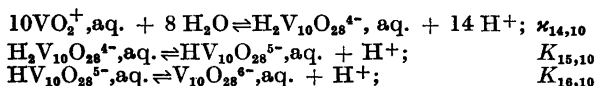# Equilibrium Studies of Polyanions

I. Isopolyvanadates in Acidic Media

F. J. C. ROSSOTTI and HAZEL ROSSOTTI

Department of Inorganic Chemistry, The Royal Institute of Technology, Stockholm 70, Sweden *

The following equilibria have been assigned to the isopolyvanadate system in the range $-0.5 < \text{pcH} < 6.5$, on the basis of spectrophotometric and potentiometric measurements (with glass electrodes) made in perchlorate media at 25°C:

$$10VO_2^+,\text{aq.} + 8\,H_2O \rightleftharpoons H_2V_{10}O_{28}{}^{4-},\text{aq.} + 14\,H^+; \quad \varkappa_{14,10}$$
$$H_2V_{10}O_{28}{}^{4-},\text{aq.} \rightleftharpoons HV_{10}O_{28}{}^{5-},\text{aq.} + H^+; \quad K_{15,10}$$
$$HV_{10}O_{28}{}^{5-},\text{aq.} \rightleftharpoons V_{10}O_{28}{}^{6-},\text{aq.} + H^+; \quad K_{16,10}$$

The cation VO_2^+,aq. is the sole species in solutions $-0.5 < \text{pcH} < 1.3$ (for a 1 M perchlorate medium in which sodium is the predominant cation), and the isoelectric point is given by:

$$\text{pcH} = 0.803 - 0.643 \log B \text{ and}$$
$$\text{pcH} = 0.715 - 0.643 \log B$$

for 1 M and 3 M perchlorate media, respectively. The values of the equilibrium constants are evaluated as: $\log \varkappa_{14,10} = -6.75 \pm 0.15$; $\log K_{15,10} = -3.6 \pm 0.3$; and $\log K_{16,10} = -5.8 \pm 0.1$ in the 1 M medium, and $\log \varkappa_{14,10} = -5.5 \pm 0.15$; and $\log K_{15,10} = -3.5 \pm 0.3$ in the 3 M medium. The application of the "core + links" treatment to the data is indicated in an appendix.

PREVIOUS WORK ON THE HYDROLYSIS OF VANADIUM(V)

Considerable uncertainty exists as to the nature of the orange-yellow vanadium(V) species which occur in acidic solution. The existence of the cation, VO_2^+, is well established, but it is not clear if less hydrolysed cations also exist. The nature of the polyvanadates in acidic media appears to be completely in doubt.

Düllberg [1] demonstrated the existence of cationic species by transport measurements in strongly acidic solutions, and the redox potentials between vanadium(V) and (IV) were first interpreted in terms of an equilibrium between

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* Present address: Department of Chemistry, University of Edinburgh, Scotland.

VO_2^+ and VO^{2+} by Foerster and Böttcher [2]. Although this interpretation has been confirmed by many other workers (cf. Hart and Partington [3] and refs. therein) several authors have mentioned the possible existence of species less hydrolysed than VO_2^+. The existence of VO^{3+} has been discussed by Meyer and Pawletta [4], Britton and Welford [5] and Jander and Jahr [6]. More recently, the existence of VO^{3+} has been proposed by Trujillo and Rios [7] and of $V(OH)_3^{2+}$ by Ramsey, Colichman and Pack [8], in order to explain the kinetics of reduction of vanadium(V) by iodide ions. The diffusion data of Jander and Jahr [6] indicate that the cations, whatever they may be, are not polymerised. No distinction can be made between alternative formulae such as VO_2^+ or $V(OH)_4^+$ by conventional equilibrium methods, but LaSalle and Cobble [9] have recently shown that the former formula is more probable on the basis of structure-entropy considerations. For simplicity, all formulae will be written here in a form stripped of the maximum possible number of molecules of water.

An isoelectric point [6,10] occurs in the region of pcH = 2 *. The orange-yellow *iso*polyvanadic acid which is then formed has been variously considered to contain 2, 4, 5, 6 and 10 vanadium atoms. The main experimental support for most of these formulations has been the occurrence of a point of inflexion in pH titration curves, or a break in conductimetric titration curves in the region 3<pcH<6. Thus Ducret [10] considers that the inflexion corresponds to the uptake of one hydroxyl ion per molecule of V_2O_5, and that the orange-yellow colour is due to $H_3V_2O_7^-$. Düllberg [1] had realised that this evidence alone cannot give the degree of polymerisation of the acid, and chose instead the formula $HV_6O_{17}^{3-}$ on the basis of molecular weight determinations and by analogy with an orange solid $Na_4V_6O_{17}$, aq. However, solid vanadates corresponding to a wide variety of ratios of $Na_2O:V_2O_5$ are claimed (see p. 978), and the molecular weights determined by a combination of cryoscopic and conductivity measurements are of doubtful validity. Nevertheless, the existence of hexavanadic acid has been supported by Bray and Tihenko [12], Carpéni and Souchay [13,14], and by Trujillo [15] mainly on the basis of the point of inflexion obtained in titration curves.

However, Britton and Robinson [16], Britton and Welford [5], and Hazel, McNabb and Santini [17] consider that the point of inflexion corresponds to the uptake of only 0.8 hydroxyl ions per molecule of V_2O_5, and formulate the species in solution as $V_{10}O_{27}^{4-}$. This choice was also supported by the existence of the salt $Na_4V_{10}O_{27}$, aq. Although the interpretation of Robinson and Sinclair's vapour pressure measurements [18] is not unequivocal, the data indicate that the molecular weight of the polyvanadate ion existing in acidic solutions is of the order of 1 000, and point to a degree of polymerisation greater than 6 and of the order of 10.

Jander and Jahr [6] assumed that the stable polyvanadate at pcH~3 is $Na_2H_4V_5O_{16}^-$, by analogy with a salt which was considered to be a pentatantalate [19], but which Lindqvist and Aronsson have subsequently shown to be a hexatantalate [20]. This erroneous assumption forms the basis of Jander and Jahr's interpretation of diffusion data for the polyvanadate system [6] in terms

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* The symbol pcH denotes —log h, where h is the free concentration of hydrogen ions cf. Ref. [11].

of Riecke's law, which is itself of doubtful validity in these systems [21]. More-over, as Carpéni and Souchay [14] have pointed out, Jander and Jahr's titration data [6] do not, in fact, appear to support these authors' interpretation of the diffusion data. Ottar [22] has recently reinterpreted the diffusion data on the basis of a kinetic theory, and has obtained the formula $V_4O_{13}^{6-}$ for the polyvanadates existing in acidic solutions. This interpretation is based on the supposition that all polyvanadates consist of chains of VO_4^{3-} tetrahedra, which share one corner, (see p. 978), and involves assumptions about the formation of hydrogen bonds between solute and solvent. Consequently, the diffusion data must still be considered to be of only qualitative interest.

It appears to be generally agreed [17] that the polyvanadates stable in acidic media depolymerise with increasing pcH to trimeric or tetrameric metavana-dates, $(VO_3^-)_n$; pyrovanadates, $V_2O_7^{4-}$; and finally to monomeric orthovanadates, VO_4^{3-}. These equilibria, however, are outside the scope of the present work.

List of symbols

A		Total concentration of A
a		concentration of free A
A_s		optical absorbancy
B		total concentration of B, or of metal
B		normalised variable defined by (25) or (31)
b		concentration of free B
c_j	$= [B(A_{st}B_s)_j]$ (51)	
E		measured potential in mV
E_j		liquid junction potential
E_0	$= E - E_j - 59.16 \log h$ (2)	
g	$= \Sigma K_j u^{sj}$ (48)	
H		total concentration of hydrogen ions, assuming all vanadium to be in the form VO_2^+ (4)
H'		total concentration of hydrogen ions, assuming all vanadium to be in the form V^{5+} (3)
h		concentration of free hydrogen ions
h		normalised variable, variously defined by (13), (28) and (36)
j		variable number of polynuclear links, $(A_{st}B_s)$, per complex $B(A_{st}B_s)_j$
$\bar{j}$		average number of polynuclear links per complex, $B(A_{st}B_s)_j$
K_j		equilibrium constant for $(1 + sj)B + sjt\ A \rightleftharpoons B(A_{st}B_s)_j$ (49)
k_0, k		parameters defined by $K_j \rightleftharpoons k_0 k^{sj}$ (54)
$K_{p,q}$		equilibrium constant for $(VO_2)_q(OH)_p^{(p-q)-} + H_2O = (VO_2)_q(OH)_{p+1}^{(p+1-q)-} + H^+$
K_w	$= [H^+][OH^-]$	
l	$= K_{16,10} K_{15,10}^{-1}$ (29)	
M		mole/l
N		unique value of n
n		variable number of mononuclear links, (A_tB), per complex $B(A_tB)_n$
P		unique value of p
p		number of hydroxyl groups in complex $(VO_2)_q(OH)_p$
pcH	$= -\log h$	
Q		unique value of q
q		number of VO_2^+ groups in complex $(VO_2)_q(OH)_p$
s		smallest integer such that product st is also integral
t		number of A groups per B group in mononuclear link (A_tB)
u	$= bh^{-t}$ (48)	
V	$= v^s$ (55)	

v $= ku$ (56)

$V_{\frac{1}{2}}$ = value of V corresponding to $y = \frac{1}{2}$

$X^{\frac{1}{2}}$ normalised variable defined by (60)

x $= \log B - t \log h$ (7)

$x_{\frac{1}{2}}$ = value of x corresponding to $y = \frac{1}{2}$

y $= Zt^{-1}$ (8)

Z average number of hydroxyl groups per VO_2^{+} group $= (h - H)B^{-1}$ (1)

Z_q $= \Sigma\, p[A_pB_q] / q\,\Sigma\,[A_pB_q]$ (19) and (34)

Z $= Z Z_{10}^{-1}$

$a_{p,q}$ $= 100q[A_pB_q]B^{-1}$ (42) and (43)

$\beta_{p,q}$ $= [A_pB_q]a^{-p}b^{-q}$ (41)

ε $= \dfrac{1}{9}(1 + \log \varkappa_{14,10} - 14 \log K_{15,10})$ (30)

η $= \log \dfrac{B}{b}$ (45)

ϑ $= P\varkappa_{P,Q}b^{Q-1}h^{-P}$ (12)

$\varkappa_{p,q}$ equilibrium constant for $q\ VO_2^{+} + pH_2O \rightleftharpoons (VO_2)_q(OH)_p^{(p-q)-} + p\ H^{+}$
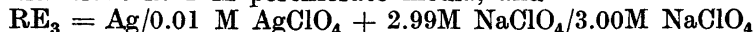
METHOD

A series of potentiometric titrations of vanadium(V) perchlorate solutions of differing concentrations, in an excess of perchloric acid, was carried out at 25° C. In each titration, the total concentration of metal, B, was held constant, and the hydrogen ion concentration was varied by additions of sodium hydroxide or sodium hydrogen carbonate. In the main series of titrations, all solutions were made 1 M with respect to perchlorate ions by the addition of sodium perchlorate. Preliminary titrations were also made in a 3 M perchlorate medium. As the concentration of metal ions and hydrogen ions never exceeded 2 % and 10 %, respectively, in the former medium, and 0.33 % and 3.3 %, respectively, in the latter medium, it may be assumed that the activity coefficients of all species remain constant. Although McKay has questioned this type of assumption [23], the simplest explanation of Biedermann and Sillén's results [24] appears to be that the activity coefficients remain constant, within the experimental error, for changes in the medium of this order of magnitude. Accordingly, it has been assumed that true stoichiometric equilibrium constants may be calculated from the measurements in each medium.

Since the hydrolysis of vanadium(IV) in a 3 M perchlorate medium has previously been reported [25], the possibility exists of interpreting vanadium (IV/V) redox equilibria as a function of hydrogen ion concentration in terms of the hydrolysis of vanadium(V). Unfortunately, equilibrium values of the redox potential could not be achieved in periods of up to 30 hours, using a number of different platinum, palladium and gold electrodes in conjunction with various potential mediators (cf. Refs.[3],[26]). Therefore, only the equilibrium hydrogen ion concentration, h, was measured. Although this quantity may often be determined most accurately with hydrogen or quinhydrone electrodes, these cannot be used in vanadium(V) solutions [27]. A glass electrode was therefore used in combination with the reference half-cells, RE_1 or RE_3, where

$RE_1 = Ag/0.01M\ AgClO_4 + 0.99M\ NaClO_4/1.00M\ NaClO_4$
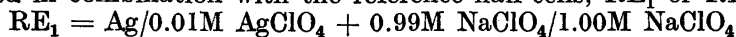
for titrations in 1 M perchlorate media, and

$RE_3 = Ag/0.01\ M\ AgClO_4 + 2.99M\ NaClO_4/3.00M\ NaClO_4$

for titrations in the 3 M medium. Since equilibrium was achieved in 2 to 15 minutes with these cells (see below), it is considered that the failure to attain equilibrium redox potentials was due to some cause other than a slow hydrolysis reaction.

The average number of hydroxyl ions bound per central group may be calculated for each point of titration, using the relationship

$$Z = (h - H) / B. \tag{1}$$

where H is the total analytical concentration of hydrogen ions, defined by eqn. (4). Thus both H and B are known from the analyses of stock solutions. The data for Z as a function of log h at different total concentrations of metal were analysed by number of methods.

The potentiometric study was supplemented by a spectrophotometric investigation of the species existing in strongly acidic solution.

EXPERIMENTAL

Reagents

Vanadium (V) perchlorate solutions were prepared by dissolving vanadium pentoxide in perchloric acid. One batch of the pentoxide was prepared by dissolving sodium vanadate (*p.a.*) in hot water, and acidifying with perchloric acid. After the solution had stood overnight, more pentoxide was precipitated by evaporating the solution to half its bulk. The product was washed by decantation, centrifuged, and washed free from sodium ions. In other cases, commercial pentoxide (*p.a.*) which had been shown by analysis for vanadium(V) to be > 99.9 % pure, was used. The solubility of vanadium pentoxide in perchloric acid is very low (*e.g.* ∼0.06 M in 0.2 M acid), and equilibration is slow, *cf.* Ref. [9]. An excess of the oxide was allowed to stand in contact with ∼0.2 M perchloric acid for about 4 weeks, and the yellow solution filtered through a very fine sintered glass disc. The concentration of vanadium(V) in the stock solution was determined as described previously [25]. The total concentration of perchlorate ions was found by titrating the eluate of aliquots passed through the hydrogen form of the resin Amberlite IR 120. Acidic solutions of vanadium(V) are reduced during passage through cation exchange resins [28] and the results were not reproducible. Accordingly, vanadium(V) was reduced to vanadium(IV) before passing aliquots through the ion-exchange column. Hydrogen sulphide was passed into the hot solution, excess of the gas expelled and sulphur coagulated by boiling, and the solution filtered.

Sodium hydroxide was freed from carbonate by allowing a 50 % solution of AnalaR grade reagent to stand for 4 weeks in a polythene bottle. Under nitrogen, the solution was filtered through a fine sintered glass disc, diluted with carbon dioxide-free water, and stored in polythene bottles. These solutions were standardised by potentiometric titration with perchloric acid, using Gran's method for calculating the end-point [29].

Sodium perchlorate solutions. One batch was prepared as described elsewhere [25]. A further stock solution was made by filtering a solution of the G. F. Smith Co. product, which had been shown to be free from iron, chlorate, hypochlorite and chloride ions. The solutions were analysed as described previously [25].

Other reagents were prepared and standardised by methods described elsewhere [25].

Procedure

The titration vessel, liquid junction, electrodes and potentiometer have also been described elsewhere [25]. The correct functioning of the Blomgren glass electrode was also tested by comparison with the quinhydrone electrode [25]. For the cell

$$RE/HClO_4 + NaClO_4/glass$$
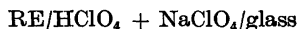
at 25°C the relationship between the measured potential, E (in mV), and the concentration, of free hydrogen ions is given by

$$E = E_0 + E_j + 59.16 \ \log \ h \qquad (2)$$

The term E_0 includes the standard potentials of the electrodes, and the asymmetry potential of the glass electrode. E_j is the liquid junction potential, which was found to be a linear function of h in the range of acidity studied ($h \leqq 0.1$ M) and in a given medium. The values of E_0 and of $E_j(h)$ were determined for each titration in the region where no hydrolysis of the ion VO_2^+ occurs (see below), and where h is identical to H. For each point, H is known from the analyses of the solution so that ($E - 59.16 \log h$) may be plotted as a function of h. The values of E_j so found

$$E_j = -16.5h \pm 0.5 \ \text{mV/mole in 3 M perchlorate}$$
$$E_j = -63h \quad \ \pm 2 \ \text{mV/mole in 1 M perchlorate}$$

are in good agreement with the values of Biedermann and Sillén [24] and of Biedermann (quoted by Hietanen) [30].

In preliminary work, values of E_0 and of $E_j(h)$ for each titration were found by first titrating acid and base in the absence of metal. However, a change of $\lesssim 0.5$ mV in E_0 usually occurred when some of the acid-base mixture was withdrawn from the titration vessel and metal solution added.

When E_0 and $E_j(h)$ are known, values of h corresponding to the measured potentials E can be found by successive approximation, using eqn. (2).

Measurements were carried out at 25.0 ± 0.1°C in a paraffin oil thermostat placed in a room also thermostated at 25°C. In a particular titration, 18.0 ml of a solution A, containing 0.04 M vanadium(V) perchlorate and 0.12 M perchloric acid was added to 18.0 ml of 0.08 M perchloric acid. This mixture was titrated with equal volumes of 0.2 M sodium hydroxide, and of solution A. (All these solutions were 1 M with respect to perchlorate ions.) Thus, the total concentration of vanadium was 0.02 M throughout the titration. A total volume of 32 ml of each titrant was added stepwise. A value of $E_0 = -314.6$ mV was obtained from the points corresponding to the addition of the first 5.0 ml of each solution. Lower concentrations of perchloric acid and of sodium hydroxide were used for measurements with lower concentrations of vanadium. Series of titrations were carried out at least in duplicate with vanadium concentrations of 0.02, 0.01, 0.005 and 0.0025 M in a 1 M perchlorate medium. Titrations at the three lowest concentrations of metal were repeated in a 3 M perchlorate medium. Higher concentrations of metal could not be used, as vanadium pentoxide is precipitated from initial solutions ($h \sim 0.1$ M) in this medium. The equilibrium hydrogen ion concentration was varied from 10^{-1} to $10^{-6.5}$ M by additions of sodium hydroxide in the 1 M medium, and of sodium hydrogen carbonate in the 3 M medium. Local excesses of hydroxyl ions were avoided by the use of the latter reagent, and it was shown by alternately bubbling nitrogen and carbon dioxide [31] that the measurements were not invalidated by complex formation between carbonate and vanadium(V) ions. The similarity between the $\bar{Z}$ (log $h)_B$ data obtained in the two media using the different bases provides a further indication of the absence of such an effect.

A steady potential was usually reached between 2 and 15 minutes after the addition of alkali; the longer times were required for high values of d $\bar{Z}$/d log h. When a steady potential had been obtained, the same value was always found when measured again after an interval of 3 hours. Individial titrations appeared to be reversible. Thus, the pcH of a 0.01 M solution of vanadium(V) was raised from ~ 1.0 to ~ 4.3 during the course of $6\frac{1}{2}$ hours. After an interval of 1 hour, the pcH was lowered stepwise to pcH ~ 1. Points for $\bar{Z}$(log $h)_B$ lay on the same curve for the forward and backward titration (cf. Fig. 2). For this reason, it is considered that the failure to achieve an equilibrium redox potential was due to some cause other than a slow hydrolytic reaction. Britton and Welford [5] have previously found that equilibrium is rapid below, but slow above, pcH ~ 5, cf. Ref. [17].

The spectrophotometric measurements were made at 25 ± 1°C with a Beckman DU Spectrophotometer, using matched 1.00 cm silica cells, and minimum slit widths.
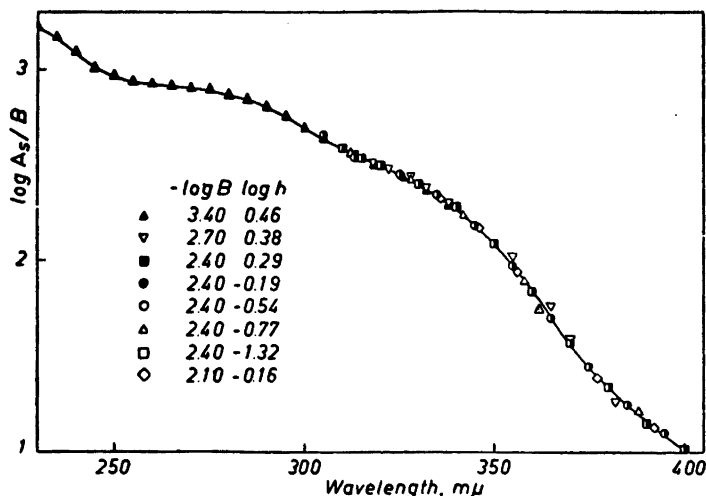
Fig. 1. Absorption spectrum of vanadium(V) perchlorate in acidic solutions 3 M with respect to perchlorate ion.

VANADIUM(V) PERCHLORATE IN STRONGLY ACIDIC SOLUTION

The total analytical hydrogen ion concentration, H', in the stock solution of vanadium(V) perchlorate and perchloric acid was first calculated assuming that all the vanadium(V) was unhydrolysed. Then

$$H' = [ClO_4^-] - 5 \ B \tag{3}$$

Preliminary titrations based on this assumption indicated that 4 hydroxyl ions are bound to each metal atom in the range 0.1 M $\geqslant h \gtrsim$ 0.04 M (for 0.01 M vanadium in the 3 M perchlorate medium), *i. e.* the species present is $[V(OH)_4^+]_x$ or $[VO_2^+]_x$.

The effect of higher acidities on the nature of this species was investigated for a range of metal concentrations by comparing the optical absorbancy, A_s, of a series of solutions, 3 M with respect to perchlorate ion. It was found that the plot of A_s/B against wavelength was independent of B in the range 0.008 M $\geqslant B \geqslant$ 0.0004 M, and of h in the range 2.89 M $\geqslant h \geqslant$ 0.048 M. The spectrum (see Fig. 1) is substantially the same as that recently obtained in $\sim$0.2 M perchloric acid by LaSalle and Cobble [9]. As the ratio A_s/B is independent of the value of B, the vanadium cation may be assumed to be the monomeric species, VO_2^+,aq.

It is therefore convenient to discuss subsequent results in terms of the combination of hydroxyl ions to a central VO_2^+ group. H is now defined as the total analytical concentration of hydrogen ions, assuming all the vanadium to be in the form VO_2^+. Thus for the stock solution of vanadium (V) perchlorate
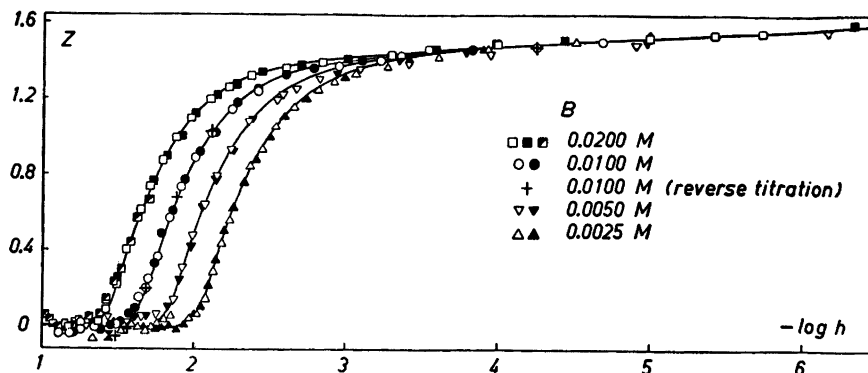
$$H = [ClO_4^-] - B \tag{4}$$

Fig. 2. The average number of hydroxyl groups, Z, bound to each VO_2^+ ion as a function of pcH for different total concentrations of vanadium, B. The lines represent theoretical formation curves calculated for: $\varkappa_{14,10} = 10^{-6.75}$, $K_{15,10} = 10^{-3.6}$ and $K_{16,10} = 10^{-5.8}$

Similarly, Z is now defined as the average number of hydroxyl ions bound to, or protons dissociated from, the VO_2^+ ion.

THE HYDROLYSIS OF THE VO_2^+ ION

Identification of the initial product of hydrolysis

In the first instance, discussion will be restricted to the potentiometric measurements made in the 1 M perchlorate medium. The data $Z(\log h)_B$ calculated for ten titrations using eqns. (1), (2) and (4) are shown in full in Fig. 2. The data for four·representative titrations at different total metal concentrations, B, are also given in Table 1.

The upper limit of 0.02 M for the metal concentrations used was imposed by the limited solubility of vanadium(V) in the perchlorate medium; and the lower limit of 0.0025 M by the limited accuracy of the glass electrode in solutions of 0.1 M$\geqslant h \geqslant$0.05 M. The random scatter about $Z = 0$ at the base of the curves lies within the experimental error of $\pm$ 0.2 mV.

As the curves referring to different values of B are not coincident, it is apparent that at least one polynuclear complex, $(VO_2)_q(OH)_p^{(q-p)+}$ is formed. The curves pass through an isoelectric point (represented by $Z = 1.0$), and each VO_2^+ ion evidently combines with a maximum of $\sim$1.6 hydroxyl ions in the range studied (pcH$<$6.5). The high values of $(- \partial Z/\partial \log h)_B$ for $Z<1.0$ indicate the formation of polynuclear species which contain a relatively high number of vanadium atoms, cf. Fig. 1 in Ref.[32]. For $Z\gtrsim$1.5, and pcH$>$4, the system is again homonuclear, since curves for different values of B are coincident.

For values of $Z\lesssim$1.2, the curves $Z(\log h)_B$ appear to be parallel, so that Sillén's "core + links" hypothesis [32],[33] may be applied. In this range, the complex, or complexes, $(VO_2)_q(OH)_p$ may be written in the form

Table 1. $Z(\log h)_B$ for four representative titrations. The symbols are those used in Fig. 2.

$B = 2 \times 10^{-2}$ M $-\log h$	□ Z	$B = 10^{-2}$ M $-\log h$	● Z	$B = 5 \times 10^{-3}$ M $-\log h$	▼ Z	$B = 2.5 \times 10^{-3}$ M $-\log h$	▲ Z
1.00	0.05	1.14	−0.05	1.27	0.00	1.34	0.00
1.05	0.08	1.18	−0.05	1.29	0.01	1.39	0.06
1.11	0.01	1.22	−0.03	1.34	−0.06	1.45	−0.05
1.16	−0.01	1.26	−0.01	1.39	−0.01	1.50	−0.01
1.21	0.01	1.30	−0.02	1.44	−0.04	1.55	0.01
1.26	0.00	1.34	−0.01	1.50	−0.02	1.61	0.06
1.43	0.130	1.39	−0.02	1.55	0.02	1.67	0.00
1.48	0.234	1.43	0.02	1.61	0.05	1.74	−0.01
1.56	0.411	1.48	0.00	1.68	0.06	1.78	0.00
1.63	0.576	1.52	0.02	1.75	0.07	1.83	0.01
1.71	0.742	1.56	0.07	1.83	0.114	1.88	−0.01
1.79	0.880	1.61	0.117	1.90	0.250	1.93	0.02
1.88	1.00	1.68	0.201	1.97	0.420	1.98	0.07
1.98	1.10	1.73	0.336	2.05	0.595	2.04	0.107
2.11	1.20	1.79	0.486	2.14	0.776	2.09	0.220
2.12	1.21	1.85	0.608	2.25	0.933	2.14	0.356
2.23	1.26	1.93	0.774	2.38	1.09	2.20	0.508
2.37	1.32	2.03	0.920	2.58	1.22	2.26	0.631
2.60	1.36	2.14	1.05	2.94	1.34	2.32	0.764
2.84	1.39	2.28	1.17	3.36	1.40	2.40	0.885
3.29	1.43	2.41	1.25	3.79	1.44	2.49	0.998
3.54	1.46	2.60	1.32	4.98	1.50	2.59	1.11
3.99	1.49	2.78	1.36			2.73	1.20
5.00	1.52	3.10	1.40			2.99	1.31
5.74	1.55	3.36	1.43			3.41	1.40
		3.82	1.46			3.92	1.46
		4.69	1.50			5.00	1.53

$VO_2((OH)_t(VO_2))_n$, where t is a constant (not necessarily integral) and where n may be a unique integer, N, or a series of integers such that the product nt is also integral. Charges are omitted for clarity. Hence, the parameter t is defined by

$$t = p/(q-1) \tag{5}$$

and p is a linear function of q. Sillén [33] has shown that

$$t = (\partial \log B / \partial \log h)_Z \tag{6}$$

The function $\log B (\log h)_Z$, which is derived from the data in Fig. 2, is plotted in Fig. 3, and it is found that $t = 1.50 \pm 0.07$. Accordingly, the different $Z(\log h)_B$ curves may be made to coincide by transforming the $\log h$ axis to

$$x = \log B - t \log h \tag{7}$$

For convenience, the Z axis is simultaneously transformed to

$$y = Z / t \tag{8}$$

The plot of $Z/1.5$ against $(\log B - 1.5 \log h)$ is not reproduced here, but as in the similar plot shown in the Appendix (Fig. 8), all points lie on a single curve, within experimental error. Now a curve $y(x)$ is analogous to the
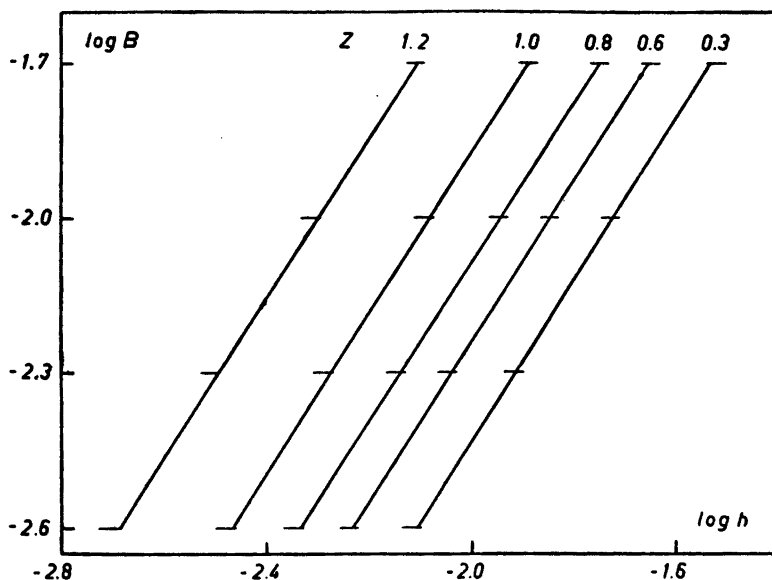
Fig. 3. Log B *as a function of log* h *for different values of* Z. *The lines are calculated for*
$$\varkappa_{14,10} = 10^{-6.75}.$$

single curve $Z(\log h)$ which obtains for a system of mononuclear hydroxyl complexes. Thus, as a first approximation, the products of the reaction between VO_2^+ ions and hydroxyl ions may be represented by the formula $VO_2((OH)_{1.5}(VO_2))_n$.

By comparing the experimental curve $y(x)$ with families of normalised curves $y(X)$ calculated for certain simplifying assumptions, the value or values of n may be found, and the formation constants for the system described in terms of two parameters. Sillén [32] has given a number of normalised curves calculated on the assumptions that:

I, no soluble complexes are formed, but an insoluble complex precipitates,

II, a unique complex $B(A_tB)_N$ is formed in solution,

III, a series of complexes $B(A_tB)_n$ is formed in solution, with values of n ranging from unity to infinity.

Although the curves given elsewhere [32] for hypotheses I and II are valid irrespective of whether t is integral or non-integral, the curves given for hypothesis III are only valid for integral values of t (cf. Appendix).

For $y \lesssim 0.5$, the curve $y(x)$ was found to fit in with the family of normalised curves for hypothesis II, with a value of $N = 8$ or 10 (odd values of N are excluded from consideration, since the product $Nt = P$ must be integral). It could therefore be tentatively inferred that the initial reaction product is a single polynuclear species $VO_2^+((OH)_{1.5}VO_2)_8^{4-}$ or $VO_2^+((OH)_{1.5}VO_2)_{10}^{5-}$, and that this species undergoes some further reaction. Even if the value of t is not exactly 1.5, it is likely that the above formulae approximate to the com-

position of the complex. Other possible combinations of values of t (within the range 1.5 ± 0.07) and of N were found by trial and error, and are given in Table 2, together with the two combinations discussed above.

Table 2. *Possible initial reaction products, $(VO_2)_Q(OH)_P$ or $VO_2((OH)_t(VO_2))_N$*

t	N	Q	P	Range fitted by hypothesis II
1.444	9	10	13	$Z \lesssim 0.6$
1.455	11	12	16	0.6
1.500	8	9	12	1.0
1.500	10	11	15	1.1
1.545	11	12	17	0.8
1.556	9	10	14	1.3

Now for the reaction

$$Q \; VO_2^+ + P \; H_2O \rightleftharpoons (VO_2)_Q(OH)_P^{(P-Q)-} + P \; H^+ \qquad (9)$$
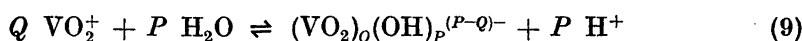
$$B = b + Q \; [(VO_2)_Q(OH)_P] \qquad (10)$$

$$\text{and } BZ = P \; [(VO_2)_Q(OH)_P] \qquad (11)$$

where b is the concentration of free VO_2^+ ions. Introducing the following auxiliary variables into eqns. (10) and (11)

$$\vartheta = Q \; [(VO_2)_Q(OH)_P] \; b^{-1} = Q\varkappa_{P,Q}b^{Q-1}h^{-P} \qquad (12)$$

where $\varkappa_{P,Q}$ is the equilibrium constant for reaction (9) and

$$\log h = \frac{1}{P} \log Q\varkappa_{P,Q} + \frac{Q-1}{P} \log B - \log h = \frac{1}{P} \log \vartheta + \frac{Q-1}{P} \log (1+\vartheta) \quad (13)$$

it may be shown that

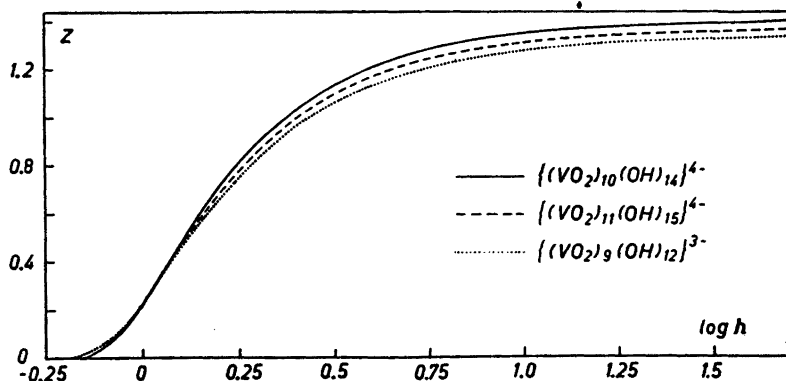$$Z = \frac{P}{Q} \frac{\vartheta}{1+\vartheta} \qquad (14)$$

Fig. 4. *Normalised curves $Z(\log h)_B$ for the single species $(VO_2)_Q(OH)_P$*

Thus a normalised set of $Z(\log h)_B$ curves may be calculated using eqns. (12) and (13), together with the values of P and Q given in Table 2, and compared with the experimental data shown in Fig. 2. Some of the normalised curves are shown in Fig. 4. A good fit could be obtained, within the limits of experimental error, with all the curves, for values of Z less than those listed in column 4 of Table 2. None of the curves fitted particularly well for values of $Z < 0.05$, but this is to be expected from the large experimental error in this region. For values of $Z \lesssim 0.8$, the data appear to be consistent with the formation of $(VO_2)_9(OH)_{12}^{3-}$, $(VO_2)_{10}(OH)_{14}^{4-}$, $(VO_2)_{11}(OH)_{15}^{5-}$ or of $(VO_2)_{12}(OH)_{17}^{5-}$, and there seems to be no reliable criterion for distinguishing with certainty between these possibilities with the present data. However, since the data are consistent with the existence of $(VO_2)_{10}(OH)_{14}^{4-}$ over the biggest range of values of Z ($\lesssim 1.3$), the simplest and most likely explanation of the hydrolysis of the VO_2^+ ion may be given in terms of the initial formation of this species.

The hydrolysis constant of $(VO_2)_{10}(OH)_{14}^{4-}$

The equilibrium constant $\varkappa_{14,10}$ for the initial reaction

$$10 \ VO_2^+ + 14 \ H_2O \rightleftharpoons (VO_2)_{10}(OH)_{14}^{4-} + 14 \ H^+ \qquad (9a)$$
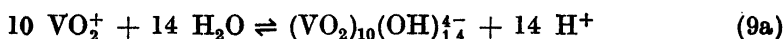
may be calculated in many ways from the data in the range where no further reaction is detectable.

(a) *Direct curve fitting.* Values of $\varkappa_{14,10}$ may be obtained directly from corresponding coordinates of experimental and theoretical curves $Z(\log h)_B$ placed in the position of best fit in the region $Z < 1.3$ (*cf.* Figs 2 and 4). When the right hand side of eqn. (13) is zero,

$$\log \varkappa_{14,10} = 14 \log h - 9 \log B - \log 10 \qquad (13a)$$

whence is obtained $\log \varkappa_{14,10} = -6.75 \pm 0.15$

(b) *Linear extrapolation.* It has been shown elsewhere [25] that

$$\log\{P^{Q-1}Z(P-QZ)^{-Q}\} = (Q-1) \log B - P \log h + \log\varkappa_{P,Q} \qquad (15)$$

for reaction (9). The data for 26 titration points in the range $0.1 < Z < 1.3$, but otherwise selected at random, were plotted in the form of $\log \{14^9 Z(14-10Z)^{-10}\}$ against $(9 \log B - 14 \log h)$; *cf.* Table 3. Since the points lie on a straight line (not reproduced here) of unit slope, and of intercept -6.8 ± 0.1, the data are consistent with the initial formation of $(VO_2)_{10}(OH)_{14}^{4-}$ with a hydrolysis constant of $\log \varkappa_{14,10} = -6.8 \pm 0.1$.

(c) *Methods based on the "core + links" hypothesis.* Values of

$$\log \varkappa_{14,10} = -6.75 \pm 0.03$$
$$\text{and} \qquad -6.75 \pm 0.07$$

were obtained by integration, and by curve fitting, respectively, of the plot of $Z/1.556$ against $(\log B - 1.556 \log h)$. Discussion of the application of the "core + links" hypothesis [32] to the present data will be deferred to an appendix to this paper.

Table 3. Data for determining $\varkappa_{14,10}$ by linear extrapolation according to eqn. (15).

$-\log B$	$-\log h$	Z	$\log\{14^9 Z(14-10Z)^{-10}\}$	$9\log B - 14\log h$
1.70	1.63	0.576	0.92	7.59
	1.79	0.880	3.09	9.75
	1.98	1.10	5.58	12.51
	2.01	1.13	6.04	12.91
	2.12	1.21	7.62	14.44
	2.37	1.32	10.70	17.91
2.00	1.83	0.569	0.88	7.60
	1.91	0.732	1.44	8.77
	2.00	0.887	3.16	10.03
	2.11	1.02	4.53	11.53
	2.24	1.14	6.32	13.35
	2.28	1.17	6.76	13.87
	2.42	1.24	8.36	15.84
2.30	1.87	0.140	-1.54	5.45
	1.99	0.480	0.36	7.10
	2.06	0.643	1.33	8.12
	2.14	0.792	2.37	9.32
	2.25	0.930	3.57	10.75
	2.37	1.08	5.29	12.43
	2.55	1.19	7.17	14.94
2.60	2.09	0.220	-1.07	5.86
	2.14	0.356	-0.32	6.60
	2.20	0.508	0.52	7.34
	2.32	0.764	2.16	9.12
	2.49	0.998	4.28	11.40
	2.59	1.11	5.70	12.87
	2.73	1.20	7.37	14.85

Straight lines of unit slope are also obtained in certain ranges for plots using the other values of P and Q listed in table 2. However, the data may be represented by equation (15) over the biggest range of values of Z ($\leqslant 1.3$) with $P = 14$ and $Q = 10$.

The secondary products of hydrolysis

If $(VO_2)_{10}(OH)_{14}^{4-}$ were the sole product of hydrolysis of VO_2^+, the plots $Z(\log h)_B$ would coincide at $Z = 1.4$, and $dZ / d \log h$ would then be zero. On the contrary, the curves do not coincide until $Z > 1.4$, and Z increases to approximately 1.6 in the range $3 \leqslant pcH \leqslant 6.5$. Within the accuracy of the experimental measurements, it appears possible to describe the upper parts of the $Z (\log h)_B$ curves mathematically in one of two ways:

(a) further hydrolysis of $(VO_2)_{10}(OH)_{14}^{4-}$ to $(VO_2)_{10}(OH)_{15}^{5-}$ and $(VO_2)_{10}(OH)_{16}^{6-}$, or

(b) formation of a series of more condensed isopolyvanadates, $(VO_2^+)_q(OH^-)_p$ where $q > 10$.

The former explanation is preferable on grounds of simplicity and in view of recent preliminary crystallographic studies of isopolyvanadates, which will be discussed later.

If $(VO_2)_{10}(OH)_{16}^{6-}$ is the ultimate decavanadate, the three isopolyvanadates may arbitrarily be assigned the formulae $H_2V_{10}O_{28}^{4-}$, aq., $HV_{10}O_{28}^{5-}$, aq., and $V_{10}O_{28}^{6-}$, aq. The dissociation constants of the first two species may be denoted

by $K_{15,10}$ and $K_{16,10}$, and the overall hydrolysis constants of the last two species by $\varkappa_{15,10}$ and $\varkappa_{16,10}$. Thus

$$\varkappa_{15,10} = \varkappa_{14,10} \cdot K_{15,10} \tag{16a}$$

$$\varkappa_{16,10} = \varkappa_{15,10} \cdot K_{16,10} \tag{16b}$$

Accordingly, for a system consisting of VO_2^+, $H_2V_{10}O_{28}^{4-}$, aq., $HV_{10}O_{28}^{5-}$, aq. and $V_{10}O_{28}^{6-}$, aq. in equilibrium

$$B = b + 10b^{10} \sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p} \tag{17}$$

and

$$h - H = BZ = 10b^{10}Z_{10} \sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p} \tag{18}$$

where Z_{10}, the average number of additional hydroxyl groups per VO_2 group in the decavanadates is defined by

$$Z_{10} = \frac{\sum\limits_{p=14}^{p=16} p[(VO_2)_{10}(OH)_p]}{10 \sum\limits_{p=14}^{p=16} [(VO_2)_{10}(OH)_p]} \tag{19}$$

where charges are omitted for clarity. Now

$$Z = \frac{10\varkappa_{14,10}b^{10}h^{-14}\,(1.4 + 1.5K_{15,10}h^{-1} + 1.6K_{15,10}K_{16,10}h^{-2})}{b + 10\varkappa_{14,10}b^{10}h^{-14}\,(1 + K_{15,10}h^{-1} + K_{15,10}K_{16,10}h^{-2})} \tag{20}$$

so that the function $Z(\log h)_B$ may be described in terms of the two variables b and h and the three parameters $\varkappa_{14,10}$, $K_{15,10}$ and $K_{16,10}$. Moreover

$$Z_{10} = \frac{1.4 + 1.5K_{15,10}h^{-1} + 1.6K_{15,10}K_{16,10}h^{-2}}{1 + K_{15,10}h^{-1} + K_{15,10}K_{16,10}h^{-2}} \tag{21}$$

so that Z_{10} $(\log h)$ may be described in terms of the single variable h and the two parameters $K_{15,10}$ and $K_{16,10}$. Combining eqns. (17) and (18)

$$\frac{b}{B} = \frac{Z_{10} - Z}{Z_{10}} \tag{22}$$

whereby b may be eliminated from eqn. (18). Thus

$$Z = 10B^9\,(Z_{10} - Z)^{10}(Z_{10})^{-9} \sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p} \tag{23}$$

By introducing auxiliary variables into this equation, it is possible to calculate theoretical (or normalised) curves, which may be superimposed on the experimental data. The required equilibrium constants are found from the differences between the coordinates of these curves in the position of best fit. This approach is analogous to that used by Lagerström and Sillén for interpreting measurements of equilibria in silicate solutions [34].

Evaluation of the decavanadate hydrolysis constants

(a) *Normalised curves log B (log Z).*
Introducing the auxiliary variables

$$\log \mathbf{Z} = \log Z - \log Z_{10} \tag{24}$$

and

$$\log \mathbf{B} = \log B + \frac{1}{9} \left(1 + \log \sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p}\right) \tag{25}$$

eqn. (23) may be rewritten in the form

$$\log \mathbf{B} = \frac{1}{9} \log \mathbf{Z} - \frac{10}{9} \log (1 - \mathbf{Z}) \tag{26}$$

The normalised curve log $\mathbf{B}$ (log $\mathbf{Z}$) may be calculated from eqn. (26) and fitted to each of the experimental curves log B (log $Z)_h$ by movement parallel to the axes, *cf.* Fig. 5. Then, for each particular value of h, the differences between the coordinates of the theoretical and experimental curves give values of Z_{10} and $\sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p}$ according to eqns. (24) and (25). The internal consistency of the values so obtained may be checked since it may be shown from eqn. (21) that

$$\frac{\mathrm{d} \log \sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p}}{\mathrm{d} \log h} = - 10 \ Z_{10} \tag{27}$$

The equilibrium constants may be found from the functions $\sum_{p=14}^{p=16} \varkappa_{p,10} h^{-p}$ (h) or $10Z_{10}(h)$ by standard methods, *cf.* Ref.[35] and parts (c) and (d) of this section.

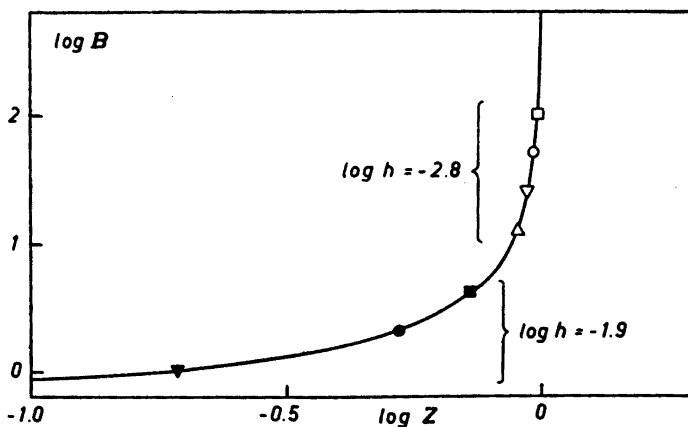*Fig. 5. Normalised curve log B (log Z) for the series of complexes $(VO_2)_{10}(OH)_P$. The lower and upper groups of experimental points show log B(log Z)$_h$ for h = $10^{-2.8}$ and $10^{-1.9}$ M in the positions of best fit.*

In the present case, reliable experimental data for $\log B (\log Z)_h$ can only be derived from the data $\log Z$ $(\log h)_B$ in the range $1.6 \leqslant pcH \leqslant 2.8$. Throughout this range it is found that

$$Z_{10} = 1.4$$
$$\text{and} \quad \log \varkappa_{14,10} = -6.7 \pm 0.2$$

In the range $2.8 \leqslant pcH \leqslant 4.0$, $d \log B/d \log h \to \infty$ so that experimental curves cannot be obtained, and fitted to the normalised curves, with any great accuracy. Nevertheless, it is evident that Z_{10} increases from 1.4 to 1.5 in this region.

(b) Normalised curves $\log B$ $(\log h)_{Z,l}$.

Alternatively, the following auxiliary variables and parameters may be introduced into eqn. (23):

$$\log \boldsymbol{h} = \log K_{15,10} - \log h \tag{28}$$

$$\log \boldsymbol{l} = \log K_{16,10} - \log K_{15,10} \tag{29}$$

$$\log \varepsilon = \frac{1}{9} (1 + \log \varkappa_{14,10} - 14 \log K_{15,10}) \tag{30}$$

$$\log \boldsymbol{B} = \log B + \log \varepsilon \tag{31}$$

and it may be shown that

$$\log \boldsymbol{B} = \log Z + \log (1.4 + 1.5\boldsymbol{h} + 1.6\ \boldsymbol{h}^2\boldsymbol{l}) - \frac{14}{9} \log \boldsymbol{h}$$

$$- \frac{10}{9} \log [(1.4-Z) + (1.5-Z)\ \boldsymbol{h} + (1.6-Z)\boldsymbol{h}^2\boldsymbol{l}] \tag{32}$$

A family of normalised curves $\log \boldsymbol{B}$ $(\log \boldsymbol{h})_{Z,l}$ may be calculated from eqn. (32) for a number of values of Z ($\leqslant 1.42$). For each family of curves, it is also necessary to assume some value of $\boldsymbol{l}$, defined by eqn. (29), cf. Fig. 6. The experimental curves $\log B$ $(\log h)_Z$ are moved over the families of normalised curves, calculated for different values of $\boldsymbol{l}$. In the position of best fit, the differences between the coordinates of the experimental and normalised curves give $\log K_{15,10}$ according to eqn. (28), and

$$\log \boldsymbol{B} - \log B = \frac{1}{9} (1 + \log \varkappa_{14,10} - 14 \log K_{15,10}) \tag{33}$$

according to eqns. (30) and (31). Log $K_{16,10}$ is found from eqn. (29).

Comparison of the experimental data $\log B$ $(\log h)_Z$ with families of normalised curves calculated for a few different values of l indicated that the best fit could be obtained with values of $l < 0.01$, i.e. in the range $Z < 1.4$, the species $V_{10}O_{28}^{6-}$,aq. is scarcely detectable. Hence a simplified form of eqn. (32) was used, with $l = 0$. From the coordinates in the position of best fit, the following equilibrium constants were evaluated: —

$$\log \varkappa_{14,10} = -6.75 \pm 0.15$$

$$\log K_{15,10} = -3.6 \pm 0.3$$
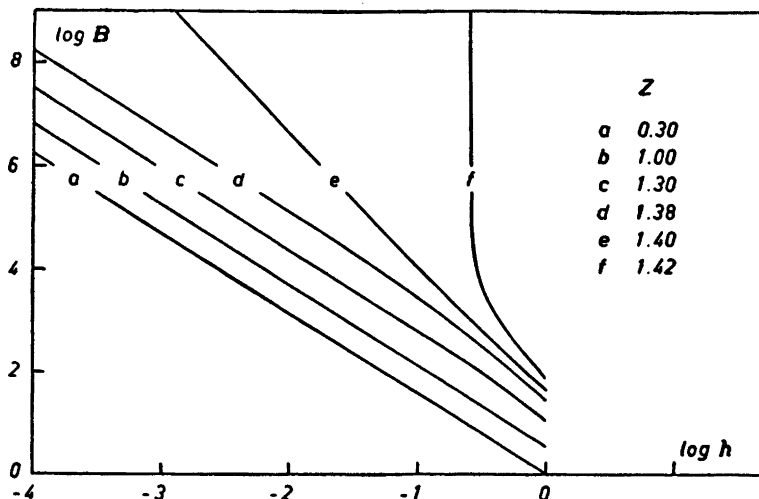
Moreover, $\log K_{16,10} < -5.6$

Fig. 6. Normalised curves log B (log h)$_{Z,l}$ for $l = 0$.

(c) *Normalised curves* $10Z_{10}$ *(log* h)$_l$

For a system consisting of a metal ion Me and of two mononuclear complexes MeOH and Me(OH)$_2$

$$Z_1 = \frac{\sum\limits_{p=1}^{p=2} p\varkappa_{p,1}h^{-p}}{\sum\limits_{p=0}^{p=2} \varkappa_{p,1}h^{-p}} \tag{34}$$

where $\varkappa_{0,1} = 1$.

Similarly, for the species $H_2V_{10}O_{28}^{4-}$ and its dissociation products $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$, eqn. (21) may be rewritten

$$10Z_{10}-14 = \frac{K_{15,10}h^{-1} + 2K_{15,10}K_{16,10}h^{-2}}{1 + K_{15,10}h^{-1} + K_{15,10}K_{16,10}h^{-2}} \tag{21a}$$

Thus, eqn. (21a) is of the same form as eqn. (34). The family of curves $10Z_{10}$(log h)$_{K_{15,10}/K_{16,10}}$ will be the same shape as the formation function Z_1 (log h)$_{K_{1,1}/K_{2,1}}$ for a mononuclear system, but will be displaced 14 units up the ordinate axis. As $b \to 0$ in the homonuclear range pcH>4, Z_{10} may be obtained as the value of Z in this region.

Introducing the auxiliary parameters and variables

$$\gamma = \tfrac{1}{2}\,(\log\,K_{15,10} + \log\,K_{16,10}) \tag{35}$$

$$l = K_{16,10}\,/\,K_{15,10} \tag{29a}$$

$$\log\,h = \gamma - \log\,h \tag{36}$$

into eqn. (21a)

$$10Z_{10} - 14 = \frac{l^{-\frac{1}{2}}h + 2h^2}{1 + l^{-\frac{1}{2}}h + h^2} \tag{37}$$

Normalised curves $10Z_{10}$ (log h)$_l$ were calculated for a number of values of $l^{-\frac{1}{2}}$, using eqn. (37) (cf.[36]), and fitted to the experimental function $10Z_{10}$(log h), by movement along the log h axis. The parameter l is that value used to calculate the curve of appropriate shape, and γ is obtained from the differences between the coordinates, according to eqn. (36). The following values of the dissociation constants of $H_2V_{10}O_{28}^{4-}$ and $HV_{10}O_{28}^{5-}$ were obtained

$$\log K_{15,10} = -3.6 \pm 0.3$$

$$\log K_{16,10} = -5.8 \pm 0.1$$

(d) *Linear Extrapolation.*

Eqn. (17) may be rewritten as

$$\frac{B-b}{10b^{10}h^{-14}} = \varkappa_{14,10} + \varkappa_{15,10}h^{-1} + \varkappa_{16,10}h^{-2} \tag{17a}$$

or

$$\frac{B-b}{10b^{10}h^{-16}} = \varkappa_{16,10} + \varkappa_{15,10}h + \varkappa_{14,10}h^2 \tag{17b}$$

Hence, if the concentration of free VO_2^+ ions, b, were known, the equilibrium constants could be found by successive extrapolations, cf. Ref.[35]. In the absence of direct measurements of b, this quantity may be calculated. Hedström [37] has shown that

$$\left(\frac{\partial \ln b}{\partial \ln h}\right)_B = \left(\frac{\partial H}{\partial B}\right)_h \tag{38}$$

Combining eqns. (1) and (38), it may be shown that

$$\ln\frac{B}{b} = \left[\int\left\{Z + \left(\frac{\partial Z}{\partial \ln B}\right)_h\right\}\mathrm{d} \ln h\right]_B \tag{39}$$

for a system which is mononuclear at the lower limit of integration, cf. Lagerström and Sillén [34]. Values of $\left(\frac{\partial Z}{\partial \log B}\right)_{h,B}$ were obtained by graphical differentiation of plots of Z (log B)$_h$, and the right hand side of eqn. (39) was evaluated by graphical integration of plots of $\left\{Z + \left(\frac{\partial Z}{\partial \log B}\right)_h\right\}_B$ against log h. Corresponding values of B, b and h were substituted into eqns. (17 a) and (17 b) and the polynomials plotted both as a function of h and of h^{-1}. The following mean values of the overall hydrolysis constants were obtained:

$$\log \varkappa_{14,10} = -\ 6.82 \pm 0.17$$

$$\log \varkappa_{15,10} = -\ 9.9\ \pm 0.6$$

$$\log \varkappa_{16,10} = -15.7\ \pm 0.6$$

Table 4. The determination of $\varkappa_{p,10}$, by successive linear extrapolations according to eqns. (17a) and (17b): an example of the calculations for $B = 2 \times 10^{-2}M$.

$-\log h.$	Z	$\left(\dfrac{\partial Z}{\partial \ln B}\right)_h$	$\log \dfrac{B}{b}$	$-\log b.$	$-\log \dfrac{B-b}{10b^{10} h^{-14}}$
1.3	0	0	0	1.698	—
1.4	0.08	0.20	0.012	1.710	6.66
1.5	0.26	0.50	0.059	1.757	7.03
1.6	0.49	0.724	0.161	1.859	7.02
1.7	0.71	0.68	0.292	1.990	6.90
1.8	0.89	0.55	0.432	2.130	6.80
1.9	1.016	0.35	0.575	2.273	6.71
2.0	1.10	0.25	0.718	2.416	6.63
2.5	1.356	0.075	1.438	3.136	6.35
3.0	1.41	0.053	2.166	3.864	6.06
3.5	1.452	0.019	2.901	4.599	5.71
4.0	1.484	0.007	3.642	5.340	5.30
4.5	1.50	0.0	4.394	6.092	4.78
5.0	1.52	0.0	5.149	6.847	4.22
5.5	1.55	0.0	5.914	7.612	3.58
6.0	1.564	0.0	6.687	8.385	2.85
6.5	1.59	0.0	7.471	9.169	2.01
7.0	1.60	0.0	8.258	9.956	1.14

Hydrolysis constants found: $\log \varkappa_{14,10} = -6.8$, $\log \varkappa_{15,10} = -9.3$, $\log \varkappa_{16,10} = -15.07$.

The large errors associated with $\varkappa_{15,10}$ and $\varkappa_{16,10}$ arise from a systematic drift in the values of the left hand side of eqns. (17a) and (17b) obtained using different total concentrations of vanadium, B. Such discrepancies are scarcely surprising as high powers of b and h are involved, and neither of these variables can be obtained very accurately from measurements made with a glass electrode of high resistance.

POTENTIOMETRIC TITRATIONS IN A 3 M MEDIUM

The preliminary titrations (like the spectrophotometric work) were carried out in a 3 M perchlorate medium in which sodium was the predominant cation, and in the region $1 < pcH < 4$, only. This work was discontinued owing to the limited solubility of vanadium(V) perchlorate in the medium. The curves, $Z (\log h)_B$, (not reproduced here) were of the same shape as those obtained in the 1 M medium, but for identical vanadium concentrations were displaced by -0.1 pcH units. Assuming the same products of reaction as in the 1 M medium the following equilibrium constants were obtained for this medium:

$$\log \varkappa_{14,10} = -5.5 \pm 0.15$$
$$\log K_{15,10} = -3.5 \pm 0.3$$

DISCUSSION

Potentiometric and absorptiometric studies indicate that vanadium(V) exists as the VO_2^+, aq. ion in the range of acidity $2.9\ M > h > 0.05\ M$. No evidence was found of less hydrolysed cations, which have been suggested by

previous investigators [4-8]. Although the interpretation of the potentiometric data in the range $1.3 < \text{pcH} < 6.5$ is not unequivocal, these data are clearly incompatible with the formation of hexavanadates [1,12-15], pentavanadates [6], or other smaller polyanions [10,22], which have also been proposed by earlier workers, and which are described in contemporary text-books. The present data may most simply be explained by assuming that the decavanadates $H_2V_{10}O_{28}^{4-}$, aq., $HV_{10}O_{28}^{5-}$, aq., and $V_{10}O_{28}^{6-}$, aq. are successively formed in solution from VO_2^+, aq. The species $H_2V_{10}O_{28}^{4-}$ corresponds to $V_{10}O_{27}^{4-}$, which has been suggested by Britton and Welford [5], and by Hazel, McNabb and Santini [17], although this species has now been shown to give rise to further decavanadates. The present data provide no evidence for the equilibrium

$$VO_2^+ \rightleftharpoons (VO_2^+)_q(OH^-)_p \rightleftharpoons V_{10}O_{27}^{4-} \quad (\text{where } q > 10)$$
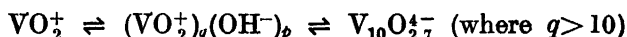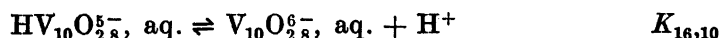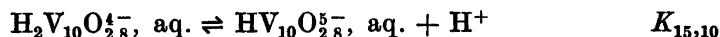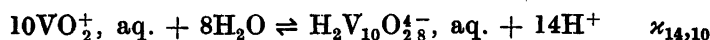
suggested by the latter workers. At higher vanadium concentrations than have been used in the present work, the pentoxide precipitates in the region of the isoelectric point, which is given by

$$\text{pcH} = 0.803 - 0.643 \log B \qquad \text{and} \qquad \text{(40a)}$$

$$\text{pcH} = 0.715 - 0.643 \log B \qquad \qquad \text{(40b)}$$

in 1 M and 3 M (sodium) perchlorate media, respectively.

Since few quantitative studies of step-equilibria of the type

$$10VO_2^+, \text{ aq.} + 8H_2O \rightleftharpoons H_2V_{10}O_{28}^{4-}, \text{ aq.} + 14H^+ \qquad \varkappa_{14,10}$$

$$H_2V_{10}O_{28}^{4-}, \text{ aq.} \rightleftharpoons HV_{10}O_{28}^{5-}, \text{ aq.} + H^+ \qquad K_{15,10}$$

$$HV_{10}O_{28}^{5-}, \text{ aq.} \rightleftharpoons V_{10}O_{28}^{6-}, \text{ aq.} + H^+ \qquad K_{16,10}$$

have been reported, values of the equilibrium constants have been obtained using a variety of methods, and are given below.

Table 5. *Hydrolysis constants valid at 25°C in a 1 M perchlorate medium, in which sodium is the predominant cation.*

Method	$-\log \varkappa_{14,10}$	$-\log K_{15,10}$	$-\log K_{16,10}$
Curve fitting: Z $(\log h)_B$	6.75 ± 0.15	—	—
$Z/1.556$ $(\log B - 1.556 \log h)$ ..	6.75 ± 0.07	—	—
$\log B$ $(\log h)_Z$	6.7 ± 0.2	—	—
$\log B$ $(\log Z)_h$	6.75 ± 0.15	3.6 ± 0.3	> 5.6
$10Z_{10}$ $(\log h)$	—	3.6 ± 0.3	5.8 ± 0.1
Linear extrapolation eqn. (15)	6.8 ± 0.1	—	—
eqns. (17a), (17b)	6.82 ± 0.17	3.1 ± 0.6	5.8 ± 0.1
Integration $Z/1.556$ $(\log B - 1.556 \log h)$	6.75 ± 0.03	—	—
Proposed values	6.75 ± 0.15	3.6 ± 0.3	5.8 ± 0.1

The hydrolysis of vanadium(V) is somewhat greater in a 3 M (sodium) perchlorate medium than in a 1 M medium, and the following equilibrium constants have been obtained;

$$\log \varkappa_{14,10} = -5.5 \pm 0.15$$

$$\log K_{15,10} = -3.5 \pm 0.3$$

The overall stability constant, $\beta_{q,p}$, for the hydroxo-complex $Me_q(OH)_p$ is related to the corresponding hydrolysis constant, $\varkappa_{q,p}$, by the expression

$$\beta_{q,p} = \frac{[Me_q(OH)_p]}{[Me]^q[OH]^p} = \varkappa_{q,p}K_w^{-p} \tag{41}$$

where K_w is the ionic product for water. Using values $K_w = 10^{-13.8}$ and $10^{-14.22}$ (Ref. 38) log $\beta_{14,10} = 186$ and 194 in the 1 M and 3 M media, respectively. An increase in the overall hydrolysis constant of $Fe_2(OH)_2^{4+}$ with increasing ionic strength has recently been reported by Milburn and Vosburgh [39].

In order to calculate the proportions of the various species present in solution, it is convenient to combine eqn. (17) with the auxiliary variables defined by eqns. (29) and (30).

$$\frac{100\ [VO_2]}{B} = 100\left[1 + 10\varkappa_{14,10}B^9h^{-14}\left(1 - \frac{Z(1+h)}{1.4+1.5\ h}\right)^9(1+h)\right]^{-1} \tag{42}$$

$$\frac{100\ [H_{16-p}V_{10}O_{28}]}{B} =$$

$$\frac{10^3\varkappa_{14,10}B^9h^{-p}\left(1 - \dfrac{Z(1+h+lh^2)}{1.4+1.5\ h+1.6lh^2}\right)^9}{1 + 10\varkappa_{14,10}B^9h^{-14}\left(1 - \dfrac{Z(1+h+lh^2)}{1.4+1.5h+1.6lh^2}\right)^9(1+h+lh^2)} \tag{43}$$

The proportions of the different species, $\alpha_{p,q}$, have been calculated as percentages of the total vanadium present for the highest (2×10^{-2} M) and lowest (2.5×10^{-3} M) vanadium concentrations used in the 1 M medium. These are plotted as functions of pcH in Fig. 7. The curves for VO_2^+ and $H_2V_{10}O_{28}^{4-}$, which are in heteronuclear equilibrium, are unsymmetrical. However, the curves $\alpha_{p,10}$ (pcH) for $HV_{10}O_{28}^{5-}$ and $V_{10}O_{28}^{6-}$, which are substantially in homonuclear equilibrium, are symmetrical (cf. mononuclear systems).
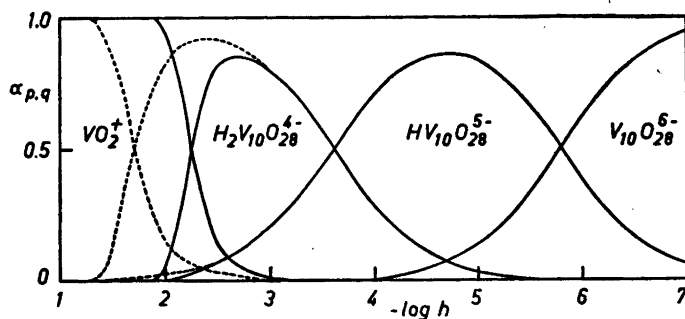

Fig. 7. The relative amounts of the hydrolysis products of vanadium (V) as a function of pcH in a 1 M perchlorate medium at 25°C expressed as percentages of the total vanadium. ———— B = 2.5×10^{-3}M and — — — B = 2×10^{-2}M.

Polyvanadates in the solid state

Orange polyvanadates crystallise from solutions of pcH < 7. The analytical ratios Me(I)/V(V) reported in the literature [40] include; 5/6, 4/5, 5/8, 2/3, 3/5, 4/7, 1/2, 3/7, 2/5, 1/3, 1/4, 2/9. Previous formulae suggested for the polyvanadates have been in accordance with one or other of these ratios. If solid vanadates of the VO_2^+ ion can be obtained from acidic solutions, as Jahr and Jander [41] have suggested, a number of these ratios may represent distinct compounds. However, in the absence of further evidence, it is somewhat doubtful whether all these ratios can represent different compounds.

Lindqvist [42], and Evans, Mrose, and Marvin [43] have recently examined crystallographically a number of orange polyvanadates, which were crystallised at pcH $\sim$ 6.5. Analytical data were in good agreement with the formulae listed in Table 6, and the salts have all been shown to contain ten, or multiples of ten, vanadium atoms per unit cell.

Table 6. *Polyvanadates examined structurally.*

Analytical formula	V atoms per unit cell.	Ref.
$(NH_4)_6V_{10}O_{28},6H_2O$	20	Lindqvist[42]
$K_6V_{10}O_{28},9H_2O$	20	Evans, Mrose & Marvin [43]
$K_6V_{10}O_{28},10H_2O$	40	»
$Ca_3V_{10}O_{28},16H_2O$ (pascoite)	20	»
$K_2Mg_2V_{10}O_{28},16H_2O$ (hummerite)	10	»
$K_2Zn_2V_{10}O_{28},16H_2O$	10	»

Although attempts to solve these structures have so far failed [42,43], it seems likely that anions which contain ten vanadium atoms exist in the solid phase.

The coordination number of vanadium(V) may be 4, 5 or 6, in solid vanadates depending upon the pcH at which the compound is obtained. Vanadium pentoxide (which precipitates at pcH $\sim$ 2) is considered to consist of chains of distorted trigonal bipyramids (Byström, Wilhelmi and Brotzen [44]) or of distorted octahedra (Magnéli and Oughton [45]). Metavanadates, $(VO_3)_n^{n-}$, crystallise from solutions of 6.5 < pcH < 8.0, and for KVO_3, H_2O, Christ, Clark and Evans [46] have shown that the basic structural unit is again the trigonal bipyramid. The metal-oxygen coordination is octahedral in the polyanions $Nb_6O_{19}^{8-}$ (Lindqvist [47]) and $Ta_6O_{19}^{8-}$ (Lindqvist and Aronsson [20]). Since, moreover, tetrahedral coordination [48] is only found in the orthovanadates, $MeVO_4$, which crystallise at pcH > 10, it is probable that vanadium is coordinated to 5 or 6 oxygen atoms in the decavanadates, which are obtained at pcH $\sim$ 6.5 (however, *cf.* Ottar [22]).

APPENDIX

The experimental data obtained in the 1 M medium are now discussed with reference to the "core + links" hypothesis [32,33]. When the parameter t is non-integral, the basic formulae [32] are still valid, but those concerned with continuous polymerisation (hypothesis III) must be modified, since some terms in the summation are now equal to zero. The "core + links" complexes
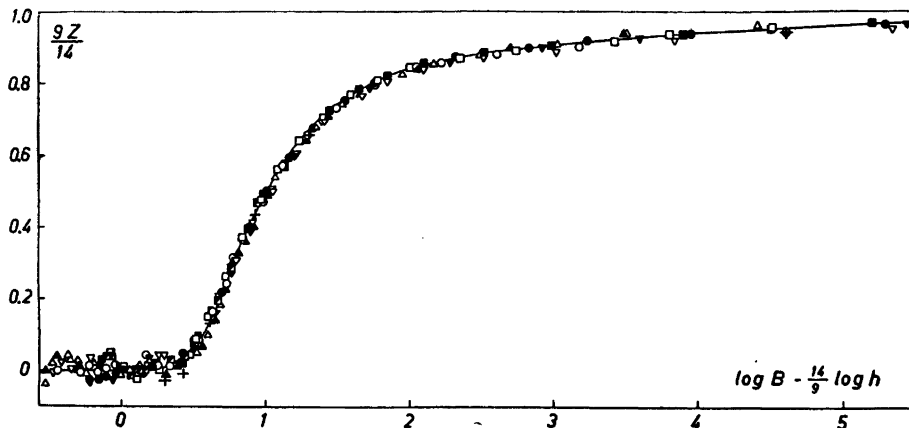
Fig. 8. y($= Z/1.556$) *as a function of* x($= log$ B $- 1.556$ *log* h). *The symbols are those used in Fig. 2. The curve is calculated from equations (59) and (60) with the two parameters, log* k$_0$ $= 2.0$ *and 9 log* k $= -8.75$.

B(A$_t$B)$_n$ only have a physical meaning when the product nt is also integral. If s is the smallest positive integer such that the product st is also integral, the possible complexes may be written as B(A$_{st}$B$_s$)$_j$, where j is either a single integer or a series of integers, and

$$n = sj \tag{44}$$

The spacing of the curves Z (log h)$_B$ indicates that the predominant complexes may be written in the form $VO_2((OH)_t VO_2)_n$, and it has been shown that the best value of t (within the experimental limit of 1.50 ± 0.07) is $14/9$, or 1.556. By plotting the data in the form $y(x)$, where

$$y = 9 \ Z \ / \ 14 \tag{8a}$$

and

$$x = \log \ B - \frac{14}{9} \log \ h \tag{7a}$$

the separate curves may be made to coincide (see Fig. 8). Hence $s = 9$, and the system may be considered as a series of complexes $VO_2((OH)_{14}(VO_2)_9)_j$. The points for $x < 2.5$ fit the curve calculated for the first complex with $sj = N=9$ (hypothesis II, Ref. [32]) in a position corresponding to log $\varkappa_{14,10} = -6.75 \pm 0.07$ for the complex $(VO_2)_{10}(OH)_{14}$. This conclusion has been reached by other methods; but the upper part of the curve $y(x)$ with $x > 2.5$ could now be interpreted in terms of continuous polymerisation.

Integration of the curve $y(x)$

Combining eqns. (5a), (8a) and (14) in Ref. [32], it may be shown that

$$\eta = \log \ \frac{B}{b} = \int_{-\infty}^{x} y \ dx + y \ \log \ e \tag{45}$$

The function $y(x)$ may be used to calculate

$$\log (1 + g) = \log (1 - y) + \eta \qquad (46)$$

and
$$\log u = x - \eta \qquad (47)$$

Here
$$g = \Sigma\, K_j u^{sj}, \qquad u = bh^{-t} \qquad (48)$$

and K_j is the equilibrium constant for the reaction

$$(1 + sj)\ \mathrm{B} + sjt\mathrm{A}\ \rightleftharpoons\ \mathrm{B}(\mathrm{A}_{st}\mathrm{B}_s)_j \qquad (49)$$

The average number, $\bar{j}$, of polynuclear links, $(\mathrm{A}_{st}\mathrm{B}_s)$, per complex is given by

$$\bar{j} = \frac{\Sigma\, j\, c_j}{\Sigma\, c_j} = \frac{\bar{n}}{s} = \frac{1}{s}\cdot\frac{\mathrm{d}\, \log g}{\mathrm{d}\, \log u} \qquad (50)$$

$$\text{where } c_j = [\mathrm{B}(\mathrm{A}_{st}\mathrm{B}_s)_j] \qquad (51)$$

As an alternative to finding $\bar{j}$ by graphical differentiation of the function $\log g$ ($s \log u$), it may be shown that

$$\bar{j} = \frac{y}{s\, (1 - y - 10^{-\eta})} \qquad (52)$$

A smooth curve was drawn through the experimental points of $Z\,/\,1.556$ plotted against $(\log B - 1.556 \log h)$, and a set of values of $\displaystyle\int_{0.35}^{x} y\, dx$ was obtained by graphical integration. The residual integral $\displaystyle\int_{-\infty}^{-\infty} y\, dx$ was assumed to be zero cf. Fig. 8. Corresponding values of $\log g$ and $\log u$ were calculated using eqns. (46) and (47), and are given in Table 7, together with values of $\bar{j}$, calculated from eqn. (52). The function $\bar{j}(x)$ is plotted in Fig. 9.
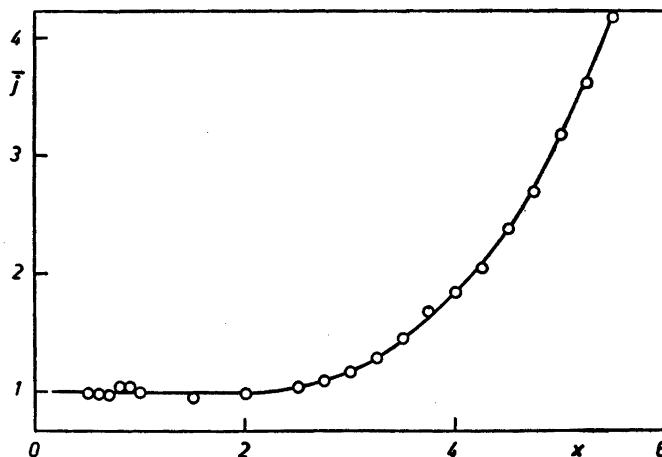

Fig. 9. The average number $\bar{j}$ of $((OH)_{14}(VO_2)_9)$ links per complex as a function of x.

Table 7. Integration of the smoothed curve y(x).

x	y	$\int_{-\infty}^{x} y\,dx$	$\log g$	$\log u$	$\bar{\jmath}$
0.50	0.040	0.0024	−2.301	0.480	0.99
0.60	0.116	0.0097	−1.824	0.540	0.98
0.70	0.212	0.0252	−1.495	0.583	0.96
0.80	0.324	0.0520	−1.276	0.607	1.04
0.90	0.420	0.0893	−1.076	0.628	1.03
1.00	0.500	0.135	−0.900	0.647	0.99
1.50	0.746	0.455	−0.277	0.721	0.94
2.00	0.844	0.856	0.205	0.777	0.98
2.50	0.884	1.289	0.649	0.827	1.03
2.75	0.896	1.511	0.861	0.850	1.09
3.00	0.906	1.736	1.067	0.871	1.17
3.25	0.916	1.964	1.263	0.889	1.28
3.50	0.926	2.194	1.450	0.904	1.44
3.75	0.936	2.427	1.629	0.917	1.67
4.00	0.942	2.661	1.827	0.930	1.83
4.25	0.948	2.898	2.022	0.940	2.04
4.50	0.955	3.136	2.201	0.949	2.38
4.75	0.960	3.375	2.393	0.958	2.68
5.00	0.966	3.616	2.566	0.964	3.17
5.25	0.970	3.858	2.802	0.970	3.60
5.50	0.974	4.101	2.939	0.976	4.17

Since $\bar{\jmath}$ is approximately unity for $x<2.5$, the single complex $VO_2((OH)_{14}(VO_2)_9)$ predominates in this region. From eqn. (48)

$$\log K_1 = \log g - 9 \log u \qquad (53)$$

whence the value

$$\log K_1 = \log \varkappa_{14,10} = -6.75 \pm 0.03$$

was obtained, in good agreement with values obtained by other methods.

Curve fitting of the function $y(x)$

It is evident from Fig. 9 that $\bar{\jmath}$ increases to values >4 at $x = 5.5$ (corresponding to pcH ~ 5 for 5×10^{-3} M vanadium). Thus within the accuracy that the data may be represented by a single curve $y(x)$, the "core + links" treatment would indicate that polymers containing at least 37 vanadium atoms are formed. This system may be described in terms of two parameters k_0 and k, provided that some assumption is made about the ratio of successive hydrolysis constants. For simplicity, attention is restricted to the hypothesis (IIIa, Ref.[32]) that this ratio is constant, and that complexes with all positive integral values of j may be formed. Sillén's treatment may be modified by defining

$$K_j = k_0 k^{sj} \qquad (54)$$

and

$$V = v^s \qquad (55)$$

where

$$v = ku = ka^t b \qquad (56)$$

On the reasonable assumption that $|V| < 1$, then

$$g = k_0 \ \Sigma \ V^j = k_0 V \ (1-V)^{-1} \tag{57}$$

and
$$v \ \frac{\mathrm{d}g}{\mathrm{d}v} = sV \ \frac{\mathrm{d}g}{\mathrm{d}V} = sk_0 V \ (1-V)^{-2} \tag{58}$$

The coordinates of normalised curves $y(X)$ are found by substituting eqns. (57) and (58) into eqns. (8a) and (9a) of Ref.[32]. For convenience, the X coordinate is defined so that the family of curves $y(X)$ passes through the point (log 2, $\frac{1}{2}$). Then

$$y = sk_0 V \ [(1-V)^2 + k_0 V \ (1 + s - V)]^{-1} \tag{59}$$

$$X = x + \log \ 2 - x_{\frac{1}{2}}$$

$$= \frac{1}{s} \log \ V + \log \ [(1-V)^2 + k_0 V \ (1 + s - V)] - 2 \ \log \ (1-V) - \log \ sk_0$$

$$- (1 + \frac{1}{s}) \ \log \ V_{\frac{1}{2}} + 2 \ \log \ (1-V_{\frac{1}{2}}) \tag{60}$$

where $x_{\frac{1}{2}} = \log \ 2sk_0 - \log \ k + (1 + \frac{1}{s}) \ \log \ V_{\frac{1}{2}} - 2 \ \log \ (1-V_{\frac{1}{2}})$ (61)

and $V_{\frac{1}{2}}$ is given by eqn. (59) when $y = \frac{1}{2}$.

Hence the value of log k may be found from the x coordinate of the point $(x_{\frac{1}{2}}, \frac{1}{2})$ of the experimental curve $y(x)$, when the normalised curve $y(X)$ of the same shape has been found. The value of k_0 is that used to calculate the appropriate curve $y(X)$.

It would thus be incorrect to compare experimental curves $y(sx)$ for systems with non-integral values of t and in which continuous polymerisation is suspected, with normalised curves calculated on the assumption that t was integral. This procedure was inadvertantly used in an earlier paper on the hydrolysis of aluminium [49]. Families of curves are required for different values of s; when $s = 1$, eqns. (59), (60) and (61) reduce to equations given previously by Sillén [32]. As $k_0 \rightarrow 0$, the curves for all values of s tend to the limiting curve calculated [32] assuming that precipitation occurs, but that no complexes are detectable in solution (hypothesis I). As $k_0 \rightarrow \infty$ then each family of curves tends to a limiting curve calculated [32] assuming that a single species is present in solution (hypothesis II, $N = s$).

The normalised curve $y(X)$, calculated using eqns. (59) and (60) with $s = 9$ and $k_0 = 100$, is shown in the position of best fit in Fig. 8. From eqn. (61) the value of 9 log $k = -8.75$ is obtained, and hence from eqn. (54), log $K_1 = -6.75$, log $K_2 = -15.5$, log $K_3 = -24.25$ . . . . . The large value of k_0 implies that the formation of the first complex with $j = 1$ dominates the first stages of the reaction.

If more accurate experimental data in the range $Z > 1.3$ were available, it might be possible to distinguish between the hypothesis of a further hydrolysis of the first decavanadate ion $(VO_2)_{10}(OH)_{14}^{4-}$, and that of a repeated "core + links" mechanism. The former would give a single curve Z (log h), indepen-

dent of B, and the latter would give a single curve $y(x)$, also independent of B, in the region $1.4 \leqslant Z \leqslant 1.6$. However, although the repeated mechanism cannot be excluded with the present data, it appears to be physically much less plausible.

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