, had proceeded to the extent of 30%. At 45° a similar curve was immediately obtained, but at 70° and 85° the inflexion was delayed until the added alkali was sufficient to form Na_2O,V_2O_5, *i.e.*, $NaVO_3$, the so-called metavanadate. At 70° the *E.M.F.*'s in the region of the end-point required several minutes to become constant. Comparable results were obtained with lime-water, and precipitation began at the stage corresponding with $2CaO,V_2O_5$, *i.e.*, $CaHVO_4$. The colour changes during the titration are of interest: the solution remained yellow until the incidence of the " metavanadate " inflexion, and then became colourless.

As found by Meyer and Aulich (*loc. cit.*), vanadium pentoxide is appreciably soluble in sulphuric acid solutions: for concentrations ranging from 8 to 64% of acid the solubility varies between 1·87 and 2·62%. This suggests that chemical union does not take place between the vanadic and sulphuric acids. The presence of vanadium pentoxide in solutions of sulphuric acid has very little effect on the p_H values as determined by the glass electrode at 18°. Alkali titrations of such solutions at 18° are rarely accompanied by the separation of any vanadium pentoxide.

The solutions remain yellow and the inflexions occur at positions corresponding to the total neutralisation of the sulphuric acid and the formation of $Na_2O,2V_2O_5$. Titration at 85°, however, postpones the end-point to the alkali metavanadate stage, and partial precipitation usually occurs from the more concentrated vanadium pentoxide solutions during the addition of the alkali required to convert $Na_2O,2V_2O_5$ into metavanadate. In the titration of a solution containing 18·25 g. of vanadium pentoxide and 40 g. of sulphuric acid per litre, this precipitation caused the inflexion to be somewhat premature, at $0{\cdot}89Na_2O,V_2O_5$.

2. *The Action of Sodium Hydroxide on Solutions of Vanadyl Sulphate and Sulphuric Acid.*— Solutions containing quadrivalent vanadium were prepared by passing sulphur dioxide through a suspension of vanadium pentoxide in sulphuric acid and boiling off the sulphur dioxide when reduction was complete. Curve *A* (Fig. 1) represents the change in hydrogen-ion concentration at 14° when 100 c.c. of 0·00997*M*-vanadyl sulphate, $VOSO_4$, and 0·00795*M*-sulphuric acid were titrated with 0·1*N*-sodium hydroxide. The solution was blue during the first stage of the reaction, which, as Curve *A* shows, was that of the neutralisation of the acid in excess of the amount required to form vanadyl sulphate. Further alkali decomposed the vanadyl sulphate with separation of a flocculent white precipitate of hydrated vanadium tetroxide. The final inflexion of the curve shows, however, that the amount of alkali required to do this was appreciably greater than is indicated by the equation $2VOSO_4 + 4NaOH = V_2O_4,2H_2O + 2Na_2SO_4$, and the reason was found in the change in the nature of the precipitate, and its subsequent dissolution, as more alkali was added, for the quadrivalent vanadium had become increasingly susceptible to aerial oxidation. Another titration was therefore performed in which a rapid stream of hydrogen (oxygen-free) was passed through the titration vessel and air was entirely excluded; the corresponding curve is *B* (Fig. 1). Precipitation again began at p_H 4·3, but the final inflexion reveals that a little more than the stoicheiometrical amount of alkali was required. Acidification and titration with potassium permanganate showed that, notwithstanding all the precautions, 4—5% of oxidation had occurred. The vanadium tetroxide did not redissolve. The curves afford definite evidence of existence of vanadyl sulphate in solution.

FIG. 1.

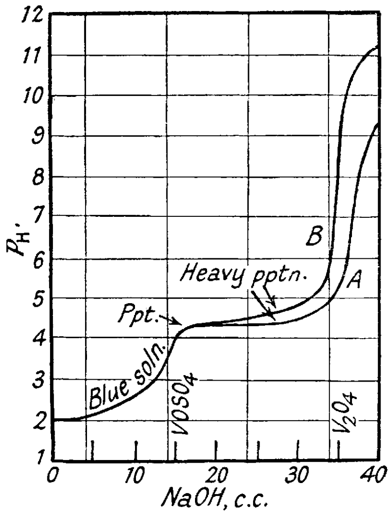

FIG. 2.

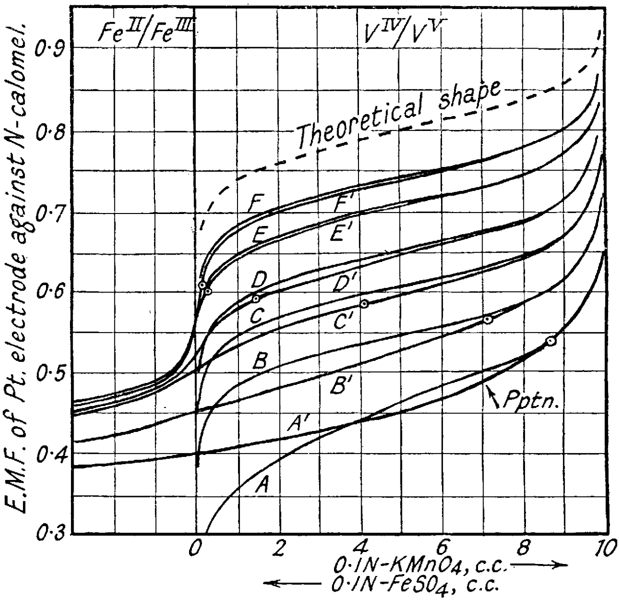

Table I illustrates the increasing susceptibility to oxidation by the air of acidified vanadyl sulphate with increasing p_H. It refers to a series of solutions prepared by mixing 100 c.c. of the solution of the concentrations used in the titrations with the amounts of 0·1*N*-alkali given in col. 1 and shaking the mixture in stoppered bottles at 14° for a week; the bottles were of 500 c.c. capacity and therefore contained adequate oxygen to effect complete oxidation to the quinquevalent state. The initial p_H may be obtained from the curve. The final p_H values, col. 6, show that decreases occurred in all cases, and especially in the alkaline solutions in which the vanadic acid formed had dissolved.

TABLE I.

NaOH, c.c.	Appearance. Initially.	After 8 hrs.	After 24 hrs.	Oxidation, %.	p_H.
10	Blue	Blue	Blue	1·5	2·48
15	Grey-blue	Green-blue	Green-blue	21·0	2·54
20	Cloudy	Yellow-green	Yellow-green	38·5	2·66
25	Ppt.	,,	,,	58·5	2·76
30	,,	,,	,,	76·0	2·90
35	,,	,,	,,	90·7	3·15
40	,,	Ppt.	Dark green soln.	95·1	6·17
45	Cloudy	Colourless soln.	Colourless	96·4	7·96
50	Brown soln.	,, ,,	,,	97·5	9·32

By mixing the above solutions at 70° in the presence of air the rate of oxidation was much enhanced, as indicated by the changes in colour and the negligible amount of precipitation that occurred.

3. *Oxidation and Reduction Reactions.*—Electrometric titrations of vanadyl sulphate solutions were performed at 22°, 50°, and 75° with 0·1*N*-potassium permanganate. The indicator electrode was bright platinum, and the titration-cell was connected, through a saturated solution of potassium chloride, to a *N*-calomel electrode. Although at 22°, the *E.M.F.*'s were slowly set up, they clearly showed the effect of the concentration of sulphuric acid. The solutions contained 1·2 g. of vanadium tetroxide and were 1·02*N* with regard to sulphuric acid. The titrated solution alone was raised to the desired temperature and the calomel was kept at room temperature. It was estimated that at 50° the increase in *P.D.* due to the difference in temperature of the two electrodes was about 0·025 volt. At 50° the stable *E.M.F.*'s were almost immediately set up, and at 75° the oxidation was even faster. The *E.M.F.*'s at half-oxidation, not including the " temperature *E.M.F.*", were 0·706 and 0·698 volt respectively, *i.e.*, assuming the *N*-calomel to be 0·283 volt more positive than the normal hydrogen electrode, 0·989 and 0·981 volt (*N*-H = 0). The effect of temperature is in accord with the observations of Müller and Just (*Z. anorg. Chem.*, 1922, **125**, 155) and Müller and Flath (*Z. Elektrochem.*, 1923, **29**, 500), who find 70—80° to be suitable in potassium permanganate titrations, and of Furman (*J. Amer. Chem. Soc.*, 1928, **50**, 1675), who prefers the range 50—60° when titrating with ceric sulphate.

In consequence, the effect of acidity on the course of oxidation of quadrivalent vanadium was investigated at 45°, and it was found that at this temperature the reaction was almost instantaneous. Fig. 2, curves *A*—*F*, represents a series of titrations of 100 c.c. of 0·00978*M*-$VOSO_4$ in the presence of sulphuric acid of the following concentrations : 0·031*N* (curve *A*), 0·071*N* (*B*), 0·174*N* (*C*), 0·398*N* (*D*), 1·01*N* (*E*), 1·81*N* (*F*). The *E.M.F.*'s at the mid-points of the titrations were 0·467, 0·545, 0·606, 0·651, 0·707, and 0·742 volt respectively with 0·1*N*-potassium permanganate, whilst curves *A'*—*F'* are the reduction sections of respective back-titrations with 0·1*N*-ferrous sulphate. An atmosphere of hydrogen was maintained in order to prevent aerial oxidation (see p. 1844).

As shown by the *E.M.F.*'s prevailing when the oxidised and reduced vanadium is present in equimolecular quantities, *viz.*, at the mid-point, and also by the positions of the curves in Fig. 2, the effect of increasing concentration of acid is to raise materially the potential ranges within which either oxidation or reduction can take place. The final positions to the left of Fig. 2, with respect to the ordinates, of the back-titration curves after the stoicheiometrical amounts of ferrous sulphate are added show that in the titrations, *A'*, *B'*, and *C'*, the potentials corresponding to the vanadium reaction and to mixtures of ferrous and ferric ions overlap. Hence, in such solutions ferrous sulphate cannot effect the complete reduction of vanadic acid to the quadrivalent state. The points marked by circles on the curves give the stages when ferrous iron could first be detected during the progressive addition of ferrous sulphate by using acidified potassium ferricyanide as an external indicator. In the least acid solution, the precipitation of basic ferric vanadate at the point marked by the arrow presented another complication.

The broken line at the top of Fig. 2 represents the change in potential calculated by means of the term $- 0{\cdot}063 \log [VO^{\cdot\cdot}]/[HVO_3]$. The shape of this curve and that of *B*, *C*, *D*, *E*, and *F* are almost identical. Attempts were made to ascertain whether the actual variations in reduction potential at the mid-points could be accounted for by the variation in hydrogen-ion concentration (or activity). It being assumed that the following equation represents the reduction : $HVO_3 + 3H^{\cdot} = VO^{\cdot\cdot} + 2H_2O + F$, then at 45°, $E_{obs.} = E_0 - 0{\cdot}063 \log [VO^{\cdot\cdot}]/[HVO_3] + 3 \times 0{\cdot}063 \log [H^{\cdot}]$.

The shape of the observed curves compared with the broken curve confirms the accuracy of the second term of this expression, whilst rough estimates of the hydrogen-ion concentration, based on the conductance ratios of sulphuric acid at 45°, lead to values of E_0 ranging from 0·77 to 0·81 volt against the *N*-calomel electrode at 18°, the average being 0·79 volt. On correction for the difference in temperature between the two electrodes, this value becomes 1·04 volt (*N*-H = 0). A more satisfactory method of correlating these variations in reduction potential would have been to determine the concentrations (or activities) at 45° of the hydrogen-ions, but the use of the glass electrode entails many assumptions. In addition to the use of the conductance ratios, the calculations cannot be entirely satisfactory, as they do not include any possible ionisation of the vanadic acid.

Rutter (*Z. anorg. Chem.*, 1907, **52**, 368) determined the potential of a single mixture of quadri- and quinque-valent vanadium in 0·5*N*-sulphuric acid at 18°. Calculation gives $E_0 = 1{\cdot}07$ volt, whilst Foerster and Böttcher (*Z. physikal. Chem.*, 1930, **151**, 321) observed at 18° potentials of 1·06, 1·012, and 1·002 volts with equimolar mixtures in 3, 1·25, and 0·75*N*-sulphuric acid respectively. Finally, Coryell and Yost (*J. Amer. Chem. Soc.*, 1933, **55**, 1909) observed similar variations in reduction potential given by solutions of vanadic acid and vanadyl chloride in the presence of varying concentrations of hydrochloric acid. In a *N*-hydrochloric acid solution the potential given at 25° by an equimolar mixture was 1·022 volt.

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