Fig. 3. Introduction of known amounts of pregnandiol without solvent showing linear response of the ionisation chamber. Stationary phase: Se-30 3 % by weight of solid support. Temperatures: Injection 245°C. Column and detector 210°C.

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On the Hydrolysis of Niobates in 3 M K(Cl) Medium

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The amount of information concerning ionic species in aqueous solutions of alkali metal niobates is rather limited. Using several different methods of investigation Jander and Ertel[1] concluded that the main species were $Nb_6O_{19}{}^{8-}$, $HNb_6O_{19}{}^{7-}$, and $(Nb_6O_{18}{}^{6-})_n$, where $n = 3$ or 4. However, later Lehné and Goetz[2] and more recently Leicht, Lehné and Rohmer[3] have studied niobate solutions by cryoscopy and emf measurements. They interpreted their data by assuming the species $Nb_5O_{16}{}^{7-}$, $HNb_5O_{16}{}^{6-}$ and $H_2Nb_5O_{16}{}^{5-}$ in the pH range $11-13.5$, and they reported mononuclear or dinuclear species in still more alkaline solutions. Furthermore an X-ray study by Lindqvist[4] indicated that hexanuclear niobate groups were present in the solid isopolyniobate, "7 $Na_2O \cdot 6$ $Nb_2O_5 \cdot 32$ H_2O".

The primary object of the present work was to decide whether hexa- or pentaniobates predominate in solution. During the experiments many difficulties were encountered but some preliminary work is reported here.

A series of emf-titrations were carried out in which the total niobium concentration, B, was kept constant whereas the total OH^--concentration in excess over $Nb(OH)_5$, $-H$, was varied. The variation of the activity factors was minimized by adding KCl to the solutions and keeping $[K^+] = 3$ M. $[OH^-]$ was obtained from the emf of the cell

$-Pt$, H_2 (1 atm)/niobate solution S/SE $+$

where SE is the reference electrode. SE $=$ 3 M KCl/3 M KCl (saturated with AgCl)/Ag, AgCl. The emf may be written $E = E_0 -59.15 \log [OH^-] + j[OH^-]$. By separate experiments without niobate in S the constants E_0 and j were determined; the latter was remarkably low (1 mV/M). From B, $-H$ and $[OH^-]$ the average negative charge per Nb atom was obtained as $Z = (-H-[OH^-])/B$.

Experimental. Two different potassium niobates were used for the preparation of the stock solutions.

$K_8Nb_6O_{19}\cdot16\ H_2O$ ("8/6") was prepared according to Jander and Ertel [1] from very pure Nb_2O_5 ("Columbium Oxide, Research Grade" from Fansteel Metallurgical Corporation, or "Niobpentoxyd, mindestens 99,6 %" from Schuckardt, München). Stock solution I was prepared from (8/6). The other niobate, $K_7HNb_6O_{19}\cdot n\ H_2O$, where $n = 13-14$, ("7/6"), was obtained by addition of alcohol to a solution of (8/6) in 0.1 M KOH. Stock solutions $II-IV$ were prepared from (7/6). The solutions were carefully protected against CO_2 in the air. All stock solutions were analyzed for K and Nb as indicated by Lindqvist.[4] The ratio K/Nb was found to be 1.330, 1.168, 1.167 and 1.171 for the solutions $I-IV$. By single crystal X-ray data the substances (8/6) and (7/6) could also be identified with those described by Halla et al.[5] except for a small monoclinic distortion in (7/6).

In order to increase the pH-range accessible to emf measurements it was necessary to acidify the niobate solutions. This could not be done with mineral acids as these immediately precipitated niobium oxide. However, the acidification could be achieved by addition of NH_4Cl solution and removing the NH_3 formed with N_2 gas. In this way solutions with log $[OH^-] = -3.3$ could be obtained. The more alkaline solutions were prepared by addition of KOH solution to the niobate solutions.

In the region where log $[OH^-] = -3.3$ to -1.75 the solutions S were generally clear but in more alkaline solutions small amounts of a precipitate were gradually formed. This, however, did not seem to have any influence on the stability of the emf. Also during the titrations it frequently occurred that the hydrogen electrodes became inactive after some hours' service, showing no well defined potentials; this may possibly be due to the adsorption of some colloidal material. The emf was restored to the equilibrium value when a fresh electrode was used.

Data and conclusions. For $B = 140$, 100 and 50 mM independent titrations (starting at log $[OH^-] \approx -3.3$) generally showed good reproducibility. In a few experiments, however, the solutions became highly turbid even at log $[OH^-]$ as low as -2.5 (approx.) and the Z-values became larger than normal (the maximum deviation was 0.01 Z-units). The data from these experiments were rejected. Finally some back titrations were carried out by adding a NH_4Cl solution to alkaline niobate solutions. When starting at log $[OH^-] = -2.4$ (symbol $\times$), complete reversibility was obtained. However, when starting at log $[OH^-] = -1.6$ a back titration (symbol $+$) showed significantly higher Z-
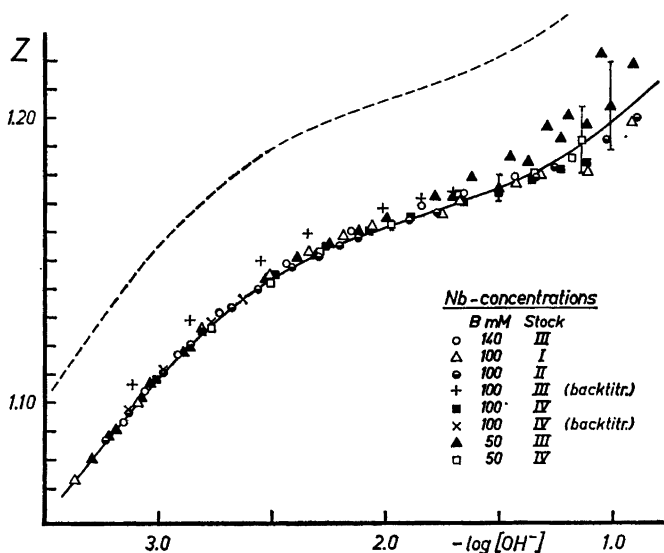

Fig. 1. Z = average negative charge per Nb atom as a function of log $[OH^-]$. Solid line = calculated curve (constants in the text). Dashed line = best curve assuming pentanuclear species. The errors indicated correspond to ± 0.2 mV (for $B = 50$ mM).
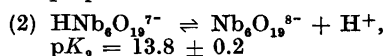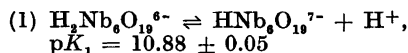
values than those obtained for the forward titrations.

The data (Fig. 1) show that the Z (log [OH$^-$]) curves for different B values coincided, indicating that all species taking part in the hydrolysis should have the same nuclearity N. The reactions can be written

$$A_pB_N + n\ A \rightleftharpoons A_{p+n}B_N \quad \text{(equilibrium constant } \beta_n)$$
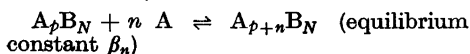
where A = OH$^-$, B = Nb(OH)$_5$ and p and n are integers. If we assume three species with $n = 0$, 1, and 2 we obtain $Z_{calc} = 1 + (\beta_1[\text{OH}^-] + 2\beta_2[\text{OH}^-]^2)/NB$. When comparing Z with Z_{calc} excellent agreement is obtained with $N = 6$, log $\beta_1 = 3.28 \pm 0.05$ and log $\beta_2 = 3.7 \pm 0.2$ (graphical estimation of errors). However, due to analytical errors in the stock solutions a correction $\Delta Z = (Z_{calc} - Z)$ had to be applied to the data. This correction has been carried out in Fig. 1. ΔZ equalled -0.002, -0.006, -0.002, and -0.010 for the solutions $I - IV$, respectively. This corresponds to a mean error in the ratio K/Nb of 0.3 %. On the other hand if $N = 5$ agreement between Z_{calc} and Z seems impossible unless $\Delta Z = 0.030$ (see Fig. 1). In the stock solutions, $\Delta Z = 0.030$ corresponds to an error in the ratio K/Nb equal to 2.5 % (approx.). Such a large systematic error is very unlikely.

From β_1, β_2, and pK_w (= 14.16) the acidity constants for the reactions are obtained in the usual way

(1) $H_2Nb_6O_{19}{}^{6-} \rightleftharpoons HNb_6O_{19}{}^{7-} + H^+$,
 p$K_1 = 10.88 \pm 0.05$

(2) $HNb_6O_{19}{}^{7-} \rightleftharpoons Nb_6O_{19}{}^{8-} + H^+$,
 p$K_2 = 13.8 \pm 0.2$

The formulas of the species are thus partly in agreement with the findings of Jander and Ertel.[1] However, the irreversibility in the most alkaline solutions and the precipitates observed must be subjected to further investigation.

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On the Occurrence of Free Selenium-Containing Amino Acids in Onion (Allium cepa)

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The incorporation of selenium — mostly as ^{75}Se — into living systems has been investigated to some extent. McConnell and Roth,[1] for instance, have shown that after administration of ^{75}Se it was present in all the rat liver fractions studied. The uptake of Se was greatest in the soluble fraction, followed by the mitochondria, the microsomes and the nuclei. Tuve and Williams[2] have identified selenomethionine and selenocystine in a hydrolysate of the proteins of *E. coli* grown in a sulfur-deficient medium containing radioactive selenite. Cowie and Cohen[3] found that selenomethionine could completely replace methionine for the normal growth of a methionine-requiring mutant of *E. coli.* Selenocystine but no selenoglutathione could be found in the hydrolysate. McConnell and Cooper[4] found that selenium was present in the albumin, globulin, euglobulin, and pseudoglobulin fractions and also in crystalline hemoglobin and in hemin and globin after subcutaneous injections of sodium selenate.

However, the part that selenium plays in metabolic reactions remains obscure. It seems to be a necessary element at least for cattle, where deficiency can cause heart-muscle degeneration.[5] The fact that selenium can substitute for vitamin E in preventing some, but not all, of the symptoms in vitamin E deficiency has led