2.25, 2.28, and 2.66 Å with standard deviations of 0.05 Å, and the shortest oxygen-oxygen distance is 2.66 ± 0.09 Å. The coordination of the bismuth atoms in the deformed layers shows thus a significant difference from what is expected for an ideal $Bi_2O_2^{2+}$ layer. The description of the structure as being built up of *separate* chains GeO_3^{2-} and *separate* layers $Bi_2O_2^{2+}$ is therefore too simplified.

A full account of the present work will appear in a forthcoming paper.

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Are Aqueous Metavanadate Species Trinuclear, Tetranuclear, or Both? Preliminary LETAGROP Recalculation of Emf Data

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A few years ago the present authors published [1,2] some emf measurements on vanadate solutions at 25°C, in alkaline 0.5 M Na(Cl) medium. In these measurements, the average charge, z, per vanadium was varied between -1 ("metavanadate") and -2 ("pyrovanadate") and the total vanadium concentration, B, ranged from 0.00062_5 to 0.0800 M.

An analysis of these data, mainly using graphical methods, indicated that the principal species are, in our notation, B^{2-} (*e.g.* $VO_2(OH)_3^{2-}$ or HVO_4^{2-}), HB_2^{3-} (*e.g.* $HV_2O_7^{3-}$) and $H_3B_3^{3-}$ (*e.g.* $V_3O_9^{3-}$), in other words the (0,1), (1,2) and (3,3) species. There was also evidence for the mononuclear (1,1) complex HB^- (*e.g.* VO_3^-).

We have written for brevity each vanadate complex in the general formula $H_pB_q^{(2q-p)-}$, and denoted it by the set (p,q). The formation constants β_{pq} (pH$_2$O + qB^{2-} $\rightleftharpoons$ $H_pB_q^{(2q-p)-}$ + pOH$^-$) and the final set proposed in these studies are shown in the first line of Table 1.

For the main "metavanadate" species (with $z = -1$), one group of workers have proposed $H_3B_3^{3-}$ (Refs.[3-7]) and another $H_4B_4^{4-}$ (Refs.[8,9,11-13]). The strongest indications for the (4,4) species come from freezing-point measurement such as those of Jahr and coworkers [12] (B between 0.20 and 0.35 M) (Ref.[12a]) or between 0.14 and 0.35 M (Ref.[12b]) and Nauman and Hallada[16] (B between 0.027 and 0.195 M).

The emf data of Schwarzenbach and Geiger [14] and spectrophotometric data of Schiller and Thilo [15] have been interpreted by trinuclear species. On the other hand, Lefebvre [10] and Sannikov and coworkers [17] have interpreted their emf measurements assuming the species (0,1), (0,2) and (4,4), Lefebvre in addition also (1,2) and (2,4).

In order to test wether our emf data could be explained equally well, assuming the (4,4) species instead of (3,3), we recently [20] carried out an analysis by means of LETAGROP.[18] In LETAGROP, the computer searches — for any combination of complexes — the combination of equilibrium constants β_{pq} that minimizes the error square sum

$U = \Sigma(Z_{\rm exp} - Z_{\rm calc})^2 = \sigma^2(Z)$. (degrees of freedom).

The closeness of the fit can thus be measured by U or σ. In a recent version of LETAGROP,[19] including operations VRID and MIKO, a complex is automatically sorted out (equilibrium constants set = 0) if the minimum would be found for a negative value for this constant.

Using an early version of the LETAGROP program,[18] we have tried [20] various combinations. As seen from Table 1, the combination (1,1) + (1,2) + (3,3) gives a much lower value for $\sigma(Z)$ than (1,1) + (1,2) + (4,4); (1,1) + (4,4) + (0,2); (1,1) + (4,4); or (1,1) + (3,3).

We have continued these calculations on our 25°C data using the version with MIKO, and some preliminary results are given in Table 1. The computer first rejected (4,4) when it was added to the earlier complexes (1,1) + (1,2) + (3,3) since a positive β_{44} gave no improvement in U. On the other hand, some improvement was found by adding (0,2), and when then the combination with (4,4),

Table 1. Sets of log β_{pq} calculated from emf data [1,2] on vanadate solutions. The first set was derived by graphical methods, the following by LETAGROP calculations (error limits = 3σ).

(1,1)	(1,2)	(3,3)	(4,4)	(2,4)	(0,2)	$\sigma(Z)$	Ref.
-6.0 ± 0.1	-3.18 ± 0.05	-10.42 ± 0.04					1,2
-5.59 ± 0.08			-13.41 ± 0.12			0.046	20
-5.61 ± 0.08			-13.32 ± 0.17		-0.13 ± 0.21	0.045	»
-5.76 ± 0.09		-10.61 ± 0.06				0.034	»
-5.68 ± 0.06	-3.12 ± 0.10		-13.16 ± 0.08			0.024	»
-5.91 ± 0.06	-3.23 ± 0.02	-10.48 ± 0.03				0.012	»
-5.90 ± 0.05	-3.25 ± 0.07	-10.48 ± 0.04	$(\beta_{44} = 0)$			0.0122	this work
-5.94 ± 0.05	-3.21 ± 0.07	-10.44 ± 0.04			0.03 ± 0.25	0.0113	»
-5.89 ± 0.06	-3.16 ± 0.08	-10.56 ± 0.08	-13.55 ± 0.18	-4.70 ± 0.18	0.44 ± 0.17	0.0091	»

(2,4) and (0,2) was tried, all came out with positive constants, and a considerable lowering of σ and U was found.

This results has been further corroborated by new emf measurements [21] in 0.5 M NaCl medium at 40°C in the range of charge z between -0.4 and -1.0. These data indicate that one must consider both the species (3,3) and (4,4) besides the decavanadate species such as (14,10), (15,10), and (16,10).

Our results would thus indicate that both trinuclear and tetranuclear species are present in the "metavanadate" solutions. The results must be considered as preliminary, since calculations and experiments are now proceeding to find out whether other species may also be present.

It is easy to see how the earlier discrepancies have occurred. In the range of low vanadate concentrations used in, *e.g.*, our emf measurements, $H_3B_3^{3-}$ predominates whereas $H_4B_4^{4-}$ becomes important in the higher B range, where most freezing point measurements are carried out.

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