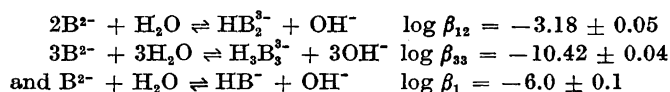# Equilibrium Studies of Polyanions

VI. Polyvanadates in Alkaline Na(Cl) Medium *

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Equilibria in alkaline vanadate(V) solutions have been studied at 25°C with 0.5 Na(Cl) as ionic medium. Emf measurements were made using a glass or a hydrogen electrode, which together gave concordant results. For an average charge, z, per vanadium, between -0.6 and -1.0 ("instability range"), equilibrium was attained very slowly. Reproducible equilibria were obtained from $z = -1$ to $z = -2$; in this range z was determined as a function of h for various total concentrations, B, of vanadium between 0.080 and 0.00062_5 M.

An analysis of the data indicated that the principal species in this range are B^{2-} [$VO_2(OH)_3^{2-}$, HVO_4^{2-}], HB_2^{3-} [$(VO_2)_2(OH)_5^{3-}$, $HV_2O_7^{3-}$] and $H_3B_3^{3-}$ [$(VO_2)_3(OH)_6^{3-}$, $V_3O_9^{3-}$]. There was also evidence for a mononuclear complex HB^- [$VO_2(OH)_2^-$, $H_2VO_4^-$, VO_3^-]. The following formation constants were obtained:

$$2B^{2-} + H_2O \rightleftharpoons HB_2^{3-} + OH^- \qquad \log \beta_{12} = -3.18 \pm 0.05$$
$$3B^{2-} + 3H_2O \rightleftharpoons H_3B_3^{3-} + 3OH^- \quad \log \beta_{33} = -10.42 \pm 0.04$$
$$\text{and } B^{2-} + H_2O \rightleftharpoons HB^- + OH^- \qquad \log \beta_1 = -6.0 \pm 0.1$$
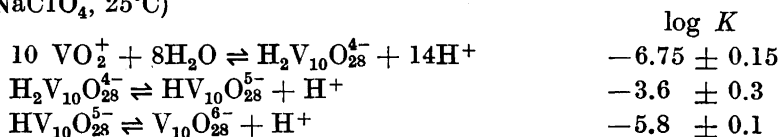
In this paper also tentative structures are given for the polynuclear complexes formed. The structures are based on five-coordination around vanadium and may give justification for the formulas $VO_2(OH)_3^{2-}$, $(VO_2)_2(OH)_5^{3-}$ and $(VO_2)_3(OH)_6^{3-}$.

The polyanions of vanadium have received a large amount of attention, but information concerning them has been most chaotic because no two workers have agreed and many different classifications, species, and types of reactions have been proposed. Among the methods used for studying these complicated equilibria the emf method seems to be the one that gives data of the highest accuracy. In a careful emf study using glass electrode, Francis and Hazel

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* The experimental part of this work was started by Nils Ingri of this laboratory, and then carried out jointly by Nils Ingri and Dr. Felipe Brito, of the University of La Laguna (Canary Islands, Spain), who is working here as a guest research associate. It was clear immediately from

Rossotti [1] investigated the polyvanadates formed in acid solutions. From these data they concluded that VO_2^+ is the only species in strong acid solution and that with increasing pH it reacts with H_2O forming a series of decavanadates. They could explain the data with the following reactions and constants (1 M $NaClO_4$, 25°C)

$$\begin{aligned} & & \log K \\ 10\ VO_2^+ + 8H_2O &\rightleftharpoons H_2V_{10}O_{28}^{4-} + 14H^+ & -6.75 \pm 0.15 \\ H_2V_{10}O_{28}^{4-} &\rightleftharpoons HV_{10}O_{28}^{5-} + H^+ & -3.6\ \pm 0.3 \\ HV_{10}O_{28}^{5-} &\rightleftharpoons V_{10}O_{28}^{6-} + H^+ & -5.8\ \pm 0.1 \end{aligned}$$

The existence of such decavanadate groups has also been indicated by X-ray investigations of crystals (Lindqvist [2], Evans, Mrose and Marvin [3]). Newman and Quinlan [4] found that their spectrophotometric data on equilibrium solutions can be explained by assuming the formation of the decavanadate ions proposed by Rossotti and Rossotti [1].

It is generally believed that these highly condensed anions are broken down with increasing pH, and that the end product in this process is the mononuclear orthovanadate ion, VO_4^{3-}. Our intention when we started this work was to use the same method as Rossotti and Rossotti but to go from the opposite direction and study the reactions taking place when H^+ is added to VO_4^{3-}; in this way we had hoped to find out the formulas and the equilibrium constants for the intermediate complexes formed when VO_4^{3-} is transformed to a decavanadate.

However, experimental difficulties reduced the range available, and the average charge per vanadium, z, could only be varied between -2 and -1. At higher z-values an "instability range" exists giving slow equilibria, and at lower z-values it is difficult to measure z accurately enough. The range studied corresponds to the transition from "pyrovanadate" ($z = -2$) to "metavanadate" ($z = -1$) following the common misleading nomenclature; the position on the pH-scale is shown in Fig. 1.
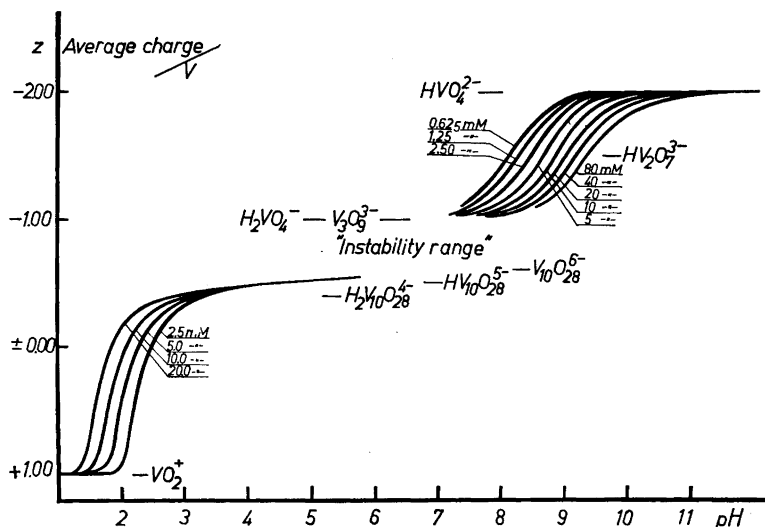
Fig. 1. Survey of data for vanadate (V) solutions: average charge, z, versus pH for various total concentrations, *B*. Curves on acid side from Rossotti and Rossotti [1] (1 M (Na) ClO$_4$). Curves on alkaline side from the present work. Between them is an "instability range", where equilibria are slowly attained. Note that the "phosphate" nomenclature has been used.

Like earlier work (Parts I[1], II[5], III[6] and IV[7] in this series) the present study was carried out as a number of potentiometric titrations at 25°C. In each titration the hydroxide ion concentration [OH$^-$] was varied, and the total vanadium concentration, *B*, was kept constant. [OH$^-$] was measured with a glass electrode with an accuracy of $\pm$ 0.3 mV. (Some experiments were also carried out using a hydrogen electrode). The variation of activity factors has largely been eliminated by keeping [Na$^+$] = constant = 0.5 M. The experimental emf gave [OH$^-$] (see eqn. 8), and the analytical composition of the solution gave *B* and *H*. *H* is the analytical excess concentration of hydrogen ions, H$^+$, assuming all vanadium to be in the form with z = $-$2, B^{2-} (= VO$_2$ (OH)$_3^{2-}$, HVO$_4^{2-}$). From these quantities one could then calculate *Z*, the average number of protons H$^+$ bound to B^{2-}, the dominating species at z = $-$2, from the relation

$$BZ = H + [\text{OH}^-] \qquad (1)$$

From *Z* we obtained z, the average (negative) charge per vanadium;

$$z = Z - 2 \qquad (2)$$

and *Z$_+$*, the average number of OH$^-$ bound to every VO$_2^+$ group (the quantity used by Rossotti and Rossotti [1]) from

$$Z_+ = 3 - Z = 1 - z \qquad (3)$$

For the mathematical treatment the experimental data have been plotted (Fig. 2) with Z and z against $-\log [OH^-]$, with a separate curve for each B-value.

NOTATIONS

The way of writing the formulas. The relationship between phosphates and vanadates was deduced from the isomorphism of the minerals vanadinite, $Pb_5(VO_4)_3Cl$, and apatite, $Ca_5(PO_4)_3F$, by the work of Rammelsberg [8]; in addition, both Rammelsberg [8] and Roscoe [9] prepared a number of crystalline vanadates with analytical formulas similar to the corresponding phosphates. From these experiments Roscoe concluded that the solid vanadates could be classified in analogy to the phosphates, and he gave the following names and formulas to three groups of vanadates.
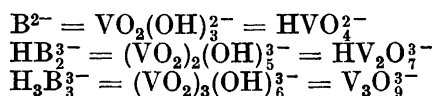
$$VO_4^{3-} \qquad\qquad V_2O_7^{4-}(\text{or } HVO_4^{2-}) \qquad\qquad VO_3^-(\text{or } H_2VO_4^-)$$

"orthovanadate"   "pyrovanadate"   "metavanadate"

These formulas, which are based upon the idea of VO_4^- tetrahedra, were soon used [10] also to describe vanadium species in aqueous solutions, and this nomenclature is still used frequently; when the "metavanadate" ions have proved to be polynuclear, formulas like $V_3O_9^{3-}$ and $V_4O_{12}^{4-}$ have been proposed, in analogy with the polymetaphosphate ions.
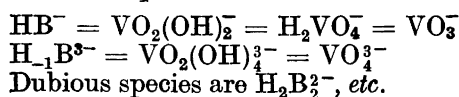
In this paper the "VO_4"-nomenclature will be used sometimes, but more often the species found in this work will be written as complexes of VO_2^+ and OH^-. Thus $H_2VO_4^-$ will be written as $VO_2(OH)_2^-$, HVO_4^{2-} as $VO_2(OH)_3^{2-}$, $HV_2O_7^{3-}$ as $(VO_2)_2(OH)_5^{3-}$, and $V_3O_9^{3-}$ as $(VO_2)_3(OH)_6^{3-}$. These formulas may have some structural justification.

In our discussion about vanadates crystallized from solution and investigated with X-ray methods, analytical formulas like $(NH_4)_6V_{10}O_{28}(H_2O)_4$, $Ca_3V_{10}O_{28}$ $(H_2O)_{16}$, KVO_3H_2O and KV_3O_8 will be used.

In the mathematical discussion, however, it will prove advantageous, for brevity and simplicity, to treat the complexes as composed of H^+ and B^{2-}, where B^{2-} is the mononuclear complex of charge 2$-$, thus HVO_4^{2-}, or $VO_2(OH)_3^{2-}$. Anticipating our results, the major complexes found by us in alkaline solutions may be written as

$B^{2-} = VO_2(OH)_3^{2-} = HVO_4^{2-}$
$HB_2^{3-} = (VO_2)_2(OH)_5^{3-} = HV_2O_7^{3-}$
$H_3B_3^{3-} = (VO_2)_3(OH)_6^{3-} = V_3O_9^{3-}$

Other complexes are

$HB^- = VO_2(OH)_2^- = H_2VO_4^- = VO_3^-$
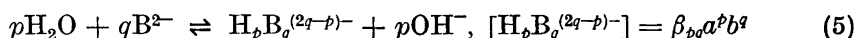$H_{-1}B^{3-} = VO_2(OH)_4^{3-} = VO_4^{3-}$
Dubious species are $H_2B_2^{2-}$, *etc.*

In essential parts the symbols are the same as in AB II[11] and Part II[5] in this series but will be repeated in order to simplify the reading.

a $\quad = [OH^-]^{-1} = h\,K_w^{-1}$; corresponds to reagent A $= -OH^-$ ($= H^+$)

B^{2-} $= $ species with one V and charge $2-$, "HVO_4^{2-}" or $VO_2(OH)_3^{2-}$; $b = [B^{2-}]$

B $\quad$ total vanadium concentration

B $\quad$ a normalized quantity corresponding to B

E $\quad$ the measured emf in mV

E_{oa} $= E + 59.15 \log [OH^-] + E_j$. $\quad$ (8)

E_j $\quad = $ const. $[OH^-]$, liquid junction emf.

H $\quad$ total analytical concentration of H^+ over B^{2-} and H_2O; H may be negative

h $\quad = [H^+]$

l $\quad = \beta_{11}\beta_{12}^2\beta_{33}^{-1}$; (27)

n $\quad$ number of links (H_tB) per complex $B(H_tB)_n$

N $\quad$ unique value for n

P $\quad$ unique value for the number of H in H_PB_Q

$\bar{p}$ $\quad$ average number of H per complex formed from B^{2-} by addition of H^+

Q $\quad$ unique value for the number of B in H_PB_Q

$\bar{q}$ $\quad$ average number of B per complex formed from B^{2-} by addition of H^+

R^{-1} $\quad$ the average degree of condensation of B^{2-}

t $\quad$ number of H per B group in the link (H_tB)

u $\quad$ normalized quantity corresponding to a $\quad$ (24)

s $\quad$ number of B^{2-} in predominating complex B_s^{2s-}

v $\quad$ normalized quantity corresponding to ab $\quad$ (24)

w $\quad$ normalized quantity corresponding to a^2b. (15 c)

x $\quad \log B - 1.5 \log [OH^-]$ (17)

y $\quad 1.5^{-1}Z$ (17)

z $\quad$ the average negative charge per vanadium (2)

Z $\quad$ the average number of H^+ bound to the dominating species of $z = -2$. (1)

Z_+ $\quad$ the average number of OH^- bound to every VO_2^+ group (the Z used by Rossotti and Rossotti [1]) (3)

The formation of a complex $H_pB_q^{(2q-p)-}$ can be written with H^+, or OH^- as reactant. We shall denote the corresponding equilibrium constants by $*\beta_{pq}$ and β_{pq}, to conform with the IUPAC tables of stability constants [12]:

$$p H^+ + q B^{2-} \ \rightleftharpoons\ H_pB_q^{(2q-p)-}; \ [H_pB_q^{(2q-p)-}] = *\beta_{pq}h^pb^q \tag{4}$$

$$p H_2O + q B^{2-} \ \rightleftharpoons\ H_pB_q^{(2q-p)-} + p OH^-, \ [H_pB_q^{(2q-p)-}] = \beta_{pq}a^pb^q \tag{5}$$

Since $[OH^-]$ is determined directly whereas h contains the uncertainty of K_w, it seems preferable to use instead of h the quantity

$$a = [OH^-]^{-1} = hK_w^{-1} \tag{6}$$

which is proportional to h. It is seen from (4), (5) and (6) that

$$*\beta_{pq} = \beta_{pq}K_w^{-p} \tag{7}$$

Chemical symbols are in Roman, concentrations in italic type. Concentrations and equilibrium constants will be expressed in M (moles per liter).

EARLIER WORK

The orthovanadate ion, VO_4^{3-}, was studied by Düllberg [10] using conducto-metric titrations. He found that, when solid orthovanadate is dissolved in water, an equivalent amount of OH^- is released. From that he concluded that the orthovanadate ion is such a strong base that it cannot exist in aqueous solution but reacts thus: $VO_4^{3-} + H_2O \rightleftharpoons HVO_4^{2-} + OH^-$.

In subsequent potentiometric studies, Britton, Robinson [13] and Ducret [14] came to the same conclusion.

However, in another paper Britton and Robinson [15] say that 49 % of the vanadate ions are hydrolysed in a solution where the total vanadium concentration = 83.3 mM.

In solubility measurements carried out by Britton and Robinson [16], an orthovanadate solution was titrated with a silver solution, and the silver concentration in the solution was measured with a silver electrode. The data obtained were in agreement with the solubility product: $[Ag^+]^3[HVO_4^{2-}][OH^-] = 10^{-24}$.

In a recent spectrophotometric investigation, Newman [17] and coworkers could explain their data on vanadium(V) in strongly alkaline solution by assuming a mixture of VO_4^{3-} and HVO_4^{2-}. They give $K = 0.097 \pm 0.005$ M for $VO_4^{3-} + H_2O \rightleftharpoons HVO_4^{2-} + OH^-$ at an ionic strength of 3.0 M.

The existence of a *"pyrovanadate"* ion, $V_2O_7^{4-}$, has been claimed by many authors. In an early cryoscopic investigation, Düllberg [10] found evidence for a dimeric vanadate species in solutions containing $2OH^-/V$. Jander and Jahr [18] reached the same conclusion from diffusion data.

Electrometric titrations [16] of sodium vanadate solution with Ag^+ (using a silver electrode) gave evidence only for the species HVO_4^{2-}, and the data could be explained assuming the solubility product $[Ag^+]^2[HVO_4^{2-}] = 10^{-13.7}$.

The solubility of $Ag_4V_2O_7$ in various solutions of sodium vanadate, $z = -2$, was measured by Souchay [19] and he found that the solubility was in accordance with the solubility product $[Ag^+]^2[HVO_4^{2-}] = $ const. However, in more concentrated solutions this constant could not explain the data which were in better agreement with $[Ag^+]^4[V_2O_7^{4-}] = $ const.

From spectrophotometric work [17] Newman claimed that the following dimerisation took place: $2HVO_4^{2-} \rightleftharpoons V_2O_7^{4-} + H_2O$ with $K = 48 \pm 5$.

From conductometric studies, Trujillo and Beltrán [20] concluded that the dimer in solutions with z between -1 and -2 has the charge -3. Emf measurements by Lefebvre [21] indicated the same complex together with its dimer.

The studies of pyrovanadate solutions by Russel and Salmon [22] with an ion exchanger also indicate that solutions with $z = -2$ contain a dimer with the charge -3.

Schwarzenbach and Parissakis [23] dissolved small amounts of $Na_4V_2O_7$ in a $Na_2SO_4(H_2O)_{10}$ melt and studied the change of the transition point. The data obtained were used for calculating the average number of vanadium atoms per complex. In concentrated solutions the ion $V_2O_7^{4-}$ was claimed to be formed whereas diluting gave equilibria $H_2O + V_2O_7^{4-} \rightleftharpoons 2HVO_4^{2-}$.

An early cryoscopic investigation *on the condensation of "metavanadate"* carried out by Düllberg [10] indicated a trimer. Jander and Jahr [18] concluded

from their diffusion data that the metavanadate ion should be a tetramer. Souchay [24] has criticized Jander and Jahr's conclusion and maintains that the solution contains trimers.

On the other hand Britton and Robinson [16] titrated vanadate solutions with Ag^+ using a silver electrode. The data could be explained assuming $[Ag^+][VO_3^-] = 10^{-6.3}$ and not by $[Ag^+]^3[V_3O_9^{3-}] = const.$ Souchay [25] says, however, that Britton and Robinson's result may be incorrect since, using the same method, he could explain the data assuming a trimer at high concentrations, and VO_3^- at low concentrations.

By studying the solubility of ammonium metavanadate Trujillo and Tejera [26] concluded that the metavandate is tetrameric. Also, Lefevbre [21] came to the same conclusion in his treatment of vanadate data with the method of "potentiometric surface".

Hazel, McNabb, and Santini [27] postulated, from emf measurements, that a complex $H_2V_2O_7^{2-}$ dimerizes to a tetramer.

From their cryoscopic studies in melting Glauber salt, Schwarzenbach and Parissakis [23] came to the conclusion that a tetramer, $V_4O_{12}^{4-}$, was formed in a range where the present work indicates a trimer, $(z = -1)$.

Russel and Salmon's ion exchange work [22] indicated a trimer with the charge 3—.

From determination of vapor pressures over solutions with $z = -1$, Robinson and Sinclair [28] could calculate the average degree of condensation in the solution, which they found to be 3.

EXPERIMENTAL DETAILS

Reagents and analysis

Sodium hydroxide free from carbonate was prepared and analysed as described in Part II [5].

Sodium chloride, Merck p.a. was used after drying at $200-300°C$ without further purification.

Hydrochloric acid, Kebo p.a. was used. Standardisation against $KHCO_3$ and standard NaOH agreed within 0.1 %.

Vanadium(V)oxide, LKB p.a. was used. The vanadium(V)oxide was analysed by reducing an acid suspension of V_2O_5 with SO_2, boiling off the excess SO_2, and titrating with standard $KMnO_4$. Analysis of the product always gave > 99.93 % V_2O_5. In order to check if the oxide contained some impurities, which could affect the result of our titrations, V_2O_5 was prepared also from sodium vanadate according to the method proposed by Rossotti and Rossotti [1], and used for preparing the solutions in some titrations. The commercial product and that one prepared from sodium vanadate gave identical titration curves.

Apparatus

As in earlier work [5-7] in alkaline solution, Jena Geräte glass has been used for titration vessels and burets.

The electrode vessel and the salt bridge were of the same type as described Part II [5]. The glass electrode was a Radiometer (Copenhagen) type G 202 BT and the emf values were read to ± 0.1 mV with a Radiometer PHM3 valve

potentiometer. The hydrogen electrode and the silver reference electrode cell were prepared as described in Part IV[7].

The cells including the titration vessel were kept in an oil thermostat at 25°C $\pm$ 0.1°C and the whole equipment kept in a thermostated room at 25°C. The solutions were introduced into the titration cell from burets calibrated by weighing water. The equilibrium solution was stirred by means of commercial nitrogen freed from O_2 which had passed through 10 % H_2SO_4, 10 % NaOH and 0.5 M NaCl.

The emf measurements

In our titrations a constant ionic medium has been maintained in order to keep the activity factors as constant as possible and thus use concentrations instead of activities in the law of mass action. To conform with earlier investigations it would be desirable to use 3 M $Na(ClO_4)$. However, in this work 0.5 M $Na(Cl)$ has been used. The concentration 0.5 M has been chosen because of the low solubility of vanadate in stronger Na^+ media.

In this work the total vanadium concentration has been varied between $0.62_5 \times 10^{-3}$ and 80.0×10^{-3} M and as the concentration of the vanadate ions and [OH^-] never exceed 20 % of the total anions, we assumed, following Biedermann and Sillén [29], the activity factors for all species to be approximately constant.

The determination of the equilibrium value for [OH^-] was made with a glass or hydrogen electrode in combination with the half-cell

SE = 0.5 M NaCl | 0.5 M NaCl saturated with AgCl | AgCl, Ag
The cell used was thus:
  — glass electrode | vanadate solution | SE +
or — Pt, H_2 (1 atm) | vanadate solution | SE +

Assuming the activity factors to be constant the emf of these cells can be written

$$E = E_{oa} + 59.15 \log [OH^-] + E_j = E_{oa} - 59.15 \log a + E_j \qquad (8)$$

where E_{oa} is a constant and E_j the liquid junction potential. The constant E_{oa} was determined from a solution of known [OH^-] and with [Na^+] = 0.5 M as described in Part II[5]. Before and after every titration, the glass electrode was checked in a solution with known [OH^-]. It was found that this check was necessary as E_{oa} sometimes could change during a titration by several millivolts, in which case the whole titration was rejected.

For the liquid junction potential we found $E_j \approx 41$ [OH^-]mV[7]; since [OH^-] was usually < 0.001 M, E_j could be neglected in the range studied.

TITRATION PROCEDURE AND ATTAINMENT OF EQUILIBRIA

The present investigation started with a number of "bottle experiments". To a number of polythene bottles containing about 50 ml strongly alkaline vanadate solution with $z \approx -3.0$ (uncolored solutions), various amounts of acid vanadate solution with $z \approx +1.0$ (yellow solution) were added. After

the addition, all solutions were at first yellow. In some of the bottles the color faded immediately, in others it faded in the course of several days, but in the bottles containing most acid the color did not change. It was found out that colorless solutions could always be obtained as long as the average charge per vanadium, z, in the mixture was ≤ -1.0; the time for discoloration increased when z approached -1.0. By mixing two solutions, both with $z < -1$, uncolored solutions were always obtained.

The experiments described above were then carried out as titrations where the acid solution was added with a buret and the alkaline solution kept in a titration vessel; the change of $[OH^-]$ was followed with a *hydrogen* electrode. As long as the measured solution with $z \leq -1$ was yellow the emf crept appreciably, whereas an uncolored solution showed a nearly constant potential. On mixing two uncolored solutions with $z \leq -1.0$, stable potentials were obtained rapidly, and only a creep of the order of 0.06 mV per hour caused by very slow reduction of vanadium(V) was observed.

From these preliminary observations we concluded that when the two solutions are mixed in such a way that the average charge per vanadium, z, is allowed even momentarily to increase above -1, equilibrium is slowly obtained, but as long as all solutions have $z \leq -1$ equilibrium is momentarily obtained.

Rossotti and Rossotti [1] found in their study of acid vanadate solutions that rapid equilibria could always be obtained when $z > -0.6$. Thus we concluded that equilibrium is obtained slowly for solutions with z ranging between -0.6 and -1.0, and in the following this range will be denoted as the "instability range" (see Fig. 1).

Even if the vanadate(V) solutions were slowly reduced by hydrogen, reproducible emfs were obtained if one consistently used the E value obtained after 20—30 min (the time usually required for H_2 electrodes to reach equilibrium) and did not allow the titration to take more than one day. However, for several reasons we decided to use the *glass* electrode for our final data. The data for our first titrations, using the hydrogen electrode, together with the glass electrode data are given in Table 1 and a comparison shows that the two electrodes give the same results within ± 0.3 mV. This agreement seems to show that no serious systematic error was involved in using glass electrodes in our alkaline vanadate solutions, which was most welcome since we do not pretend to understand how the glass electrode works.

Remembering the fact that rapid equilibria can always be obtained when $z \leq -1$ for all solutions, the following two titration procedures have been worked out, and both have been used.

1) $z(\log[OH^-])_B$-titrations. In these titrations the total concentration of vanadium, B, has been kept constant and $\log[OH^-]$ and thus z has been varied. The total hydroxide ion concentration was varied usually by decreasing z; then the solution in the titration vessel had $z \approx -1.03$ and was titrated with a more alkaline solution with $z < -2$. In a check titration with increasing z, the solution with $z \approx -1.03$ was in the buret and the alkaline solution in the titration vessel. The points so obtained, (see Fig. 2, 0.010 M points □) were on the same titration curve as the others (■), and there was no difference in the time for attainment of equilibria.

2) $B(\log[OH^-])_z$-titrations. In these titrations two ways for changing the total concentration of vanadium have been used. In one of them the solution in the titration vessel was 0.5 M Na(Cl), and a solution with known z and B was added; in the other way the solution containing the vanadium (known z and B) was kept in the titration vessel, and 0.5 M Na(Cl) was added by buret. From eqn. (1) and (2) it can be seen that during these titrations z was nearly constant, (In the range studied $[OH^-]$ can be neglected in comparison with H).

All these methods for getting experimental data have given consistent results, and equilibrium was always obtained rapidly.

Preparation of the vanadate solutions

Solution for the titration vessel. A weighed quantity of vanadium(V) oxide was added to a volumetric flask (of Jena-Geräte glass) and a calculated amount of standard sodium hydroxide was added. The addition of NaOH was chosen so as to make $z \approx -1.03$. In the preparation of the solutions with the lowest vanadium concentrations, the oxide dissolved rapidly giving an apparently colorless solution, but for higher concentrations it was necessary to dilute with de-aerated distilled water and raise the temperature to about $50-80°C$ for a short time. After dissolution of the vanadium(V) oxide, calculated amounts of solid NaCl were added. After waiting until the temperature had fallen to 25°C, the flask was carefully filled to the mark with de-aerated water. It was checked that the volume of the flask had not changed after heating and cooling. The manipulations described above were always carried out in a CO_2-free N_2 atmosphere.

The buret solution was prepared as described above except that the solutions were made more alkaline.

TREATMENT OF EXPERIMENTAL DATA

The primary experimental data: the emf values and the analytical composition of the solution were recalculated using eqns. (1), (2) and (8), to give z $(\log[OH^-])_B$. The data are given in this form in Fig. 2 and Table 1.

If mononuclear complexes only were formed, z would be a function of $[OH^-]$ only. From Fig. 2 it is seen that z is a function of both B and $[OH^-]$, and so, apparently, one polynuclear complex at least must be formed.

The $z(\log[OH^-])_B$ curves range between two z limits, $z = -1$ and $z = -2$. The complex or the complexes predominating at $z = -2$ and $z = -1$ may be polymers, and for our analysis it is convenient to start with one of these limiting complexes. As a concentrated vanadate solution became more acid on dilution (see Fig. 2) we concluded that $(B^{2-})_s$, the complex at $z = -2$, is of lower nuclearity than the complex at $z = -1$. To conform with previous methods we decided to study a condensation reaction and thus analyse the reactions taking place when H^+ is added to $(B^{2-})_s$. Before starting this analysis it is, however, necessary to find the value for s.
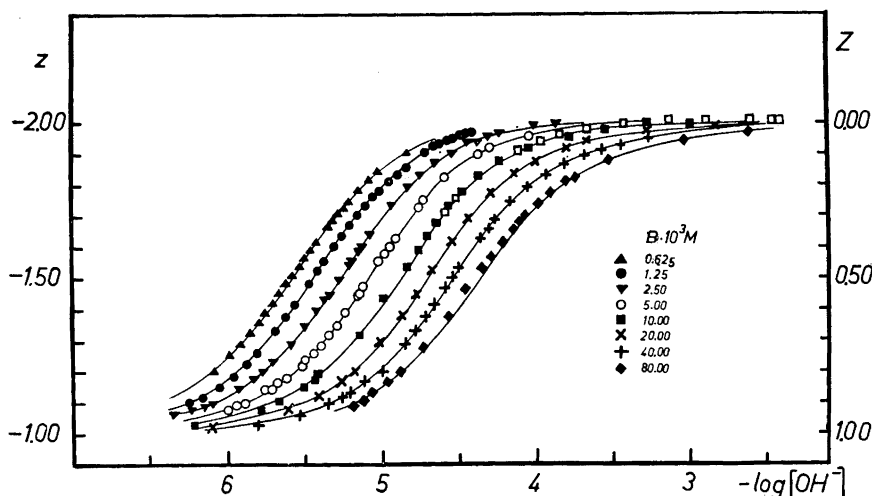
Fig. 2. Experimental data plotted as z $(\log[OH^-])_B$. The average number, $Z = (2-z)$, of H^+ bound to B^{2-} is also given. The curves are calculated assuming the formation of HB_2^{3-} ($\log \beta_{12} = -3.19$) $H_3B_3^{3-}$ ($\log \beta_{33} = -10.42$) and HB^- ($\log \beta_1 = -6.04$). The open symbols for $B = 0.010$ M represent a back titration.

Table 1. Vanadates at 25°C in 0.5 M Na(Cl).

Data $z(\log[OH^-])_B$ obtained with glass electrode.

$B = 0.000625\,M. -z, -\log[OH^-]$: 1.202, 6.086; 1.250, 5.990; 1.286, 5.920; 1.323, 5.860; 1.354, 5.811; 1.386, 5.762; 1.416, 5.713; 1.450, 5.669; 1.480, 5.625; 1.509, 5.581; 1.538, 5.544; 1.565, 5.501; 1.590, 5.466; 1.614, 5.425; 1.669, 5.348; 1.685, 5.319; 1.704, 5.285; 1.723, 5.249; 1.744, 5.214; 1.781, 5.151; 1.813, 5.087; 1.842, 5.030.

$B = 0.00125\,M. -z, -\log[OH^-]$: 1.018, 6.697; 1.062, 6.363; 1.112, 6.159; 1.145, 6.056; 1.180, 5.973; 1.219, 5.885; 1.259, 5.812; 1.282, 5.770; 1.328, 5.694; 1.374, 5.628; 1.418, 5.567; 1.486, 5.474; 1.526, 5.418; 1.566, 5.364; 1.602, 5.314; 1.632, 5.263; 1.668, 5.212; 1.701, 5.160; 1.733, 5.109; 1.760, 5.058; 1.782, 5.006; 1.811, 4.952; 1.832, 4.896; 1.851, 4.840; 1.925, 4.663; 1.934, 4.627; 1.945, 4.578; 1.953, 4.538; 1.962, 4.490; 1.969, 4.453; 1.974, 4.416.

$B = 0.00250\,M. -z, -\log[OH^-]$: 1.080, 6.233; 1.112, 6.078; 1.148, 5.932: 1.176, 5.839; 1.232, 5.701; 1.288, 5.593; 1.340, 5.500; 1.392, 5.423; 1.444, 5.347; 1.492, 5.276; 1.544, 5.212; 1.644, 5.079; 1.740, 4.940; 1.836, 4.751; 1.904, 4.549; 1.944, 4.389; 1.960, 4.308; 1.968. 4.238; 1.996, 4.012; 2.008, 3.866.

$B = 0.005\,M. -z, -\log[OH^-]$: 1.093, 5.911; 1.148, 5.701; 1.179, 5.620; 1.258, 5.443; 1.442, 5.157; 1.540, 5.030; 1.603, 4.951; 1.754, 4.736; 1.922, 4.300; 1.978, 3.614; 2.016, 3.207, 2.892, 2.015; 2.016, 2.800; −1.708, 6.004; 1.152, 5.695; 1.219, 5.521; 1.282, 5.397; 1.344, 5.296; 1.449, 5.144; 1.546, 5.019; 1.630, 4.914; 1.727, 4.768; 1.826, 4.593; 1.899, 4.375; 1.960, 4.042; 1.993, 3.661; 2.005, 3.369; 2.008, 3.178; 2.009, 2.929; 2.009, 2.975; 2.009, 2.929; 2.009, 2.838; 2.011, 2.767.

$B = 0.010\,M. -z, -\log[OH^-]$: 1.078, 5.794; 1.101, 5.674; 1.147, 5.513; 1.172, 5.444; 1.316, 5.148; 1.484, 4.907; 1.537, 4.841; 1.593, 4.768; 1.634, 4.716; 1.682, 4.652; 1.735, 4.573; 1.785, 4.483; 1.832, 4.375; 1.878, 4.236; 1.920, 4.042; 1.957, 3.788; 1.977, 3.543; 1.990,

3.278; 1.996, 2.994; 2.001, 2.703; 2.002, 2.456; --- 2.005, 2.005; 2.000, 2.039; 2.004, 2.081;
2.003, 2.125; 2.006, 3.129; 1.996, 3.424; 1.980, 3.667; 1.960, 3.846; 1.943, 3.968; 1.914,
4.118; 1.824, 4.397; 1.761, 4.521; 1.713, 4.597; (titration in reversed direction).

$B = 0.020$ M. $-z$, $-\log[OH^-]$: 1.018, 6.098; 1.071, 5.610; 1.117, 5.407; 1.165, 5.258; 1.211,
5.156; 1.291, 5.010; 1.378, 4.872; 1.448, 4.776; 1.525, 4.675; 1.615, 4.550; 1.690, 4.436;
1.773, 4.296; 1.834, 4.144; 1.874, 4.000; 1.914, 3.794; 1.943, 3.567.

$B = 0.040$ M. $-z$, $-\log[OH^-]$: 1.028, 5.804; 1.059, 5.542; 1.098 ,5.352; 1.119, 5.258; 1.128,
5.210; 1.164, 5.117; 1.208, 5.011; 1.248, 4.894; 1.291, 4.850; 1.332, 4.786; 1.375, 4.720;
1.415, 4.663; 1.467, 4.593; 1.502, 4.546; 1.529, 4.507; 1.593, 4.421; 1.629, 4.369; 1.661, 4.303
1.692, 4.269; 1.747, 4.164; 1.795, 4.052; 1.834, 3.932; 1.866, 3.811; 1.895, 3.672; 1.912, 3.564;
1.928, 3.447; 1.938, 3.538; 1.948, 3.261; --- 1.094, 5.368; 1.155, 5.146; 1.205, 5.016; 1.247
4.933; 1.316, 4.813; 1.363, 4.739; 1.429, 4.649; 1.487, 4.566; 1.543, 4.495; 1.615, 4.396;
1.658, 4.330; 1.719, 4.227; 1.782, 4.095; 1.890, 3.718; 1.940, 3.395; 1.980, 2.818; 1.986, 2.594.

$B = 0.080$ M. $-z$, $-\log[OH^-]$: 1.094, 5.181; 1.109, 5.124; 1.130, 5.059; 1.170, 4.970; 1.207,
4.869; 1.279, 4.731; 1.465, 4.446; 1.530, 4.352; 1.576, 4.282; 1.619, 4.218; 1.657, 4.154;
1.681, 4.107; 1.702, 4.069; 1.740, 3.987; 1.773, 3.905; 1.825, 3.743; 1.878, 3.522; 1.946,
3.038; 1.975, 2.607; 1.989, 2.240.

Data $B(\log[OH^-])_z$ obtained with glass electrode

$z \approx 1.09$. $B.10^3$, $-\log[OH^-]$, $-z$; 0.62$_5$, 6.543, 1.091; 1.29, 6.343, 1.092; 2.50, 6.154, 1.091;
5.04, 5.951, 1.091; 10.00, 5.757, 1.091; 19.97, 5.560, 1.092; 40.00, 5.368, 1.093.

$z \approx 1.29$. $B.10^3$, $-\log[OH^-]$, $-z$; 0.62$_5$, 5.919, 1.282; 1.250, 5.779, 1.288; 2.50, 5.591, 1.290;
5.00, 5.403, 1.292; 10.00, 5.212, 1.294; 20.00, 5.023, 1.296; 40.00, 4.837, 1.296.

$z \approx 1.43$. $B.10^3$, $-\log[OH^-]$, $-z$; 0.62$_5$, 5.741, 1.422; 1.25, 5.566, 1.429; 2.51, 5.380, 1.434;
5.00, 5.189, 1.437; 10.00, 4.996, 1.440; 20.00, 4.801, 1.442; 40.00, 4.614, 1.444;

$z \approx 1.59$. $B.10^3$, $-\log[OH^-]$, $-z$; 0.62$_5$, 5.444, 1.585; 1.27, 5.312, 1.587; 2.50, 5.150, 1.588;
5.02, 4.972, 1.589; 10.03, 4.778, 1.589; 21.34, 4.568, 1.590.

$z \approx 1.90$. $B.10^3$, $-\log[OH^-]$ $-z$; 0.62$_5$, 4.825, 1.903; 1.25, 4.725, 1.903; 2.50, 4.588, 1.903.

Data $z(\log[OH^-])_B$ obtained with hydrogen electrode

$B = 0.040$ M. $-z$, $-\log[OH^-]$: 1.59, 4.43; 1.61, 4.41; 1.71, 4.25; 1.84, 3.92; 1.94, 3.38; 1.99,
2.60; 2.00, 2.44; 2.00, 2.33; ---- 1.09, 5.37; 1.16, 5.15; 1.21, 5.02; 1.25, 4.93; 1.32, 4.81; 1.36,
4.74; 1.43, 4.65; 1.49, 1.57; 1.54, 4.50; 1.62, 4.40; 1.66, 4.33; 1.72, 4.23; 1.78, 4.10; 1.89,
3.72; 1.94, 3.40; 1.98, 2.82; 1.99, 2.59.

$B = 0.010$ M. $-z$, $-\log[OH^-]$: 1.07, 5.76; 1.21, 5.33; 1.47, 4.94; 1.56, 4.82; --- 1.70, 4.62.
1.80, 4.42; 1.86, 4.23; 1.97, 3.27.

Data $B(\log[OH^-])_z$ obtained with hydrogen electrode

$z \approx 1.59$. $B.10^3$, $-\log[OH^-]$, $-z$: 40.00, 4.42, 1.59; 35.00, 4.45, 1.59; 30.00, 4.49, 1.59; 2.50,
4.54, 1.59; 20.00, 4.60, 1.59; 10.00, 4.78, 1.59; 5.10, 4.88, 1.59; 2.50, 4.92, 1.59.

The nuclearity at $z = -2$

For $B = 0.0025-0.0200$ M and for z from -1.0 to -1.5 the experimental
$z(\log[OH^-])_B$-curves are parallel within the limits of experimental errors, and
according to AB I[29] the complex or the complexes formed may be written in
the "core and links" form $(B^{2-})_s[(B^{2-})_sH_t]_n^{[2s+n(2s-t)]-}$ where t and n are quantities

which can be determined independently of the value of s. In our "core + links" analysis, which will be described in a following section, we found $t = 1.5$ and $n = N = 2$. With these values for t and n the upper limiting value for z may be expressed as a function of s

$$z_{\lim} = \frac{t \ N - 2(N + 1)s}{(N + 1)s} = \frac{1 - 2s}{s}$$

and for $s = 1$, $z_{\lim} = -1.0$; $s = 2$, $z_{\lim} = -1.5$; $s = 3$, $z_{\lim} = -1.67$. Experimentally, $z_{\lim} = -1.00$ (see Fig. 2) and consequently our data are in agreement only with $s = 1$, and the species at $z = -2$ must be monomeric with the charge -2, B^{2-}, whereas the limiting species at $z = -1$ would be $H_3B_3^{3-}$.

The first step in our analysis of the experimental curves $z(\log[OH^-])_B$ will be a determination of $\bar{q}$, the average number of vanadium atoms in all complexes except B^{2-}, and $\bar{p}$, the average number of protons bound (in excess to B^{2-}) in these complexes. A description of this calculation will be given in a following section, (in connection with eqns (10), (11) and (12)), but a part of it will be given here as it gives a further proof of the mononuclearity for vanadium at $z = -2$.

As pointed out earlier the complex dominating at $z = -2$, may be written in the form $(B^{2-})_s$. If H^+ is added, a condensation takes place and the average degree of condensation, R^{-1}, increases as H^+ increases. Sillén [30] has shown that R^{-1} may be calculated from the experimental $Z(\log a)_B$-curves and the general formula he gives may be written

$$R = R_0 - \int_{\log a_1}^{\log a} \left(\frac{\partial \ (2 + z)}{\partial \log B} \right)_a \mathrm{d} \log a = \frac{1}{s} - \int_{\log a_1}^{\log a} \left(\frac{\partial \ Z}{\partial \log B} \right)_a \mathrm{d} \log a \quad \text{at constant } B \quad (9)$$

In this formula $R_0 = \dfrac{1}{s}$ is an integration constant, the value of which can be determined from the lower limit of integration, s is the number of B^{2-} units in $(B^{2-})_s$, $\log a_1$ the value of $\log a = -\log [OH^-]$ where the integration starts and $(2 + z) = Z$, the average number of H^+ bound per $(B^{2-})_s$.

For obtaining R^{-1} at an arbitrary point on the $z(\log a)_B$-curve the value of s and the integral in (9) must be known. The calculated values for the integral at various $-\log [OH^-]$ obtained from our experimental data are given in Table 2. From this table it is evident that low experimental z-values and high B-values give integrated quantities > 0.5; if $s \geq 2$ negative values for R^{-1} would then be obtained, according to (9). That must mean that the integrated area is too large to be in agreement with other s-values than $s = 1$.

Again we conclude $s = 1$. The complex with $z = -2$, B^{2-}, is mononuclear.

The mean composition of the polynuclear complexes

To find the species in these vanadate solutions we shall start with the "direct integration method", previously used in the borate study [5], which gives the *mean composition of the complexes formed*. With this integration as

Table 2. Values for $\bar{q}$ and $\bar{p}$ obtained with the "direct integration" method.

-log a	*	**	$\bar{q}$	$\bar{p}$	-log a	*	**	$\bar{q}$	$\bar{p}$
$B = 1.25 \cdot 10^{-3}$ M					5.40	0.53	0.801	2.7	2.6
					5.50	0.56	0.896	2.8	2.7
4.20	0.01	0.008	1.0	0.7	5.60	0.58	0.991	2.9	2.7
4.40	0.01	0.008	2.0	1.5					
4.60	0.03	0.029	2.0	1.9					
4.80	0.05	0.056	1.7	1.7	$B = 20 \cdot 10^{-3}$ M				
5.00	0.09	0.106	1.7	1.6					
5.20	0.15	0.189	1.7	1.6	4.00	0.08	0.082	2.1	1.3
5.40	0.12	0.298	1.8	1.6	4.20	0.13	0.124	2.1	1.3
5.60	0.19	0.425	1.9	1.8	4.40	0.19	0.185	2.2	1.4
5.80	0.36	0.592	1.9	1.9	4.60	0.26	0.271	2.3	1.7
6.00	0.40	0.777	1.9	1.9	4.80	0.36	0.392	2.5	1.9
					5.00	0.44	0.640	2.6	2.2
$B = 2.5 \cdot 10^{-3}$ M					5.20	0.50	0.700	2.7	2.4
					5.40	0.56	0.890	2.8	2.5
4.60	0.07	0.048	2.1	1.5	5.60	0.60	1.080	2.9	2.7
4.80	0.10	0.086	2.1	1.5					
5.00	0.17	0.148	2.2	1.8					
5.20	0.24	0.243	2.3	2.0	$B = 40.0 \cdot 10^{-3}$ M				
5.40	0.32	0.368	2.3	2.0					
5.60	0.41	0.523	2.4	2.3	3.00	0.02	0.017	2.0	1.2
5.80	0.48	0.700	2.5	2.5	3.20	0.04	0.030	2.1	1.3
6.00	0.52	0.880	2.5	2.4	3.40	0.06	0.048	2.1	1.2
6.10	0.54	0.967	2.5	2.5	3.60	0.08	0.075	2.0	1.1
					3.80	0.11	0.100	2.1	1.3
$B = 10 \cdot 10^{-3}$ M					4.00	0.16	0.160	2.0	1.2
					4.20	0.22	0.233	2.1	1.4
4.20	0.10	0.085	2.1	1.5	4.40	0.29	0.333	2.2	1.6
4.40	0.15	0.137	2.2	1.5	4.60	0.38	0.463	2.4	1.9
4.60	0.22	0.214	2.3	1.7	4.80	0.47	0.620	2.5	2.3
4.80	0.30	0.321	2.4	2.0	5.00	0.50	0.706	2.6	2.4
5.00	0.39	0.460	2.5	2.2	5.20	0.56	0.889	2.8	2.7
5.20	0.47	0.623	2.6	2.4	5.40	0.60	1.079	2.9	2.8
					5.60	0.63	1.274	3.0	2.9

$$* \int \left(\frac{\partial Z}{\partial \log B} \right)_a d \log a \qquad ** \int \left[Z + \left(\frac{\partial Z}{\partial \log B} \right)_a \right] d \log a$$

the basis we shall try to find the *formulas of the complexes;* the final step in the analysis will be a confirmation of the complexes with one or two *projection maps.*

In the foregoing we have shown that there is a single monomeric complex, B^{2-}, at $z = -2$, $(Z = 0)$, and thus polynuclear complexes must be formed when Z increases (see Fig. 2). For high Z values there is a mixture of mononuclear and polynuclear complexes. If direct measurements on $b = [B^{2-}]$ were possible it should be very easy to obtain

$$\bar{q} = \frac{B-b}{BR-b} \qquad (10) \qquad \text{and} \qquad \bar{p} = \frac{BZ}{BR-b} \qquad (11)$$

In these formulas B is the total concentration of vanadium and R is the reciprocal of the average degree of condensation of B^{2-}; so, $(BR-b)$ is the total molar concentration of all species except B^{2-}.

However, even in absence of direct measurements on b, this quantity may be calculated. General expressions for this calculation have been given by Sillén [30] and his formulas will be used here for getting R and b. The formula for getting R has already been given in eqn. (9) and the formula for calculating b is

$$\log \frac{B}{b} = \int\limits_{\log a_1}^{\log a} \left[Z + \left(\frac{\partial Z}{\partial \log B} \right)_a \right] \, d \log a \qquad \text{at constant } B \qquad (12)$$

Log a_1 is the log a value where the integration starts, B the total concentration of vanadium and $Z = (z + 2)$, the average number of H^+ bound to B^{2-}, the dominating species at $z = -2$; at $a = a_1$, $b \approx B$ and log $B/b \approx 0$.

The integration has been carried out numerically from the experimental Z (log a)-curves at a given value of B. $(\partial Z/\partial \log B)_a$ was obtained as the average of the quotients $(\Delta Z/\Delta \log B)_a$ from the plot Z (log $B)_a$ for two neighbouring intervals.

In Table 2 a part of our result from the integration is given, and in Fig 3 $\bar{q}$ and $\bar{p}$ for some concentrations have been plotted against $-\log [OH^-]$. It is indicated by this integration that complexes are formed with $\bar{q}$ ranging bet-
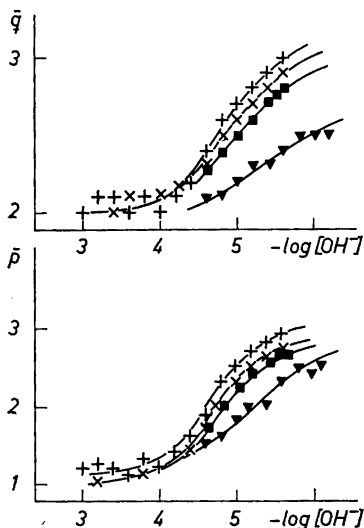

Fig. 3. Analysis by "direct integration"; $\bar{q}$ and $\bar{p}$ plotted against $-\log[OH^-]$. $+ = 0.040$ M; $\times = 0.020$ M: $\blacksquare = 0.010$ M and $\blacktriangle = 0.0025$ M.
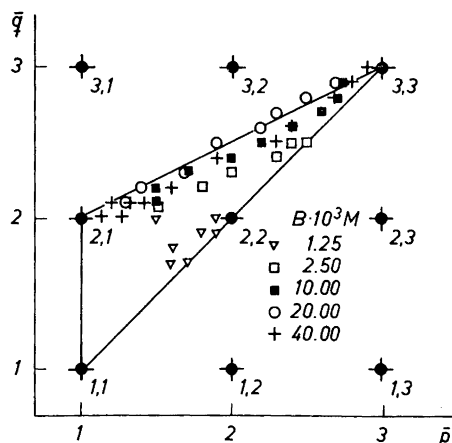
Fig. 4. $\bar{q}$ versus $\bar{p}$; note that all points fall within the triangle between (2,1), (3,3) and (1,1).

ween 2.0 and 3.0 and $\bar{p}$ between 1.0 and 3.0. The plot $\bar{q}$ against $\bar{p}$ for $B = 0.040$, 0.020, 0.010 M in Fig. 4 gives a nearly straight line between the sets $(\bar{q}, \bar{p}) = (2,1)$ and $(3,3)$, indicating that the main complexes for these concentrations are HB_2^{3-} and $H_3B_3^{3-}$.

At lower concentrations, $B = 0.0025$ and 0.0012_5 M, the $(\bar{q}\ \bar{p})$ points deviate markedly from this line, thus indicating the formation of some additional complex or complexes at lower B. If one tries to explain these deviations with the formation of a single complex, $\bar{q}$ for this complex must be <3; thus the species may be a monomer $H_{p'}B$ or a dimer $H_{p'}B_2$; p' must be <2 and p'' <3 as the deviations are found at low Z-values and Z is ranging between 0.00 and 1.00. Then only the complexes HB^- and $H_2B_2^{2-}$ remain and of these two HB^- seems to be the more likely one as all data, $\bar{q}$ $(\bar{p})$ in that case fall within the triangle formed by the $(\bar{q}\ \bar{p},)$-coordinates, $(3,3)$; $(2,1)$ and $(1,1)$ corresponding to the composition of the complexes $H_3B_3^{3-}$, HB_2^{3-} and HB^-.

If the two complexes HB_2^{3-} and $H_3B_3^{3-}$ only were formed (10) and (11) may be written

$$\bar{q} = \frac{2[HB_2] + 3[H_3B_3]}{[HB_2] + [H_3B_3]} = \frac{2 + 3\beta_{33}\beta_{12}^{-1}a^2b}{1 + \beta_{33}\beta_{12}^{-1}a^2b} \tag{13}$$

$$\bar{p} = \frac{[HB_2] + 3[H_3B_3]}{[HB_2] + [H_3B_3]} = \frac{1 + 3\beta_{33}\beta_{12}^{-1}a^2b}{1 + \beta_{33}\beta_{12}^{-1}a^2b} \tag{14}$$

or in a normalized form

$$\bar{q} = \frac{2 + 3w}{1 + w} \quad \text{(15a)} \qquad\qquad \bar{p} = \frac{1 + 3w}{1 + w} \quad \text{(15b)}$$

where $w = \beta_{33}\beta_{12}^{-1}a^2b$ (15c)

With (15a) and (15b) it is possible to construct two theoretical curves $\bar{q}$ (log w) and $\bar{p}$ (log w) and compare them with the experimental $\bar{q}$ (log a^2b)- and $\bar{p}$ (log a^2b)-curves. If the assumption is right the experimental $\bar{q}$ and $\bar{p}$ values plotted against log a^2b must give two single curves with the same shape as the calculated $\bar{q}$ (log w)- and $\bar{p}$ (log w)-curves. In Fig. 5 experimental and calculated curves are compared and the fit must be considered satisfactory (except for $B = 2.5.10^{-3}$ M). The difference in coordinates between log a^2b and log w in the position of best fit gives the ratio $\beta_{33}\beta_{12}^{-1}$:

log w — log $a^2b = $ log β_{33} — log $\beta_{12} = -7.40 \pm 0.20$. (The final constants give log $\beta_{33}\beta_{12}^{-1} = -7.24 \pm 0.10$).

Thus this treatment has indicated the species $H_3B_3^{3-}$ and HB_2^{3-} and given an approximate relationship between their formation constants. For low B values indications were found for a complex HB^- or $H_2B_2^{2-}$.

<center>"C o r e   a n d   l i n k s"   t r e a t m e n t</center>

In the first instance only the data for $B = 0.0025-0.020$ M and for Z from 0.45 to 1.00 will be discussed. In this range the Z(log a)$_B$-curves form within
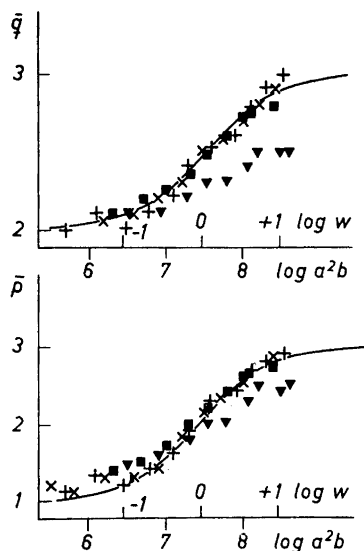
Fig. 5. $\bar{q}$ and $\bar{p}$ plotted against log a^2b. Full curve calculated assuming only HB_2^{3-} and $H_3B_3^{3-}$ (log $\beta_{33}\beta_{12}^{-1} = -7.40 \pm 0.20$) + = 0.040 M; × = 0.020 M; ■ = 0.010 M and ▲ = 0.0025 M.
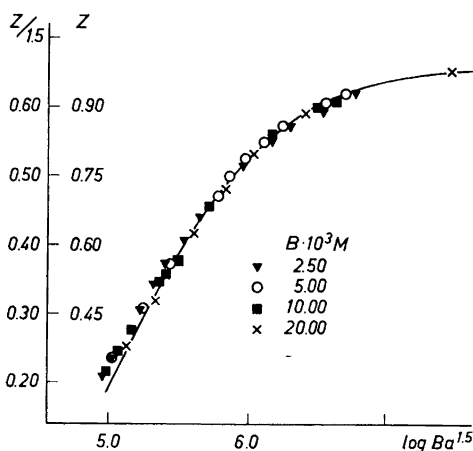
Fig. 6. Z or $y = 1.5^{-1}$ Z as a function of $x = \log B + 1.5 \log a$; Data for $B = 0.0025$ to 0.020 M, and for Z from 0.45 to 1.00 are given. Full curve calculated assuming the single complex $H_3B_3^{3-}$; with log $\beta_{33} = -10.50$.

the limits of experimental error, apparently parallel curves. That should mean that the complex or the complexes formed may be written in the "core + links" form $B(BH_t)_n^{[2+n(2-t)]-}$; t is a constant and n may be an unique integer N or a series of integers such that the product nt is an integer. In ABI[31] it has been shown that

$$t = -\left(\frac{\partial \log B}{\partial \log a}\right)_Z \qquad (16)$$

From our experimental $Z(\log a)_B$-data in Fig. 2 it is easily found that $t = 1.5$. That should mean that the main species formed have the composition $B(BH_{1.5})_n^{(2+0.5\ n)-}$. If only complexes with that composition are formed, the validity of (16) can be tested, as all experimental points should lie now on a single $y(x)$-curve, with the coordinates

$$x = \log B - 1.5 \log [OH^-] \qquad y = 1.5^{-1} Z \qquad (17)$$

In Fig. 6 the experimental plot of y against x is shown. It is seen that the experimental points according to (16) lie satisfactorily on a single curve and the "core + links" hypothesis may be considered as a good explanation of these data.
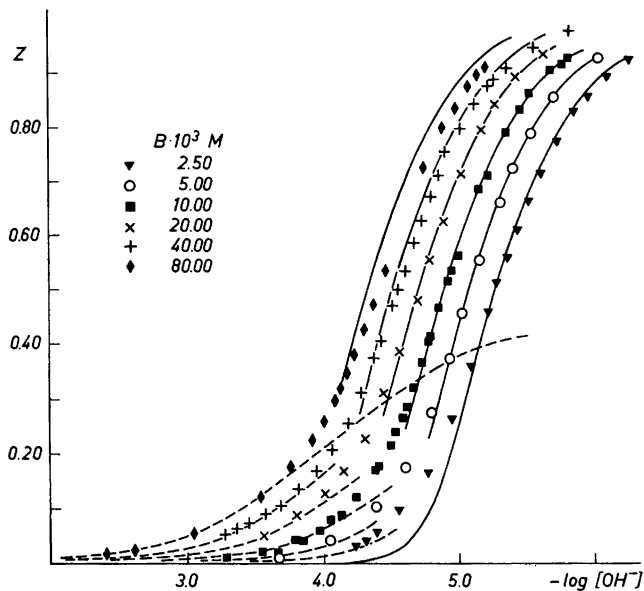
Fig. 7. Data Z (log $[OH^-])_B$. Full curves calculated assuming only $H_3B_3^{3-}$ (log β_{33} = -10.48). Dotted curves calculated assuming only HB_2^{3-} (log β_{12} = -3.12).

To decide whether n is a constant or not the curve $y(x)$ was compared with the normalized $y(X)$-curves calculated on the following three assumptions given in ABII [11] page 321:

I   no soluble complexes are formed but a precipitate is obtained
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.

This comparison indicated a single complex, $H_3B_3^{3-}$, with $N = 2$. The normalized $y(x)$-curves used were so constructed that the difference in reading on the X- and log $Ba^{1.5}$-coordinates in the position of best fit gave log β_{33} (see eqns. (24) and (25) in ABII [11]). We found log $\beta_{33} = -10.50 \pm 0.10$.

In order to get further confirmation for that complex and to check the shape of the experimental curves, a normalized $Z(X)_{PQ}$ curve was constructed under the assumption that a single complex H_PB_Q with $P = 3$ and $Q = 3$ was formed. If only one complex is formed, we have

$$B = b + Q\,[H_PB_Q] = b + Q\beta_{PQ}a^Pb^Q$$
$$BZ = P\beta_{PQ}a^P\,b^Q$$

Elimination of b and rearranging gives:

$$Q\beta_{PQ}B^{Q-1}a^P = w(1-w)^{-Q} = 10^{PX}$$

where $w = QZP^{-1}$. Using w as auxiliary variable it is possible to calculate a normalized $Z(X)_{PQ}$-curve where

$$X = P^{-1} \log w - QP^{-1} \log (1-w) \tag{18a}$$

and $Z = wPQ^{-1}$. $\tag{18b}$

The normalized curve with $Q = 3$ and $P = 3$ was found to fit well with the experimental $Z (\log a)_B$-curves (see Fig. 7) for low Z values and the concentrations $B = 0.0025 - 0.020$ M; the difference in coordinates on the horizontal axis gave $\beta_{33} = -10.48 \pm 0.1$

$$\log a - X = -P^{-1} | \log \beta_{PQ}Q - (Q-1)P^{-1} \log B = -\tfrac{1}{3} \log 3\beta_{33} - \tfrac{2}{3} \log B \tag{19}$$

The main product is thus $H_3B_3^{3-}$, which, however, does not suffice to explain the data in the range for $B = 0.0025 - 0.080$ M and for Z from 0.00 up to 0.45.
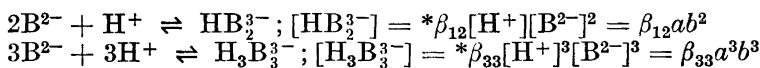
In the direct integration we found that $\bar{q}$ and $\bar{p}$ approach the limiting values $\bar{q} = 2$ and $\bar{p} = 1$ when $Z \to 0$. From that we may conclude that the polynuclear complex first formed must be HB_2^{3-}.

With the aid of (18a) and (18b) a normalized $Z(X)_{PQ}$ curve was constructed for a single complex H_PB_Q with $Q = 2$ and $P = 1$ and compared with the experimental $Z(\log [OH^-])_B$-data at low Z-values. An acceptable fit (see Fig. 7) was obtained for the four highest vanadium concentrations, $B = 0.080 - 0.010$ M, and the difference in reading on the horizontal axis gave, for all concentrations $\log \beta_{12} = -3.12 \pm 0.1$.

Confirmation of HB_2^{3-} and $H_3B_3^{3-}$ with a normalized graph $\log B(\log u)_Z$

In order to get a final confirmation for the formation of the complexes HB_2^{3-} and $H_3B_3^{3-}$, a normalized graph [31a] for the three species, B^{2-}, HB_2^{3-} and $H_3B_3^{3-}$ was constructed and compared with the experimental data. Reactions:

$$2B^{2-} + H^+ \rightleftharpoons HB_2^{3-}; [HB_2^{3-}] = {}^*\beta_{12}[H^+][B^{2-}]^2 = \beta_{12}ab^2$$
$$3B^{2-} + 3H^+ \rightleftharpoons H_3B_3^{3-}; [H_3B_3^{3-}] = {}^*\beta_{33}[H^+]^3[B^{2-}]^3 = \beta_{33}a^3b^3$$

The condition for the concentrations gives

$$B = b + 2\beta_{12}ab^2 + 3\beta_{33}a^3b^3 \tag{20}$$

$$BZ = \beta_{12}ab^2 + 3\beta_{33}a^3b^3 \tag{21}$$

We wish to transform these expressions to the normalized form

$$Bu = v(1 + 2v + 3uv^2) \quad (22), \qquad BZu = v(v + 3uv^2) \tag{23}$$

and this is achieved by the substitutions

$$u = \beta_{33}\beta_{12}^{-2}a \; ; v = \beta_{12}ab \; ; B = B\beta_{12}^3\beta_{33}^{-1} \tag{24}$$

Elimination of u from (22) and (23) gives

$$u = (Z + v(2Z-1))(1-Z)^{-1}(3v^2)^{-1}$$

and $B = 3v^3(1 + v) (Z + v(2Z-1))^{-1}$

With these formulas it is possible to calculate log B as a function of Z and log u.

The calculated log $B(\log u)_Z$ graph was compared with the experimental log $B(\log a)_Z$-data and in the position of best fit the difference in reading along the coordinate axes on the two graphs gives the constants β_{12} and β_{33}

$$\log B - \log B = 3 \log \beta_{12} - \log \beta_{33} \tag{25}$$

$$\log u - \log a = \log \beta_{33} - 2 \log \beta_{12} \tag{26}$$

and $\log \beta_{12} = -3.12 \pm 0.05 = \log \beta_{33} = -10.42 \pm 0.05$.

The dotted curves in Fig. 8 are calculated with these constants. It is seen from this figure, that the agreement is satisfactory. However, small deviations at $B = 0.00125$ M, $B = 0.00062_5$ M and low z-values were found.

Deviations caused by additional complex

It remains now to explain the deviations from the dotted curve in Fig. 8. Such low total concentrations as 0.00125 and 0.00062_5 M can usually be studied with high accuracy only in very favorable cases. Now in our case measurements on low vanadium concentrations can be made in a very sensitive pH-range, and the deviations cannot be due only to experimental error but must be caused also by the formation of some additional complex.

In our treatment of the experimental data with the direct integration method the main part of the data could be explained with HB_2^{3-} and $H_3B_3^{3-}$ but deviations were found for low B and if a single additional complex was formed this could indicate either HB^- or $H_2B_2^{2-}$. These two possibilities have been tested with the aid of normalized graphs log $B(\log a)_{Z,l}$, and it was found that only the combination with the species B^{2-}, HB^-, HB_2^{3-} and $H_3B_3^{3-}$ gave normalized graphs, which fitted satisfactorily with the experimental data (see Fig. 8). The equations valid for the construction of this normalized graph are

$$Bu = v(1 + lu + 2v + 3uv^2)$$
$$BZu = v(lu + v + 3uv^2)$$

where the same substitutions as in (22) and (23) has been used and

$$l = \beta_1 \beta_{12}^2 \beta_{33}^{-1} \tag{27}$$

Elimination of u gives

$$u = (Z + v(2Z-1))(1-Z)^{-1}(3v^2 + l)^{-1} \tag{28}$$

and $B = v(1 + v) (3v^2 + l) (Z + v(2Z-1))^{-1}$ \hfill (29)

From (28) and (29) two log B (log $u)_Z$ graphs with different values of l, $l = 0.005$ and $l = 0.010$, were constructed and compared with the experimental graph. From the calculated graph which fitted best with the experimental
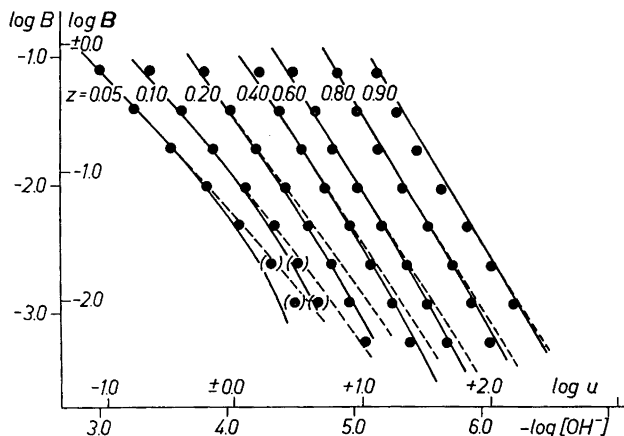
Fig. 8. Projection maps experimental data $\log B(\log[OH^-])z$ and normalized curves $\log B(\log u)z$ calculated for a) HB_2^{3-} and $H_3B_3^{3-}$ (dotted curve) b) HB^-, HB_2^{3-} and $H_3B_3^{3-}$ assuming $\beta_{11}\beta_{12}^2\beta_{33}^{-1} = 0.01$ (full curve). The position of best fit gave $\log \beta_1 = -6.04 \pm 0.08$, $\log \beta_{12} = -3.19 \pm 0.05$ and $\log \beta_{33} = -10.42 \pm 0.05$.

data, the full curve in Fig. 8, we obtained the constants β_{12} and β_{33} from (25) and (26)

$$\log \beta_{12} = -3.19 \pm 0.05; \quad \log \beta_{33} = -10.42 \pm 0.05$$

and the constant β_1 from eqn. (27) and the value of l giving the best fit ($l = 0.01$).

$$\log \beta_1 = -2 \pm 0.03 - 4.04 \pm 0.05 = -6.04 \pm 0.08$$

Final sets of equilibrium constants

Our potentiometric measurements give a set of data (B,Z,a) for concentrations 0.080 M $< B < 0.00062_5$ M, which may be explained most simply by a successive condensation of B^{2-} to HB_2^{3-} and $H_3B_3^{3-}$. Low concentrations indicated also a mononuclear species HB^-. No evidence has been found for the existence of higher polyions e.g. tetranuclear species.

The equilibrium constants obtained in this work have been deduced according to the methods developed in this institute and are summarized in Table 3.

Table 3.

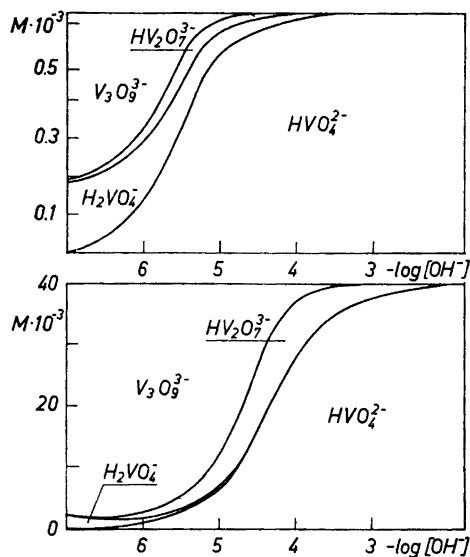| The constants deduced by:	$\log \beta_1$	$\log \beta_{12}$	$\log \beta_{33}$
Curve fitting $1.5^{-1}Z(\log Ba^{1.5})$			-10.50 ± 0.1
$Z(X)_{PQ}$		-3.12 ± 0.1	-10.48 ± 0.1
Normalized graph $\log B$ $(\log u)_{z,l}$, $l = 0$		-3.19 ± 0.05	-10.42 ± 0.05
Normalized graph $B(\log u)_{z,l}$	-6.04 ± 0.08	-3.19 ± 0.05	-10.42 ± 0.05
"Best values" of Nils Ingri	-6.04 ± 0.08	-3.19 ± 0.05	-10.42 ± 0.05

Fig. 9. Distribution of complexes as a function of $-\log[OH^-]$ for the total vanadium concentrations $B = 0.0062_5$ M and $B = 0.040$ M. The formulas have been written with the "phosphate" nomenclature.

The constants obtained in Felipe Brito's calculation [1a] (see the note on page 1971) are summarized in Table 4.

Table 4.

$\log \beta_1$	$\log \beta_{12}$	$\log \beta_{33}$	Method for deducing the constant
-5.97 ± 0.04	-3.16 ± 0.03	-10.42 ± 0.03	normalized map $\log B(\log u)z$
-5.97 ± 0.04	-3.16 ± 0.03	-10.42 ± 0.03	„ „ $\log BZ(\log Bu^{1.5})z$
-5.95 ± 0.06	-3.17 ± 0.04	-10.41 ± 0.03	„ „ $\log BZ(\log Bu)z$
-5.96 ± 0.06	-3.17 ± 0.04	-10.42 ± 0.03	„ „ $\log BZ(\log B(1-Z)u)z$
-5.97 ± 0.05	-3.17 ± 0.04	-10.42 ± 0.03	"Best values" of Felipe Brito.

After we had finished our calculations we discussed the methods used and have agreed on the following set of constants.

$$\log \beta_1 = -6.0 \pm 0.1; \log \beta_{12} = -3.18 \pm 0.05; \log \beta_{33} = -10.42 \pm 0.04$$

Fig. 9 shows the distribution of the various species as a function of log $[OH^-]$ for the total concentrations $B = 0.00062_5$ M and 0.040 M.

Possible structures of the complexes

Now one may ask if the ions found can be given a reasonable structural interpretation. There are many different methods for evaluating the structure of complexes in aqueous solution (X-ray diffraction of solutions, thermodynamic considerations, various types of spectra *etc.*) but very few of them have been used for studying vanadate(V) solutions.

From a structure-entropy consideration, however, La Salle and Cobble [42] have shown that VO_2^+ rather than $V(OH)_4^+$ is the more probable form of vanadium(V) in very strong acid solution.

Siebert [41] has studied strong alkaline vanadate(V) solutions, using Raman spectra, and from similarities between spectra obtained and spectra of PO_4^{3-} solutions he concluded that the vanadate ion in these solutions is tetrahedral, VO_4^{3-}.

For solutions of intermediate pH this kind of data is lacking. In this case one may guess from what is known on the solid state and assume that vanadium(V) forms the same type of ions or units or least has the same coordination number in solutions as in the solid.

Previous X-ray studies of crystalline vanadium(V) compounds prepared from water solutions indicate that the coordination number of vanadium(V) may be 4,5, or 6.

In solid V_2O_5 investigated by Byström, Brotzen and Wilhelmi (1950) [32], vanadium is surrounded by five oxygen atoms forming a distorted trigonal bipyramid. The bipyramids are coupled by sharing two edges giving infinite chains. These chains are linked laterally to sheets. The lateral linking is established by the attraction between a vanadium atom and an oxygen in two different chains. Thus the coordination around vanadium is between 5 and 6. From water solution V_2O_5 is precipitated at pH$\approx$1.6. The same type of V-O-sheets have also been found in the mineral hewettite $CaV_6O_{16}(H_2O)_9$ (Barnes, Qurashi [33]).

Evans [34] has pointed out that it may be reasonable to expect the same type of bipyramidal chains, modified to give vanadium a distorted octahedral coordination, also in the solid decavanadates, crystallizing at pH$\approx$6.5, $(NH_4)_6$ $V_{10}O_{28}(H_2O)_6$ (Lindqvist [2]) $K_6V_{10}O_{28}(H_2O)_9$, $K_6V_{10}O_{28}(H_2O)_{10}$, $Ca_3V_{10}O_{28}(H_2O)_{16}$ (pascoite), $K_2Mg_2V_{10}O_{28}(H_2O)_{16}$ (hummerite) and $K_2Zn_2V_{10}O_{28}(H_2O)_{16}$ (Evans, Mrose and Marvin [3]).

KV_3O_8 belongs to this group also and has been investigated with X-rays by Evans and Block [34]. According to Evans [34] this vanadate contains bipyramidal chains "folded in a herringbone fashion".

At higher pH, 6—8, colorless "metavanadates" may be crystallised and among then KVO_3 (Evans and Block [35], 1954, Petràsovà, Madar and Hanic [36] 1958) and $KVO_3(H_2O)$ (Christ, Clark and Evans [37] 1954) have been investigated by X-ray analysis. In $KVO_3(H_2O)$, the units are trigonal bipyramids which share edges forming a chain. In the structure two V-O-distances are shorter than the other and Hanic [38] has pointed out that this should indicate the existence of VO_2^+ groups in the crystal.

In KVO_3 which crystallizes together with $KVO_3(H_2O)$ one would expect the same trigonal staggered chain but here vanadium is four-coordinated and the tetrahedra share corners forming a string similar to diopside. It is easy to derive the diopside chain from the staggered trigonal bipyramid by a simple stretching process. In fact it may be possible also to convert $KVO_3(H_2O)$ to KVO_3 by grinding (Evans [35]). Diopside structures have been found also for $NaVO_3$ (Sörum [39] 1943) and NH_4VO_3 (Lukesh [40] 1950).

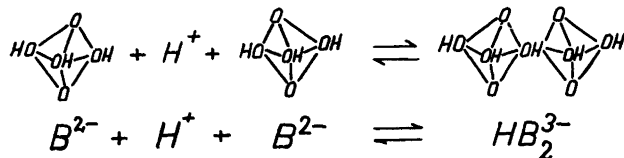$$B^{2-} + H^+ + B^{2-} \rightleftharpoons HB_2^{3-}$$

Fig. 10.

From the most alkaline solutions "orthovanadates" may be crystallized, and tetrahedral VO_4^- groups have been established in a number of vanadium compounds especially minerals ($BiVO_4$ [43], (Pb, Zn, Cu)(OH)(VO_4) [44], Pb_3 ($VO_4)_2$ [45], $ScVO_4$ [46], and others).
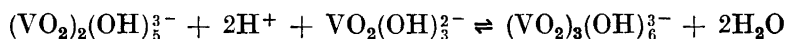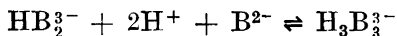
From the configurations in the solid vanadate(V) crystals investigated with X-rays it seems reasonable to propose, for the polynuclear complexes in solution, structures where vanadium either is four- or five-coordinated.

Assuming four-coordination, the vanadium species $H_3B_3^{3-}$ may be given the formula $V_3O_9^{3-}$; structurally that means three VO_4 tetrahedra sharing two corners forming a 6-membered ring. With VO_4-tetrahedra, however, it is difficult to understand the formation of HB_2^{3-}.

On the other hand assuming vanadium to be five-coordinated it is possible to give a mechanism for formation of both HB_2^{3-} and $H_3B_3^{3-}$. In this case the first step in the condensation reaction may be written (Fig. 10)

$B^{2-} + H^+ + B^{2-} \rightleftharpoons HB_2^{3-}$

$VO_2(OH)_3^{2-} + H^+ + VO_2(OH)_3^{2-} \rightleftharpoons (VO_2)_2(OH)_5^{3-} + H_2O$
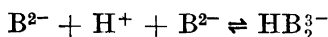
and for the reaction (Fig. 11) when HB_2^{3-} reacts with H^+ and B^{2-} forming the trimer $H_3B_3^{3-}$

$HB_2^{3-} + 2H^+ + B^{2-} \rightleftharpoons H_3B_3^{3-}$

$(VO_2)_2(OH)_5^{3-} + 2H^+ + VO_2(OH)_3^{2-} \rightleftharpoons (VO_2)_3(OH)_6^{3-} + 2H_2O$

Instead of a ring structure $H_3B_3^{3-}$ may also be a chain, coupled as in KVO_3 (H_2O), but in this case it is difficult to explain why higher complexes e.g. four — or five-nuclear complexes, have not been detected in our solutions.
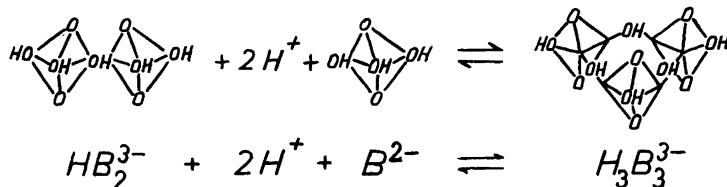

$$H_3B_2^{3-} + 2H^+ + B^{2-} \rightleftharpoons H_3B_3^{3-}$$

Fig. 11.

Added in proof: Recently K. F. Jahr and L. Schoepp *(Z. Naturforsch. 14 b* (1959) 467, 468) presented the results from an investigation of water solutions of metavanadate using three different cryoscopic methods. They used much higher concentrations than that one used in this work ($C \approx 0.140-0.196$ moles $NaVO_3$ per kg) and concluded that the solutions contained the tetrameric ion, $V_4O_{12}^{4-}$. In addition to that they also found that thallium(I)metavanadate is dissolved in tertbutylchloride giving the compound $(C_6H_9)_4V_4O_{12}$. Whatever the reason for the discrepancy between cryoscopic measurements of Schwarzenbach and Jahr on one side and our emf work on the other side may be, our data certainly cannot be explained by a mechanism where $V_4O_{12}^{4-}$ is the main product.

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