

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 $\text{VO}_2(\text{VO}_2(\text{OH})_t)_N$ where $-tN$ must be integers. With the value of $t = -1.40$ only values of $N = 5, 10, 15$ etc. are possible. The primary hydrolysis product would therefore be expected to be $\text{VO}_2(\text{VO}_2(\text{OH})_{1.40})_5 (= (\text{VO}_2)_6(\text{OH})_7)$ as also found by me. It is, however, certain that some of the additional complexes of composition $(\text{VO}_2)_{11}(\text{OH})_{14}, (\text{VO}_2)_{16}(\text{OH})_{21}$, etc. do also exist which I have not pointed out in my paper. If the primary hydrolysis product is $(\text{VO}_2)_6(\text{OH})_7$, the limiting slope of a plot of $\log(-Z/(t+Z))$ versus $(\log C_B - 1.40 \log [\text{H}^+])$ 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 reaction(s) start around $Z \approx 1.35 \pm 0.03$, a value which corresponds closely to the "core-link" product of composition $\text{VO}_2((\text{VO}_2)_5(\text{OH})_7)_5$ 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 $\text{VO}_2((\text{VO}_2)_5(\text{OH})_7)$ actually to be as formulated in the "core-link" approach, i.e. as oxyvanadium(V) pentavanadate, a formulation which has also been proposed by Jander⁵ for some solid vanadates, the existence of the solid decavanadates mentioned by Rosotti⁴ 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.

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4. Rosotti, F. J. C. and Rosotti, H. S. *Ibid.* **10** (1956) 957.
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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 VOOH^+ and $\text{VO}(\text{OH})_2$ are present but that $[\text{VOOH}^+] > [\text{VO}(\text{OH})_2]$ in the range studied. To determine both constants independently, more data would be needed.

Vanadium(V) is the main problem. Whereas the orange-colored vanadates (the first hydrolysis product of VO_5^{+}) were earlier supposed to be penta- or hexavanadates, Rosotti's work¹ strongly indicated that they are deca-vanadates. Later work by various methods²⁻⁷, 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 paper⁸ he deduced from Rosotti's data a set of reactions and equilibrium constants. However, a check⁹ showed, that with Jensen's theory one would calculate curves $Z(\log h)_B$ 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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sen has produced either better data of his own or at least a complete alternative explanation (reactions and equilibrium constants), which can be compared with experimental data.

I might add, that a limited set of core-links complexes, (especially a set of only two species) has often proved a useful approximation but cases with a considerable number of core-links complexes do not seem to be as frequent as I may once have thought on the basis of our earliest data. It is an irony of fate that B. S. Jensen now is trying to revive these concepts too.

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9. Sillén, L. G. *Acta Chem. Scand.* **15** (1961) 1421.

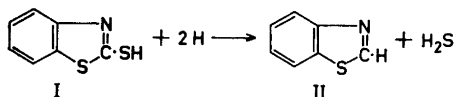
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Reduction of 2-Mercaptobenzothiazole to Benzothiazole

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2-Mercaptobenzothiazole (I) is widely used as a component in corrosion inhibitors for automotive anti-freezes¹. 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):



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-methoxybenzothiazole did not yield identifiable products², so the reaction is not of general applicability. Reductive degradation of 2-mercaptobenzothiazole under more drastic conditions has been reported. Treatment with Raney nickel³ or Raney cobalt⁴ thus yielded benzothiazole and further degraded compounds. Hydrogenation over a cobalt sulphide catalyst at high pressure and elevated temperature gave equal parts of *o*-aminothiophenol and benzothiazole⁵.

Experimental. The directions of Blomquist and Diuguid² 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° 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. 93.0–93.5°/8 mm Hg. Titration with perchloric acid in glacial acetic acid gave equiv. wt. 135.2, calc. for II 135.18. Picrate, m.p. 169° (depends upon rate of heating), lit.³ 169.5–170°. 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.*⁶

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