SHORT COMMUNICATIONS

The deviation of experimental data corresponding to the lowest total concentration of vanadium may be due to experimental error or may be due to new reactions occurring in this concentration range.

To perform an analysis these data will in any case be neglected in the first attempt and may later be included in a refinement. The constancy of $t$ over almost the whole range of $Z$ does strongly indicate the existence of series of "core-link" complexes of the general formula VO$_4$(VO$_2$(OH)$_2$)$_n$ where $-nT$ must be integers. With the value of $t = -1.40$ only values of $N = 3$, 10, 15... etc. are possible. The primary hydrolysis product would therefore be expected to be VO$_2$(VO$_2$(OH)$_2$)$_{1.40/5}$ (=(VO)$_3$(OH)$_2$)$_5$ as also found by me. It is, however, certain that some of the additional complexes of composition (VO)$_n$(OH)$_m$(VO)$_b$(OH)$_a$, etc. do also exist which I have not pointed out in my paper. If the primary hydrolysis product is (VO)$_2$(OH)$_2$, the limiting slope of a plot of log$(-Z/[t + Z])$ versus ($logC_{0} - 1.40 log [H^+]$) should be 5. That this is the case is seen from Fig. 2.

An enlarged plot of log(1.60$-Z$) versus pH, (not shown), indicates that new reactions start around $Z = 1.35 \pm 0.03$, a value which corresponds closely to the "core-link" product of composition VO$_4$(VO$_2$(OH)$_2$)$_5$ with $Z = 1.35$. The pure "core-link" polymerisation does therefore seem to end with this product. The nature of the final reaction(s) cannot be determined with any certainty, but might well be represented by some selected but hypothetical reactions.

Assuming the structure of the hexavanadate VO$_4$(VO$_2$(OH)$_2$)$_5$ actually to be as formulated in the "core-link" approach, i.e. as oxyvanadium(V) pentavanadate, a formula which has also been proposed by Jander$^8$ for some solid vanadates, the existence of the solid decavanadates mentioned by Rosotti$^4$ to support his proposal for the existence of the decavanadate in solution might well be explained. The deviation of the experimental data for low concentrations of vanadium might also be explained as formation of pentavanadates or polypentavanadates in this concentration range.

The formation constants for the species of "core-link" composition can be determined by curve-fitting or other means. When an electronic computer will be at hand I intend to do this determination.

That I still claim—as cited by Sillén with some malice—"A distinct advantage is that the primary polymerisation product often can be determined with certainty", will be obvious from the examples given above.

References


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Comments to B. S. Jensen's Paper
"The Formation of Polynuclear Complexes"

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Vanadium(IV) is a minor point. From experience on other systems it seems likely that both VO(OH)$^+$ and VO(OH)$_2$ are present but that [VO(OH)$_3$]$^+$ [VO(OH)$_4$]$^-$ in the range studied. To determine both constants independently, more data would be need.

Vanadium(V) is the main problem. Whereas the orange-colored vanadates (the first hydrolysis product of VO$^+$) were earlier supposed to be penta- or hexavanadates, Rosotti's work$^1$ strongly indicated that they are deca-vanadates. Later work by various methods$^2$, seems to confirm Rosotti's deca-vanadate hypothesis.

B. S. Jensen wants to revive the hexavanadate theory, perhaps with a subsequent series of "core-links" complexes. In his first paper$^8$ he deduced from Rosotti's data a set of reactions and equilibrium constants. However, a check$^1$ showed, that with Jensen's theory one would calculate curves $Z/log(h)$ far from Rosotti's experimental data, on which the calculations were allegedly founded. In Jensen's new contribution the long discussion does not even end with a set of equilibrium constants. There is little point in continuing this discussion of the revived hexavanadate hypothesis until B. S. Jen-...


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Reduction of 2-Mercaptothiazole to Benzothiazole

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2-Mercaptothiazole (I) is widely used as a component in corrosion inhibitors for automotive anti-freezes. Accordingly, its stability in the presence of iron is of great importance. In neutral or alkaline solution it was found to be quite stable, but in acid solution it was reduced by iron powder to benzothiazole (II):

\[
\text{I} \quad \text{N} \quad \text{S} \quad \text{C-SH} + 2\text{H} \rightarrow \text{II} \quad \text{N} \quad \text{S} \quad \text{C-H} + \text{H}_2\text{S}
\]

This simple reduction seems not to have been observed for the unsubstituted compound. However, the corresponding reaction was reported for 2-mercapto-6-methylbenzothiazole, while 2-mercapto-4-nitro-6-methyl- and 2-mercapto-4-nitro-6-methoxy-benzothiazole did not yield identifiable products, so the reaction is not of general applicability. Reductive degradation of 2-mercapto-benzothiazole under more drastic conditions has been reported. Treatment with Raney nickel or Raney cobalt thus yielded benzothiazole and further degraded compounds. Hydrogenation over a cobalt sulphide catalyst at high pressure and elevated temperature gave equal parts of o-aminophenol and benzothiazole.

Experimental. The directions of Blomquist and Diuguid were partly followed. I (10 g) was mixed with iron powder (Ferrum reductum, 10 g), glacial acetic acid (90 ml), ethanol (25 ml), and water (10 ml). The mixture was heated at 100°C for 36 h, after which time no more hydrogen sulphide was evolved. The mixture was made strongly alkaline and distilled with steam until the distillate was clear. It was extracted with ether, the ether solution dried over potassium carbonate, the ether evaporated, and the residue fractionated in vacuum. The main fraction (4.1 g; 51 %) had b.p. 93.5–93.8°/6 mm Hg. Titration with perchloric acid in glacial acetic acid gave equiv. wt. 135.2, calc. for II 135.18. Pierate, m.p. 169° (depends upon rate of heating), lit. 169.5–170°. The identity of the compound was further confirmed by its infrared spectrum, which was found to coincide with that given for benzothiazole by Randall et al.

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