On the Hydrolysis of Niobium(v) and Tantalum(v) in 3 mol dm⁻³ KCl at 25 °C. Part 1. Construction of a Thermodynamic Model for Nbⱽ

Nestor Etxebarria, Luis A. Fernández and Juan M. Madariaga
Kimika Analitikoaren Saila, Zientzi Fakultatea, Euskal Herriko Unibertsitatea (UPV/EHU),
P.K. 644 Bilbao 48080, Spain

The hydrolysis of Nbⱽ in 3.0 mol dm⁻³ KCl has been studied by potentiometric measurement of the H_3O^+ ion concentration with a glass electrode. The results have been treated both graphically and numerically, and show that the hydrolysis process can be considered to be homonuclear. A comparison has been made with other data in the literature and a hydrolysis model for Nbⱽ proposed using the modified Bromley theory.

The hydrolysis of Nbⱽ and Taⱽ has been disregarded in most metal hydrolysis reviews owing to the scarce and sometimes controversial information about the nature of species found in solution. Moreover, most of the information on hydrolysis equilibria is quite old while the majority of the present studies are related to applications in metal alloys[1] and to the development of separation methods.[2,3] The geochemistry and mineralogy of Nb and Ta have been particularly well studied[4] owing to their economic and industrial importance. However, the study of the hydrolysis of these metals has never been easy because of the difficulties in preparing pure and stable solutions.[5]

In general, niobium and tantalum show almost identical solution and solid-phase behaviour and their ionic radii are also almost the same. Related to their tendency to hydrolyse, the polymerization of these metals leads to the gradual formation of colloidal solutions.[5] Excluding complexation with different inorganic or organic ligands their hydrolytic behaviour varies with acidity of the solution, and may be divided into reactions occurring under very acidic conditions, during the formation of a solid phase, and those occurring in alkaline solutions.

The formation of the solid oxides is the most important hydrolysis process. According to Babko *et al.*[6] niobium oxide (Nb_2O_5) is stable in the range pH 0–7, and dissolves to form only mononuclear species. However, according to Fairbrother,[7] Nb_2O_5 and Ta_2O_5 do not show a stoichiometric solubility owing to the formation of colloidal species and to the variation in the solid-phase composition and/or structure. The amphoteric behaviour of Nb_2O_5 together with the higher solubility of potassium compared to sodium salts[7] makes this possible; fusion of the oxides with potassium carbonate or potassium hydroxide followed by leaching of the cooled melt with water leads to a niobate solution. Although the structure of the dissolved salts is controversial, a general stoichiometry $xK_2O \cdot yM_2O_5$ (M = Nb or Ta) with different $x:y$ ratios has been proposed,[1] and hexaniobates ($[Nb_6O_{19}]^{8-}$) were frequently obtained.

The first experimental studies on the hydrolysis of Nbⱽ were performed by Jander and Ertel.[8–11] Three kinds of reactions were observed although the formation quotients were not accurately defined: the formation of the hexaniobate $[Nb_6O_{19}]^{8-}$ from $[NbO_4]^{3-}$, the hydrolysis of the hexaniobate and the formation of the solid oxide. Subsequently, two protonation reactions of the most basic hexaniobate $[Nb_6O_{19}]^{8-}$ were proposed by Neumann[12] and their formation constants were determined in 3 mol dm⁻³ at 25 °C. This system was also studied potentiometrically by Spinner,[13] in the same KCl media but at different ionic strengths and three

protonation steps were proposed, together with formation constants determined, and spectrophotometrically in 1 mol dm⁻³ KCl by Goiffon *et al.*,[14] and as a result of this work, the three steps proposed by Jander and Ertel were also defined. Goiffon *et al.*[14] proposed that at pH < 13.97 protonation of hexaniobate occurred with the formation of species with stoichiometry $[H_xNb_6O_{19}]^{(x-8)}$ (x = 0–3), that at pH 13.97–14.47 there was an equilibrium between the hexaniobate and tetraniobate $[H_4Nb_4O_{16}]^{8-}$ and finally, at pH > 14.47 an equilibrium existed between $[Nb_4O_{16}]^{12-}$ and $[NbO_4]^{3-}$. Some time later Goiffon and Spinner[15] confirmed these species, and also proposed the formation of dodecaniobates according to Raman spectroscopy.

It is certainly difficult to establish a suitable model for the hydrolysis of this metal. Thus, we have conducted a potentiometric study to define the number of stoichiometries of the hydrolysed species of Nbⱽ as well as to calculate their formation constants in 3 mol dm⁻³ KCl.
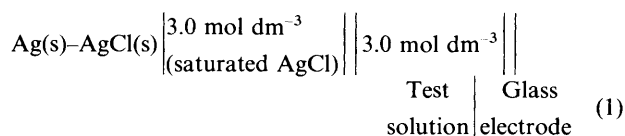
Experimental

Reagents and Solutions.—For preparing stock solutions of Nbⱽ, solid Nb_2O_5 (Merck p.a.) was fused with KOH (Merck p.a.) in a zirconium crucible. The maximum yield (>95%) was obtained using a 7:1 ratio of KOH:Nb_2O_5. Following fusion, the mixtures were cooled, dissolved in water (MilliQ), filtered with a cellulose nitrate filter (Sartorius, 13107-ACN) and kept in a polyethylene flask under a nitrogen atmosphere.

The metallic solutions were standardized by a gravimetric method based on precipitation with 8-hydroxyquinoline.[16] A suitable aliquot of the solution was diluted to 100 cm³. An excess of 8-hydroxyquinoline (3%, w/v) solution was added and *ca.* 0.1 mol dm⁻³ HNO_3 was added dropwise until the pH of the solution was *ca.* 6. After 30 min the yellow precipitate formed was filtered off with a Sartorius 13107-ACN filter and washed with hot water. Finally, it was ignited in a furnace at 900 °C and was weighed as Nb_2O_5. Each determination was repeated five times and the standard deviation of the mean value was <0.1%.

Other reagents used were KCl (Merck p.a.), HCl (Fluka p.a.) and NH_4Cl (Merck p.a.). The concentration of the ionic medium was checked gravimetrically after evaporating aliquots of the stock solutions, while the acid solutions were standardized volumetrically with tris(hydroxymethyl)aminomethane using both colorimetric indication (methyl red) and potentiometric detection (Gran's method).[17] The ammonium chloride solutions were standardized by back titration using hydrochloric acid.[18]

Potentiometric Experiments.—A series of potentiometric titrations were carried out automatically at 25.0 ± 0.1 °C conducted by a system developed in this laboratory.[19] The glass electrode was standardized (to determine $E°$, the standard potential) coulometrically before each titration. Owing to the irreversible hydrolysis which occurs under strongly acidic conditions[12] most titrations were divided into two steps. In the first step the pH was lowered from the initial value (≈ 13) to ≈ 10.5 using NH_4Cl as titrant, the acidity gradient being such as not to precipitate the oxide. The NH_3 formed was removed by bubbling N_2 through the solution for 90 min. The second step of the titrations was performed coulometrically in order to control the rate of increase in acidity. On average, the whole titration at any total metal concentration used lasted around 7 d.

The potentiometric system comprised a glass electrode (Metrohm 6.0101.100) and a double-junction reference electrode [Ag–AgCl(s) Metrohm 6.0726.100] which were placed in the titration vessel and immersed in a thermostatted oil-bath. The electrodes were connected to a preamplifier in order to boost the electric signal to the voltmeter. Electromotive force measurements were carried out with Hewlett-Packard HP3421A or HP-E1326B voltmeters. The volumetric additions were performed with a Metrohm Dosimat 665 burette while the coulometric additions were carried out with an Advantest TR6142 programmable power supply; in the latter case a platinum net was immersed in the solution and connected to a mercury counter electrode through a Wilhelm bridge. The potentiometric measurements were performed with the cell shown in equation (1) which gave a good performance at high pH values.

$$\text{Ag(s)–AgCl(s)} \left| \begin{array}{c} 3.0 \text{ mol dm}^{-3} \\ \text{(saturated AgCl)} \end{array} \right| \left| \begin{array}{c} 3.0 \text{ mol dm}^{-3} \\ \hline \begin{array}{c|c} \text{Test} & \text{Glass} \\ \text{solution} & \text{electrode} \end{array} \end{array} \right| \quad (1)$$

Determination of h.—The free concentration of hydrogen ions (h) was calculated using the Nernst equation where the measured potential can be expressed in (2), j_{bas} is the alkaline

$$E = E° + 59.16 \log h + j_{bas}K_w \quad (2)$$

liquid-junction coefficient and K_w ($= [H_3O^+][OH^-]$) is the stochiometric autoprotolysis constant of water, determined previously by means of coulometric $E°$ titrations as $-\log K_w = 14.12 \pm 0.01$ and $j_{bas} = 22 \pm 1$ mV dm³ mol⁻¹.

Results

In order to determine the proton transfer and polymerization equilibria the number of protons involved must be calculated. Therefore, a graphical treatment has been carried out using the function Z applied to reaction (3), where A is the monometallic

$$pA + iH^+ \rightleftharpoons H_iA_p \quad (3)$$

species and H_iA_p represents the different polyoxoniobates formed. The function Z is defined as the average number of protons bound to the metal ion,[20] equation (4). If the nuclearity

$$Z = \frac{[H^+]_{tot} - h + K_w h^{-1}}{p[A]_{tot}} = \frac{\sum\limits_{p=1}\sum\limits_{i=0} i\beta_{pi}[A]^p[H^+]^i}{\sum\limits_{p=0}\sum\limits_{i=0} p\beta_{pi}[A]^p[H^+]^i} \quad (4)$$

of the central ion does not change in the species formed ($p = 6$) then the Z function will be 'homonuclear'[20] in nature and its values will follow the series $0 \longrightarrow 1 \longrightarrow 2 \longrightarrow i$. The

results obtained show that the Z values only follow this series when $p = 6$ and are independent of the total concentration of Nb^V, so it was concluded that hexaniobates are formed. Meaningless results were obtained for other values of p.

Similar results have been obtained by other groups,[12,13] so the hexameric species $[Nb_6O_{19}]^{8-}$ was assumed to be formed. Thus, the corresponding overall formation constants are given by equation (5), where $B = [Nb_6O_{19}]^{8-}$.

$$\beta_i = [H_iB]/([H^+]^i[B]) \quad (5)$$

The experimental Z values for Nb^V ranged between 0.7 and 2 in the pH range 9.7–13.1, as shown in Fig. 1. At higher pH values the Nernst equation (2) is not followed while at pH < 9.7 the slight formation of a solid was observed. The four sets of data coincided within the limits of the experimental errors. Thus, assuming $p = 6$, the shape of the Z functions indicates the presence of at least two protonation steps in the experimental pH range studied.

In order to give a suitable model and to obtain an initial estimation of the formation constants, the classical Z treatment[20] was applied to one normalized variable X and two variable parameters p and q for three protolytic steps. In this case the theoretical Z functions[20] can be written as in equation (6). The comparison of the experimental Z ($-\log h$) values with

$$Z = \frac{\beta_1 h + 2\beta_2 h^2 + 3\beta_3 h^3}{1 + \beta_1 h + \beta_2 h^2 + \beta_3 h^3} = \frac{pX + 2qX^2 + 3X^3}{1 + pX + qX^2 + X^3} \quad (6)$$

the theoretical Z ($-\log X$) curves for different values of p and q yields the best-fit values of the formation constants.

Fig. 1 shows the experimental Z values in the position of the best fit, together with a theoretical Z function for a triple protonation step (solid line) which shows a better fit to the experimental data than a double protonation step (not shown).

The values of the three protonation constants calculated graphically were refined numerically by means of the NYTIT[21] version of the LETAGROP program[22] which minimizes the sum of the square of the absolute error of the measured potential. The values of the protonation constants obtained by graphical and numerical methods are in good agreement. Other chemical models were also tried in the numerical calculations but none of them improved the fit.

The results of the numerical calculations as well as the goodness of fit are listed in Table 1 together with literature data under the same conditions. The values calculated in this work were used to construct the theoretical Z function plotted in Fig. 1.

Discussion

At first glance it would appear that there is some disagreement between the values obtained here and those reported previously.
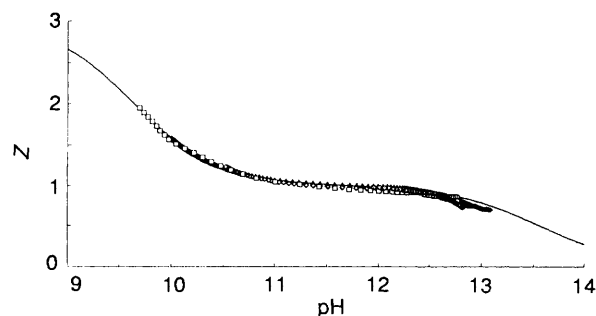
Fig. 1 Experimental Z values plotted as a function of pH for varying total concentrations of Nb^V: $c_{Nb} = 2.49 \times 10^{-2}$ ($\triangle$), 2.49×10^{-3} ($\diamond$), 4.87×10^{-3} ($\square$) and 9.14×10^{-3} mol dm⁻³ ($\bigcirc$). The continuous line represents the theoretical function calculated for the three protonation step model

**Table 1** Protonation constants of the hydrolysis products of Nb^V in 3.0 mol dm^{-3} KCl

Reaction	log β_i		
$[Nb_6O_{19}]^{8-} + H^+ \rightleftharpoons$ $[HNb_6O_{19}]^{7-}$	13.8 ± 0.2^a	12.60^b	13.63 ± 0.04^c
$[Nb_6O_{19}]^{8-} + 2H^+ \rightleftharpoons$ $[H_2Nb_6O_{19}]^{6-}$	24.68 ± 0.05	23.46	23.55 ± 0.04
$[Nb_6O_{19}]^{8-} + 3H^+ \rightleftharpoons$ $[H_3Nb_6O_{19}]^{5-}$	—	32.85	32.90 ± 0.07

^{a} Ref. 12. ^{b} Ref. 13. ^{c} This work. Values were calculated by the NYTIT version of LETAGROP program minimizing the sum of the squares of the absolute error of the measured potential. 247 Measurements with a standard deviation of 1.45 mV, Hamilton R factor $= 0.006\,77$.

Table 2 Protonation constants of Nb^V at 25 °C in KCl at different ionic strengths *

Protonation constant	Ionic strength/mol dm^{-3}					
	0.0	0.1	0.5	1.0	2.0	3.0
log β_1	11.90	11.98	12.17	12.30	12.44	12.60
log β_2	22.90	22.99	23.14	23.24	23.35	23.46
log β_3	32.90	32.93	32.95	32.95	32.89	32.85

* All values taken from ref. 13.
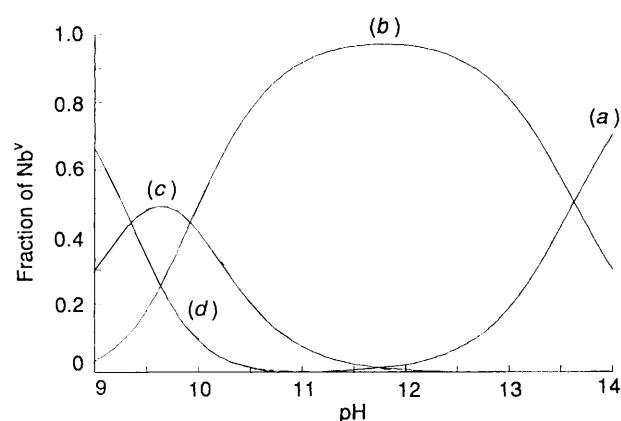
Fig. 2 Distribution diagram for Nb^V in 3.0 mol dm^{-3} KCl, $[Nb_6O_{19}^{8-}]_{total} = 1.00$ mmol dm^{-3}. Species: (a) $[Nb_6O_{19}]^{8-}$, (b) $[HNb_6O_{19}]^{7-}$, (c) $[H_2Nb_6O_{19}]^{6-}$ and (d) $[H_3Nb_6O_{19}]^{5-}$

In particular there is some discrepancy between the first protonation constant of Nb^V obtained by us and by Spinner.[13] The other values are within the experimental error. The value of the first protonation constant is closer to that calculated by Neumann[12] although only two equilibria were proposed. This can, however, be explained by the fact that formation constants were only obtained at pH > 10, and the third protonation occurs at lower pH values. Using the values obtained in this work (see Table 1) a distribution diagram for Nb^V has been plotted in Fig. 2. It should be noted that the solutions are free of the solid phase only over a very narrow pH range.

In order to obtain further information and to complete the hydrolysis scheme of niobium(V) the protonation constants obtained in this work together with those obtained previously[13] (see Table 2), were treated by a modification of Bromley's theory[23,24] using molar concentrations. In this way the values of the thermodynamic protonation constants (log °β_i) as well as the interaction parameters between the protonated species and anions in the ionic media may be calculated. This calculation is directly performed using molar concentrations. Taking into account equation (6), the general expression (7) can be used to

$$\log \beta_i = \log °\beta_i - \log \gamma_{H,B} + i\log \gamma_{H^-} + \log \gamma_B \quad (7)$$

correlate the experimental data in this chemical system. The individual activity coefficients γ_i of the charged species can be substituted by Bromley's equation (8), where $A = 0.5109$ dm$^{\frac{3}{2}}$

$$\log \gamma_M = -\frac{Az_M^2 I^{\frac{1}{2}}}{1 + I^{\frac{1}{2}}} + \sum_x \mathring{B}_{MX}(|z_M| + |z_X|)^2 c_X/4 \quad (8)$$

mol$^{-\frac{1}{2}}$, I is the ionic strength in mol dm^{-3}, z_M is the ionic charge of the cation M, z_X is the charge of the anion X with an opposite sign to M and c_X is its molarity. The parameter $\mathring{B}_{MX}$ can be expressed as in equation (9), where B_{MX} represents the interaction parameter of the ion pair MX.

$$\mathring{B}_{MX} = \frac{(0.06 + 0.6B_{MX})|z_M z_X|}{[1 + (1.5I/|z_M z_X|)]^2} + B_{MX} \quad (9)$$

The main feature of the modified Bromley theory is that it can be applied to molar instead of molal concentrations, which were required in the original theory. In order to convert the interaction parameters to the molar scale, they were recalculated from the γ_t and c_{MX} data.[25]

By rearranging equation (7) and incorporating (8) and (9) the protonation constants at different ionic strengths, can be correlated [equation (10)] where $D = AI^{\frac{1}{2}}/(1 + I^{\frac{1}{2}})$ and F is the

$$\log {}^I\beta_i = \log °\beta_i - (i^2 - 17i)D + iF_{H^+,Cl^-} +$$
$$F_{Nb_6O_{19}^{8-},K^+} - F_{H_iNb_6O_{19}^{i-8},K^+} \quad (10)$$

term expressed in equation (9), $\mathring{B}_{MX}$, for each ionic species. If these equations are applied to the three protonation reactions three similar equations can be written and the thermodynamic protonation constant of each reaction (log °β_i) and the interaction parameters $(B_{Nb_6O_{19}^{8-},K^-}$, $B_{HNb_6O_{19}^{7-},K^+}$, $B_{H_2Nb_6O_{19}^{6-},K^+}$ and $B_{H_3Nb_6O_{19}^{5-},K^+})$ can then be calculated.

The values collected in Table 2 deserve some comment. First the values proposed at 0.1 mol dm^{-3} are not reliable because the ionic strength is not strictly constant; these values were therefore ignored in the following calculations. Secondly, the constants of infinite dilution were calculated by graphical extrapolation[13] and were thus not included in our calculations. Finally, as mentioned before, the first protonation constant calculated in this work was significantly different to that found by Spinner and co-workers, and therefore instead of using all the log β_1 values it was considered better not to use any of them and to estimate the parameters by other means.

The results of the application of the modified Bromley theory are listed in Tables 3 and 4 together with estimates of the first thermodynamic protonation constant and the interaction parameter that was not calculated with the rest of the values. A comparison of the experimental protonation constants and those calculated by the modified Bromley theory is also shown in Fig. 3.

The thermodynamic constants and the interaction parameters were estimated as follows: if the relationship between the interaction parameter and the charge: ionic radius ratio[25,26] of Nb^V is taken into account, the interaction parameter of $[HNb_6O_{19}]^{7-}$ and K^+ can be obtained from $B_{Nb_6O_{19}^{8-},K^+}$, $B_{H_2Nb_6O_{19}^{6-},K^+}$ and $B_{H_3Nb_6O_{19}^{5-},K^+}$. Using this value, it is then possible to calculate the thermodynamic protonation constant (°β_1) of the first equilibrium from the respective stoichiometric protonation constant obtained in this work.

Finally, the formation of the solid oxide should also be considered although this is the most controversial part of the model. The solubility data reported by Babko et al.[6] (see Table 5) were used; however in their study the ionic medium was 1 mol

**Table 3** Thermodynamic protonation constants for hydrolysis of Nb^V

Reaction	log $^0\beta_i$
$[Nb_6O_{19}]^{8-} + H^+ \rightleftharpoons [HNb_6O_{19}]^{7-}$	$(16.11 \pm 0.14)*$
$[Nb_6O_{19}]^{8-} + 2H^+ \rightleftharpoons [H_2Nb_6O_{19}]^{6-}$	27.97 ± 0.13
$[Nb_6O_{19}]^{8-} + 3H^+ \rightleftharpoons [H_3Nb_6O_{19}]^{5-}$	39.91 ± 0.18

* Calculated from the estimated interaction parameter of the first protonated species and formation constants obtained in this work.

Table 4 Interaction parameters for hydrolysed niobium(v) species H$_i$B and K$^+$

| H$_i$B	B_{H_iB,K^+}
$[Nb_6O_{19}]^{8-}$	-0.027 ± 0.085
$[HNb_6O_{19}]^{7-}$	$(-0.024 + 0.003)*$
$[H_2Nb_6O_{19}]^{6-}$	-0.019 ± 0.002
$[H_3Nb_6O_{19}]^{5-}$	-0.006 ± 0.004

* Estimated from the relationship between the interaction parameters and the ratio for ionic charge:ionic radius of the rest of the couples in this system. See text for further details.
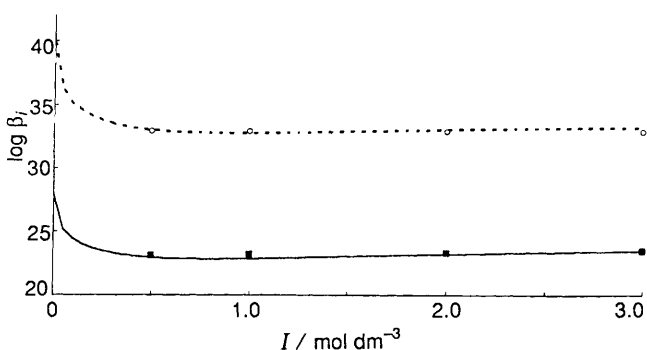
Fig. 3 Comparison between the experimental values ($\bigcirc$, log β_3; $\blacksquare$, log β_2) of the protonation constants in KCl medium at different ionic strength and the theoretical values (-----, log $^i\beta_3$; ——, log $^i\beta_2$) calculated by Bromley's equation

Table 5 Solubility data* for niobium oxide (s) and Nb(OH)$_5$ (s_o)

pH	$10^5 s$/mol dm^{-3}	$10^5 s_o$/mol dm^{-3}
6.50	1.4	1.4
7.00	1.4	1.4
7.67	9.7	1.4
7.82	16.4	1.4

* All values from ref. 6.

Table 6 Protonation constants for the hydrolysis reactions of Nb^V in 1.0 mol dm^{-3} KNO$_3$

Reaction	log β_i
$6Nb(OH)_5 - 5H^+ \rightleftharpoons [H_3Nb_6O_{19}]^{5-} + 11H_2O$	-14.46
$6Nb(OH)_5 - 6H^+ \rightleftharpoons [H_2Nb_6O_{19}]^{6-} + 11H_2O$	-24.06
$6Nb(OH)_5 - 7H^+ \rightleftharpoons [HNb_6O_{19}]^{7-} + 11H_2O$	-33.49
$6Nb(OH)_5 - 8H^+ \rightleftharpoons [Nb_6O_{19}]^{8-} + 11H_2O$	-47.04
$2Nb(OH)_5 \rightleftharpoons Nb_2O_5(s) + 5H_2O$	9.71
$H_2O - H^+ \rightleftharpoons OH^-$	-13.71

Fig. 4 Distribution diagram for Nb^V in 1.0 mol dm^{-3} KNO$_3$; $[Nb(OH)_5]_{total} = 0.10$ mmol dm^{-3}. Species: (a) Nb$_2$O$_5$(s), (b) Nb(OH)$_5$, (c) $[H_3Nb_6O_{19}]^{5-}$, (d) $[H_2Nb_6O_{19}]^{6-}$, (e) $[HNb_6O_{19}]^{7-}$ and (f) $[Nb_6O_{19}]^{8-}$

dm^{-3} KNO$_3$ so the values of the protonation constants in Table 3 had to be recalculated accordingly. These calculations only involve the interaction coefficients of H$^+$ with Cl$^-$ and NO$_3^-$ and the values were:[24] $B_{NO_3^-,K^+} = 0.1027 \pm 0.0008$ and $B_{Cl^-,H^+} = 0.1648 \pm 0.00$ 12.

Attempts were made to rationalize the solubility data reported by Babko et al.[6] using a combination of the protonated species previously defined. The model which gave the best fit involves reaction (11) and the solubility of niobium

$$6Nb(OH)_5 \xrightarrow{K_{-5,6}} [H_3Nb_6O_{19}]^{5-} + 5H^+ + 11H_2O \quad (11)$$
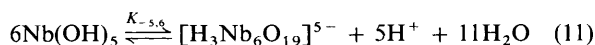
oxide can therefore be attributed to the formation of Nb(OH)$_5$ and its equilibrium with the species $[H_3Nb_6O_{19}]^{5-}$. From the reaction (11) the corresponding mass-balance equation (12) can be written. Using the data in Table 5 and equation

$$s = [Nb(OH)_5] + 6K_{-5,6}[Nb(OH)_5]^6[H^+]^{-5} \quad (12)$$

(12), the value $\log K_{-5,6} \pm 3\sigma = -14.46 \pm 0.30$ can be calculated.

Also, the solubility product (K_{so}) of equilibrium (13) can be

$$Nb_2O_5(s) + 5H_2O \rightleftharpoons 2Nb(OH)_5 \quad (13)$$
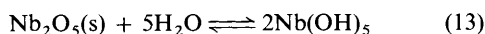
estimated to be 1.96×10^{-10} dm^9 mol^{-3} in 1.0 mol dm^{-3} KNO$_3$. The thermodynamic solubility product of reaction (13) is written as $K_{so} = \{Nb(OH)_5\}^2\{H_2O\}^{-5}$.
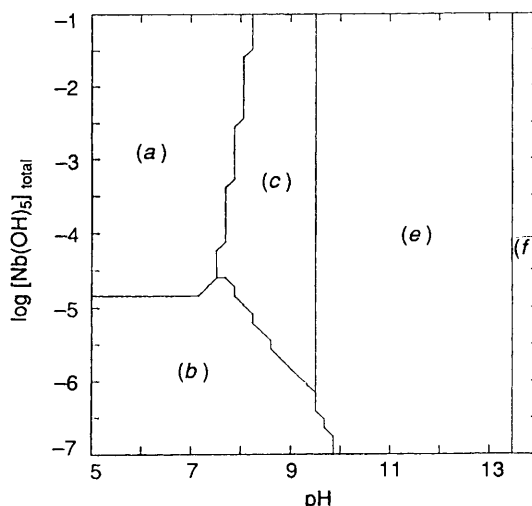

Fig. 5 Predominance diagram for Nb^V in 1.0 mol dm^{-3} KNO$_3$. Species (a)–(f) as in Fig. 4

If the values of β_1, β_2 and β_3 calculated here are expressed in terms of equilibria involving Nb(OH)$_5$ a hydrolysis model can be constructed which accounts for the behaviour from highly acidic to highly alkaline conditions as seen in Figs. 4 and 5

where the distribution and predominance diagrams have been plotted using the formation constants and reactions listed in Table 6.

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