Ru dtp$_3$. However, the band is considerably broader in the latter case ($\delta(-)$ is only 2000 cm^{-1} in Rh dtp$_3$) as may be explained by the more complicated structure of the excited configuration $\pi^{-1}\gamma_5^5\gamma_3$ of the Ru(III) complexes. Similar remarks apply to the highest band observed at 41 700 cm^{-1} of Ru dtp$_3$ which may be compared to the band of Rh dtp$_3$ at 38 800 cm^{-1}.

Experimental 3.8 g ”potassium chlororuthenite” (predominantly $K_2[RuCl_5(H_2O)]$ or K_2RuCl_5) from H. Drijfhout and Zoon, Amsterdam, was heated with 100 ml 0.5 M perchloric acid. An olive-brown precipitate (0.9 g) was filtered off, and the filtrate added 40 ml 1 M aqueous solution of ammonium diethyldithiophosphate (from American Cyanamid, Stamford, Conn.). By heating at 80° for 6 h, under stirring, a dark brown precipitate was formed. When boiled with ethanol, this precipitate left 0.6 g of a yellow-brown powder (believed possibly to be dtp$_3$ RuORu dtp$_3$, having nearly the same analysis as Ru dtp$_3$: C 20.93; H 4.39; P 14.79; S 32.67. It is nearly insoluble in ethanol. A solution in dichloroethane shows a broad band at 380 mμ but no maxima in the visible), and the hot filtrate deposited various fractions of dark red, nearly black, crystals. The latter fractions were mixed with small amounts of a brown substance, reversing the intensity ratio between the 420 and 400 mμ bands. On the other hand, the first fraction so prepared (only 0.1 g) was identified as genuine Ru dtp$_3$. This was not so much because of the analysis. (Found: C 21.50; H 4.52; P 15.18; S 32.95. Calc. for $C_{12}H_{30}O_6P_3S_6Ru$: C 21.92; H 4.66; P 14.14; S 29.27) as because of the fact that colourless In dtp$_3$, when recrystallized from boiling ethanol together with one of the mixed fractions, syncrystallized with a clear red colour, leaving an orange solution. The visible absorption spectrum of a solution of these In(III), Ru(III) containing crystals was identical with that given above. The reflection spectrum of the red crystals was measured on the attachment to the Cary 14 recording spectrophotometer (on which all solutions were also measured) and showed maxima of the optical density at 509 and 421 mμ and a shoulder at 400 mμ.

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Received April 23, 1962.

”The Formation of Polynuclear Complexes”

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In a recent contribution to *Acta Chem. Scand.*[1] professor L. G. Sillén has critisized my paper ”The Formation of Polynuclear Complexes.”[2]

The display presented by Sillén clearly shows that I have drawn some wrong conclusions in the case of the hydrolysis of the VO_2^+-ion, but apart from this his criticism is rather surprising both in its form as well as in its examples as will be evident from the following.

It will be clear for readers of my paper that the analysis of experimental data by the method proposed by me is in its present form limited to cases where only two complexes exist simultaneously in major amounts. This is the cause why I did not intend to identify the mononuclear species being formed in the case of the hydrolysis of the vanadyl ion.

Sometimes, however, the trends in the limiting slopes may be of some aid in identifying the new species arising when new reactions start. Such a case do we in fact have in the hydrolysis of the VO^{2+}-ion.

Rosotti by curve-fitting methods claimed the monomeric hydrolysis product to be VO(OH) with a stability constant of $\beta_{11} = 10^{8.2} \pm ^{0.1}$ and showed how well the calculated curve fitted the experimental data. In his contribution Sillén used this example to demonstrate the superiority of the treatment of experimental data used by him and his group.

By considering the trends shown by the limiting slopes in a log Z *versus* pH plot of the available data it is obvious that the monomeric species $VO(OH)_2$ might as well be the actual species being formed. From the limiting tangent the formation constant is estimated to $\beta_{21} \simeq 10^{19}$.

In Fig. 1 a plot of Z *versus* pH calculated by means of the following formula is compared with experimental data

$$(Z-1) = ((\beta_{21}[OH]^2-1)/(4C_B\beta_{22}[OH]^2))\left(\sqrt{(\beta_{21}[OH]^2+1)^2+8\beta_{22}[OH]^2C_B} -(\beta_{21}[OH]^2+1)\right)$$

where C_B is the total concentration of vanadium and with $\beta_{21} = 10^{18.8}$ and $\beta_{22} = 10^{21.5}$.

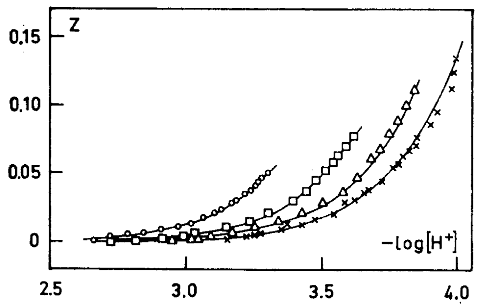

Fig. 1. Hydrolysis of VO^{2+}. Z (average number of OH^- bound per VO^{2+}) as a function of pH for different total concentrations of vanadium. The lines represent theoretical formation curves calculated for $\beta_{22} = 10^{21.5}$ and $\beta_{21} = 10^{18.8}$.

This representation does fit the experimental data as well as does the representation proposed by Rosotti (Fig. 2 of Ref.[3]).

By slight changes in the stability constants it is possible to find fits, some of which may suit the investigator better, but with the present set of data it will not be possible to decide, by visual examination, which secondary species is actually being formed.

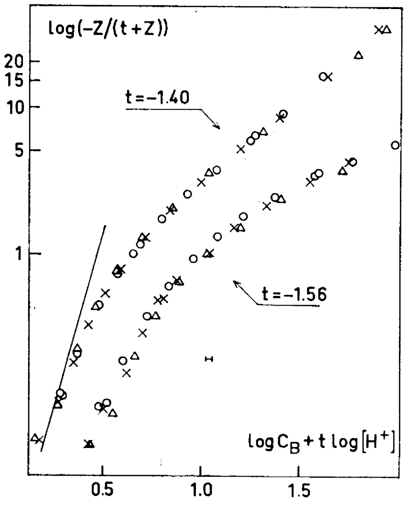

Fig. 2. Hydrolysis of VO_2^+. Values of log $(-Z/(t + Z))$ plotted *versus* ($\log C_B + t\log$ H^+) for $t = -1.40$ and $t = -1.56$. The estimated error is shown in the figure (H). A line of slope 5 is also shown.

To decide which representation does fit the best elaborate least squares calculation might be done leaving the investigator to the choice of regarding a difference found to be significant or not.

To me it seems wise not to state more about the nature of the secondary hydrolysis product than to state it is monomeric as neither of the proposals for the monomeric hydrolysis are much more than guesses. Curve fitting of approximate solutions to experimental data has no chemical meaning and can only be a mathematical art even when it is skillfully done.

To consider my analysis of the hydrolysis of the VO_2^+-ion, the criticism seems at first sight well founded as seen from the comparison of experimental data with theoretical curves based on my formation constants — as displayed by Sillén. The disagreement is impressive but does in fact only prove that my constants are more or less in error.

Whereas a reasonable fit at the onset of the hydrolysis can be obtained by correcting the primary constant within the uncertainty connected to it, this is not the case for the final reaction proposed. If one therefore accepts my proposal for the primary hydrolysis product, additional intermediates must be formed.

As a basis for the analysis by the one or the other method the value of t (for definition see Ref.[2]) is used. In my analysis I used the value $t = -1.40$ whereas Rosotti used the value $t = (-)1.56$.

As a check of which value is to be preferred in the analysis, a plot of log $(-Z/(t + Z))$ *versus* ($\log C_B + t\log[H^+]$) can be made. For the best value of t the best fit with a single curve should be obtained. In Fig. 2 such plots for the experimental data are shown for $t = -1.40$ and $t = -1.56$.

Apart from data referring to the lowest total concentration of vanadium, which are not included in either plot, all experimental data fit very well on a single curve for $t = -1.40$. This is, as is seen from the figure, not the case of $t = -1.56$. The estimated error for the abscissae is shown in the figure. If the actual error is larger, which I do not believe, many reasonable fits can be constructed which are, however, often improbable from a chemical point of view.

Accepting the best fit, an analysis on the basis of the value $t = -1.40$ will be the most reasonable.

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 $VO_2(VO_2(OH)_{-t})_N$ 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 $VO_2(VO_2(OH)_{1.40})_5$ $(=(VO_2)_6(OH)_7)$ as also found by me. It is, however, certain that some of the additional complexes of composition $(VO_2)_{11}(OH)_{14}$,$(VO_2)_{16}(OH)_{21}$, etc. do also exist which I have not pointed out in may paper. If the primary hydrolysis product is $(VO_2)_6(OH)_7$ the limiting slope of a plot of $\log(-Z/(t + Z))$ *versus* $(\log C_B - 1.40 \log [H^+])$ 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 reaction(s) start around $Z \simeq 1.35 \pm 0.03$, a value which corresponds closely to the "core-link" product of composition $VO_2((VO_2)_5(OH)_7)_5$ 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 $VO_2((VO_2)_5(OH)_7)$ actually to be as formulated in the "core-link" approach, *i.e.* as oxyvanadium(V) pentavanadate, a formulation which has also been proposed by Jander [5] 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.

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Received April 26, 1962.

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 $VO(OH)_2$ are present but that $[VOOH^+] > [VO(OH)_2]$ 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_2^+) were earlier supposed to be penta- or hexavanadates, Rossotti's work[1] strongly indicated that they are deca-vanadates. Later work by various methods [2-7], seems to confirm Rossotti'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 Rossotti's data a set of reactions and equilibrium constants. However, a check [9] showed, that with Jensen's theory one would calculate curves $Z(\log h)_B$ far from Rossotti'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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* *Acta Chem. Scand.* **16** (1962) 1049.