

TARTRATE COMPLEXES OF MOLYBDENUM(VI)

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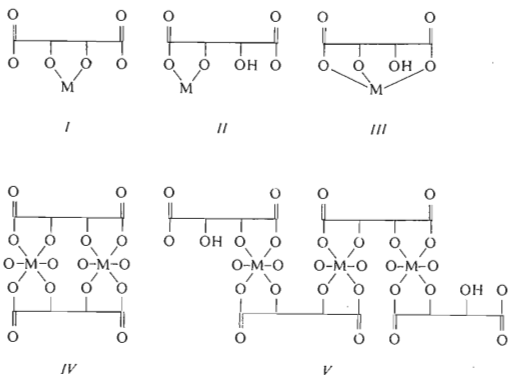
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The formation of $\text{MoO}_2(\text{TH}_{-1})_2^{4-}$ and $(\text{MoO}_2)_2(\text{TH}_{-2})_2^{4-}$ complexes was proved in roughly neutral aqueous solutions and their equilibrium constants were determined by potentiometric neutralization titrations. The possible ways of bonding of the tartrate ligand to the central Mo(VI) atom and the compositions of the Mo(VI) tartrate chelates are discussed.

In aqueous solutions of tartaric acid (H_2T), both of the two carboxy groups dissociate, $\text{p}K_{a1}$ 2.9, $\text{p}K_{a2}$ 4.0 (I 0.1, $t = 21^\circ\text{C}$; ref.¹). The protons of the alcohol groups split off in concentrated alkali hydroxide solutions or during complex formation. Anions of the type HTH_1^{2-} can occur as ligands in complex compounds¹ (the symbol is used to denote tartaric acid from which two hydrogen atoms have split off, one from a carboxy group and one from an alcohol group). The central atom is bonded to the tartrate ligand² either *via* the two oxygen atoms of the alcohol groups (*I*) or *via* the oxygen atoms of the neighbouring carboxy and alcohol groups (*II*); in view of the analogy of tartaric and aspartic acids, bonding *via* the two carboxy and an alcohol functional groups (*III*) is also conceivable. If a central atom is capable of formation of tartrate complexes of both *I* and *II* types, then the latter appear in more acidic solutions than the former². In type *II* complexes only "a half" of the tartrate ligand is exploited, so that another central atom can bond to the other half; in this manner polynuclear complexes involving a tartrate bridge are formed³.

The MoO_4^{2-} or $\text{MoO}_2(\text{OH})_4^{2-}$ molybdate anions are mononuclear in dilute aqueous solutions at $\text{pH} \geq 6$. Formation of oligomolybdates⁴ in weakly acidic solutions is associated with a consumption of hydrogen ions; the oligonuclear species decompose⁵ on additional acidification in solutions at $\text{pH} < 3.5$. The formation of oligonuclear Mo(VI) compounds can be prevented⁵ by chelating agents. Electroneutral molecules of molybdic acid predominate⁶ in solutions, at $\text{pH} \approx 2$, Mo(VI) cations have been detected^{6,7} in solutions at $\text{pH} < 2$. The Mo(VI)-tartaric acid system has been extensively studied, *e.g.* in the works⁸⁻¹⁵, by employing diverse physico-chemical methods, but the published data on the complex composition and stability are not clearcut and also are not quite mutually consistent.



The present work is a continuation of the study of Mikanová¹⁶, who investigated potentiometrically the formation of Mo(VI) chelates with hydroxyacetate, malate, and tartrate, respectively, in solutions at pH 6–7. For all of these aliphatic α -hydroxyacids, she established the occurrence of complexes of the type *II*, the M : L ratio being invariably 1 : 2. She has given evidence that two mol of hydrogen ions are taken up in the chelation of one mol of molybdate¹⁰, and suggests that the interaction of molybdate with tartrate can be represented by the equation:



EXPERIMENTAL

The chemicals used were of reagent grade purity (Lachema, Brno). Sodium molybdate was recrystallized from hot water, the concentration of its solutions was checked by acidimetric titration in sorbitol medium¹⁷. No specification was given by the manufacturer of the commercial tartaric acid and sodium potassium tartrate preparations, but the optical activity measurements indicate that D-tartaric acid was involved which is in accordance with the fermentation manufacturing procedure.

For the cryoscopic measurements, a test tube containing about 5 ml of solutions was cooled with a mixture of ice and sodium chloride, the temperature was read by means of a Beckmann thermometer graduated to 0.01°C divisions.

Titrations with 0.1M-HNO₃ were performed at 20 ± 1°C on ABU-12, PHM-26, TTT-11, and SBR instruments for automatic titration (Radiometer, Copenhagen). The electrode response of the glass electrode used in conjunction with a saturated calomel electrode was checked by titration of a strong acid (HNO₃) with a strong base (NaOH). The pH-meter was adjusted prior to each titration by using a phosphate buffer of pH 6.50 ± 0.02 (Radiometer).

The \bar{z} function is used to indicate the average number of mol of hydrogen ions bonded to a mol of molybdate ion MoO_4^{2-} . The equilibrium constant calculation proceeded from the activity of hydrogen ions and concentrations of the remaining components involved. The obtained values are presented as $\log \bar{K} \pm s(\log K)$, where \bar{K} is the mean value and $s(\log K) = [\log(\bar{K} + s) - \log(\bar{K} - s)]/2$, where s is the standard deviation of the mean.

The POT-LETAG program used¹⁸ employs a minimization procedure to seek for the "optimum" constants for the input equilibria. The U quantity is the sum of squares of the differences between the observed \bar{z} values and those calculated for the chosen constants of the equilibria considered; the minimum U value is indicative of the "optimum" constants, which are regarded as correct. The program also affords the S quantity characterizing the standard deviation calculated from the differences between the observed and calculated \bar{z} values. The calculations using the POT-LETAG program were carried out on an EC1033 computer at the Computer Centre, Purkyně University, Brno.

Electrophoresis experiments were performed on Niederschlag 29 F 11 paper (GDR) cut to 23.5×8 cm stripes, using the arrangement devised by Jokl¹⁹. The electrophoresis proceeded for 45 min, the applied voltage gradient was 10 V/cm, the metal plate was thermostatted to $20.0 \pm 0.1^\circ\text{C}$ with flowing-through water. Hydrogen peroxide served as the electroosmosis indicator, bromate ion, as the mobility standard. The reported¹⁹ values of the relative mobility represent the ratios of the observed mobilities of Mo(VI) or W(VI) compounds to the standard. The electrophoresis was conducted in tartrate, acetate, pyridine, and ammoniacal buffer solutions. The ionic strength was adjusted to 1.07 by adding potassium nitrate; except for acidic solutions, in which an insoluble precipitate of KHT formed. The chromatographic treatment of the systems used in the electrophoresis gave evidence that the sorption of the Mo(VI) or W(VI) compounds by the paper was negligible, the R_F values found were 0.9–1.0. Approximately 1 μl of solution prepared by mixing equal volumes of 0.05M- Na_2MoO_4 and tartrate-containing buffer solutions was applied to the start by means of a micropipette; spraying of a saturated solution of chloranilic acid in a 2 : 1 mixture of ethanol with concentrated hydrochloric acid served for the detection²⁰.

RESULTS

Potentiometric Titrations

Two series of solutions containing sodium potassium tartrate and disodium molybdate were titrated with the acid titrant solution. In the first series, the tartrate was present in a high excess and the ionic strength was adjusted to 1.04 with potassium nitrate; the composition of the solutions is given in Table I (No 1–6). The acid consumption in the titrations of solutions containing the two components was observed at higher pH values as compared with titrations of solutions in which only one of the components was present. This implies that protons are taken up for complex formation. Assuming the occurrence of reaction (A), the \bar{z} value is given by the relation

$$\bar{z} = 2[\text{MoO}_2(\text{TH}_{-1})_2] / \{[\text{MoO}_2(\text{OH})_4] + [\text{MoO}_2(\text{TH}_{-1})_2]\} \quad (1)$$

and the constant of the reaction can be calculated from the equation

$$K_A = \bar{z}/2(1 - \bar{z}/2)(c_T - \bar{z}c_M)^2 [\text{H}]^2 \quad (2)$$

(the ion charges are omitted for simplicity). As Table I (No 1–6) demonstrates, the K_A values calculated from a total of 41 experimental points for various concentration of the reacting components differ only very slightly, thus warranting the assumption that only reaction (A) takes place in the solutions under study.

Approximately equimolar solutions of molybdate and tartrate were treated likewise (Table I, No 7, 8). The results indicate that at the beginning of the complex formation, at $\text{pH} \sim 7$, when free tartrate is still present in a rather high concentration, equilibrium (A) predominates, but the assumption of the reaction (A) solely cannot account for the experimental data in the region $\text{pH} 6.5\text{--}6.0$, where oligomolybdates do not yet form in solutions in which molybdate is present in the c_M concentration used and from which tartrate is absent.

Based on reaction (A), use can be made of the titrations for a determination of Na_2MoO_4 as a dihydric "complex base" in solutions containing excess tartrate. However, since the consumption of the acid for this reaction is closely followed by its consumption for the protonation of the tartrate T^{2-} anion, no pH jump appears in the equivalence point. The titration end point was therefore sought by applying Gran's type linear graphical transformation^{21,17}. Denoting the volume of the added acid solution v and that corresponding to the equivalence point v_e , the equilibrium constant can be expressed as

$$K_A = v/(v_e - v)(c_T - 2c_M v/v_e)^2 [\text{H}]^2, \quad (3)$$

with the limit

$$\lim_{v \rightarrow v_e} v[\text{H}]^{-2} (c_T - 2c_M v/v_e)^{-2} = 0. \quad (4)$$

TABLE I

Results of the potentiometric study of the complexes for $c_T \geq c_M$; $I 0.4$, $t = 20 \pm 1^\circ\text{C}$

| No | c_M mmol l^{-1} | c_T mmol l^{-1} | pH | \bar{z} | n^a | $\log K_A$ |
|----|-------------------------------|-------------------------------|---------------|-----------|-------|------------------|
| 1 | 16 | 120 | 7.8–6.7 | 0.1–1.7 | 7 | 16.40 ± 0.01 |
| 2 | 10 | 120 | 7.3–6.7 | 0.9–1.8 | 4 | 16.47 ± 0.02 |
| 3 | 16 | 80 | 7.5–6.3 | 0.1–1.8 | 7 | 16.53 ± 0.02 |
| 4 | 10 | 80 | 7.7 \pm 6.3 | 0.1–1.9 | 8 | 16.43 ± 0.02 |
| 5 | 16 | 40 | 7.7 \pm 6.6 | 0.1–1.0 | 7 | 16.52 ± 0.02 |
| 6 | 10 | 40 | 7.6 \pm 6.1 | 0.1–1.8 | 8 | 16.52 ± 0.01 |
| 7 | 16 | 16 | 7.1–6.6 | 0.1–0.3 | 4 | 16.69 ± 0.02 |
| 8 | 10 | 16 | 7.1–6.3 | 0.1–0.7 | 5 | 16.48 ± 0.02 |

^a Number of experimental points.

Providing that the free tartrate concentration does not change considerably during the titration, the end point can be determined by the simple graphical transformation

$$v \cdot 10^{2\text{pH} + \text{const}} = f(v) \quad (5)$$

If, however, the condition of a constant tartrate concentration is not met, Gran's function (5) is nonlinear (Fig. 1, curve 1), and a linear Gran's transformation is only obtained by introducing the appropriate correction for the variation in the tartrate concentration brought about by the dilution of the solution titrated and by the complex formation,

$$v \cdot 10^{2\text{pH} + \text{const}}(V + v)^2 (c'_T - 2c'_M v/v_e)^{-2} = f(v) \quad (6)$$

(Fig. 1, curve 2). Here V is the volume of the titrated solution and c'_T and c'_M are the concentrations of the two components, all at the beginning of the titration. The v_e value requisite for the calculation of the corrected Gran's function (6) is estimated graphically by using the simple Gran's function (5) (Fig. 1, curve 1). For a sufficient excess of tartrate ($c'_T - 2c'_M \geq 0.02 \text{ mol l}^{-1}$) the inaccuracy in the estimate does not affect the linearity of the function (6). The linear Gran's function (6) (Fig. 1, curve 2) served also as a test for verifying that the assumption of a single reaction (A) occurring in the solution was correct.

In the second series of the solutions titrated, molybdate was present in excess and their ionic strength was $I \ 0.2$ (KNO_3); a survey is given in Table II. Here, too, the consumption of acid in titrations of solutions containing both of the components

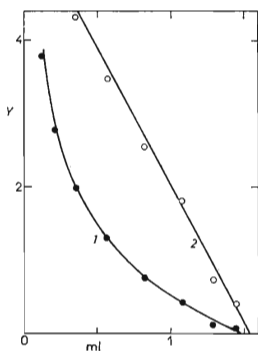
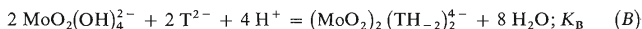
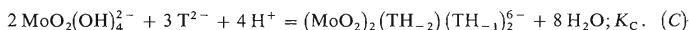


FIG. 1
Gran's transformations for the titration of 5 ml of 0.016M- Na_2MoO_4 and 0.080M- NaKT with 0.1M- HNO_3 . 1 Eq. (5), 2 Eq. (6)

was observed at higher pH than in titrations of solutions containing only one of them in the same concentration. The titrations were evaluated only in that pH region in which the formation of oligomolybdates in solutions with the same molybdate concentrations and free of tartrate was negligible. The assumption of the occurrence of reaction (A) solely was unable to account for the experimental data obtained. At $c_M > c_T$, both halves of the tartrate anion take probably part in the complex formation. In the analogous reaction of molybdate with hydroxy acetate, no $M : L = 1 : 1$ complexes have been detected. Thus, formation of chelates in which the central Mo(VI) atom is bonded to a single tartrate anion is rather unlikely. One can expect the formation either of binuclear $(MoO_2)_2 (TH_{-2})_2^{4-}$ complexes *via* the reaction



(formula IV), or of $(MoO_2)_n (TH_{-2})_{n-1} (TH_{-1})_2^{(2n+2)-}$ oligonuclear chains *via* reactions such as that for $n = 2$,



Formula V represents a chain complex with $n = 3$.

The computer-evaluated experimental data indicate that in the first stage of the titration, hence at higher pH values, small amounts of the mononuclear $MoO_2 \cdot (TH_{-1})_2^{4-}$ complex are formed in the solutions, whereas additional acidification leads to the predominant formation of the binuclear $(MoO_2)_2 (TH_{-2})_2^{4-}$ complex. In the latter stage the concentration of the species not bonded in the complexes as well as that of the mononuclear chelate decrease. No chain-type polynuclear

Table II

Results of the potentiometric study of the complexes for $c_M > c_T$; $c_M = 0.04 \text{ mol l}^{-1}$, $I 0.2$, $t = 20 \pm 1^\circ C$. $\alpha_1 = 2[MoO_2(TH_{-1})_2]/c_T$, $\alpha_2 = 2[(MoO_2)_2(TH_{-2})_2]/c_T$

| c_T mmol l ⁻¹ | pH | $\bar{z} \cdot 10^2$ | $\alpha_1 \cdot 10^2$ | $\alpha_2 \cdot 10^2$ | Parameters ^a |
|-------------------------------|---------|----------------------|-----------------------|-----------------------|------------------------------|
| 2 | 6.7–6.1 | 2–10 | 14–24 | 5–67 | $U = 0.016$ |
| 4 | 7.0–6.1 | 2–20 | 15–30 | 2–70 | $S = 0.016$ |
| 8 | 7.3–6.1 | 2–35 | 6–37 | 1–72 | $\log K_A = 16.64 \pm 0.005$ |
| 12 | 7.4–6.0 | 2–56 | 6–40 | 1–80 | $\log K_B = 30.90 \pm 0.003$ |
| 16 | 7.5–5.9 | 2–78 | 5–43 | 1–85 | $\log K_C = 30.9 \pm 1.2$ |

^a Found by the POT-LETAG program for 62 experimental points.

complexes could be detected in the systems under study; only a very low concentration, below $0.001c_T$, of the complex with $n = 2$ and zero concentrations of complexes with $n = 3, 4$, and 5 were found by the computer. The computed negligible concentrations of the chain-type complex with $n = 2$ in conjunction with the high s ($\log K_c$) value (Table II) imply that this complex virtually did not form in the solutions investigated.

Sodium molybdate (0.04 mol l^{-1}) was also titrated with the acid in the presence of glycerol in concentrations $0.08, 0.04, 0.016$, and 0 mol l^{-1} . The acid consumption for the formation of oligomolybdates at pH 6.0 – 4.7 in such solutions is unaffected by the glycerol present, hence the latter does not form complexes with Mo(VI).

Electrophoresis

The electrophoretic mobility of Mo(VI) and W(VI) was studied in tartrate solutions of concentration 0.2 mol l^{-1} . At pH 8 – 10 , constant values of the relative mobility were observed, $u_1 - 1.01$ (Mo) and -0.95 (W). As the acidity increased in the region of pH 8 – 6 , the anionic mobility decreased until at pH 6 – 4 it was constant again, $u_2 - 0.77$ (Mo) and -0.80 (W). At pH < 4 the anionic mobility dropped further with increasing acidity; for Mo(VI) the decrease did not stop at pH > 1 , for W(VI) a constant value of $u_3 - 0.40$ was attained at pH 2 – 1 . Graphical evaluation of the $u = f(\text{pH})_{c_T}$ dependence afforded the $u = (u_1 + u_2)/2$ value for pH $_{1/2} \sim 6.8$ (Mo) and 7.3 (W). Supposing that the mobility change at pH 6 – 8 was due to transformation of the non-complex MO_4^{2-} anions ($M = \text{Mo}, \text{W}$) into complexes by virtue of reaction (A), we calculated the approximate $\log K_a$ values, 15.0 (Mo) and 16.0 (W), from the known pH $_{1/2}$ and c_T values, by using the equation

$$\log K_A = 2 \text{pH}_{1/2} - 2 \log c_T. \quad (7)$$

The $u = (u_2 + u_3)/2$ value for W(VI) was attained at pH ~ 3 , which indicates that for the carboxy groups not bonded to the central atom in the complex there is $\text{p}K_a \sim 3.0$. Jokl's equation²²,

$$u/Z = aM^{-1/2} + b, \quad (8)$$

interrelates the mobility u , molecular weight M , and the ion charge Z . For the arrangement used, the values obtained were $a = 8.0$, $b = -0.16$. The observed u_2 and u_3 mobilities obeyed Jokl's relation for the presumed formation of the $\text{MO}_2(\text{TH}_{-1})_2^{4-}$ and $\text{WO}_2(\text{HTH}_{-1})_2^{2-}$ ions.

Cryoscopy

Sodium molybdate solutions of the concentrations 0.066 and 0.022 mol l^{-1} exhibited pH 6.8 and 7.0 and freezing point depression $\Delta T_1 = 0.33$ and 0.11 K , respectively.

Equimolar solutions of sodium molybdate and tartaric acid with concentrations 0.066 and 0.022 mol l⁻¹ displayed pH 4.8 and 4.7 and $\Delta T_2 = 0.09$ and 0.06 K, respectively. Thus, solutions of sodium molybdate alone give a neutral reaction and the ΔT values decrease linearly with the decreasing concentration. By addition of tartaric acid the molybdate solutions become acidic; if the reaction (B) proceeded quantitatively, the solution would remain practically neutral and the freezing point depression would obey the relation $\Delta T_2/\Delta T_1 = 5/6$. The freezing point depression in solutions of molybdate alone can be divided into the contributions from the sodium and the molybdate ions, making 2/3 and 1/3 of the total ΔT_1 value, respectively. If tartaric acid reacted with Mo(VI) solely, leaving the sodium ions intact, the ratio would be $\Delta T_2/\Delta T_1 \geq 2/3$. The observed ΔT values indicate that on the addition of tartaric acid to the molybdate solution the number of cryoscopically active sodium ions diminishes too. We suggest that this is accounted for by the formation of oligonuclear complexes possessing a high negative charge, imparting to the complexes the nature of a cation exchanger capable of binding sodium ions. Such anions with a high charge may be chain-type Mo(VI) complexes with tartrate. In concentrated solutions there are more favourable conditions for the formation of polynuclear complexes, in dilute solutions the electrolytes dissociate more readily; therefore, the observed $\Delta T_2/\Delta T_1$ ratio decreases with increasing concentration.

DISCUSSION

In approximately neutral aqueous solutions containing tartrate in a sufficient excess, only reaction (A) takes place. Protons are consumed in this reaction, and consequently, the complex created is steady in acidic solutions and decomposes in basic solutions. During the formation of the $\text{MoO}_2(\text{TH}_{-1})_2^{4-}$ tartrate complex, similarly as in the case of the Mo(VI)-pyrocatechol system⁵, no stepwise coordination of the ligands was established. The central Mo(VI) atom in the $\text{MoO}_2(\text{TH}_{-1})_2^{4-}$ complex is coordination-saturated, a next ligand can only be bonded after some of the existing ligands is split off; tartrate ligands can be exchanged for hydroxy ligands in alkaline solutions, oxide ligands do not split off in aqueous solutions. The complex $\text{MoO}_2 \cdot (\text{TH}_{-1})_2^{4-}$ anion is a base, the dependence of the electrophoretic mobility on pH points to protonation of the carboxy groups not bonded in the complex, $\text{p}K_a \approx 3$, and to $\text{MoO}_2(\text{HTH}_{-1})_2^{2-}$ complex formation; the occurrence of the $\text{MoO}_2(\text{HTH}_{-1}) \cdot (\text{TH}_{-1})^{3-}$ ion is also conceivable. Protonation of the $\equiv\text{MoO}_2$ group, reported for the catechol complexes², could not be established by the potentiometric titrations, as the resolving power of the technique at $\text{pH} \approx 3$ in solutions with the requisite excess of tartaric acid is insufficient.

As the acid is gradually added to a neutral solution containing molybdate and tartrate, $c_T < c_M$, a small amount of the mononuclear $\text{MoO}_2(\text{TH}_{-1})_2^{4-}$ chelate forms first, in the next stage the formation of the binuclear $(\text{MoO}_2)_2(\text{TH}_{-2})_2^{4-}$ complex

prevails. In the latter, all of the four functional groups are coordination-bonded. The coordinative saturation of the central Mo(VI) atom in the binuclear complex is of the same nature as in the mononuclear tartrate complex. The binuclear chelate was only examined in solutions at $\text{pH} \geq 6$; its formation is conditioned by a low tartrate concentration. In acidified solutions, formation of a complex mixture is to be expected containing also oligomolybdates free of the tartrate ligand and oligomolybdates to which one or more tartrate ligands are attached. The complexity of the mixture of complexes formed in weakly acidic solutions in which tartrate is not present in a sufficient excess is indicated by cryoscopy experiments, pointing to the occurrence of bulky anions of ion exchanger nature. Presumably, in such bulky oligonuclear anions the central Mo(VI) atoms are joined *via* tartrate bridges.

In all of the complexes observed, molybdenum is bonded to one alcohol and one carboxy group of the tartrate. Consequently, two mol of hydrogen ions were found consumed in the chelation of one mol of molybdate in neutral solutions. Binding of one mol of tartrate in molybdate complex calls for one or two mol of protons in neutral solutions, for the formation of the mono- or binuclear complex, respectively. The possibility of Mo(VI) bonding to tartrate *via* two oxygens of the alcohol groups has been suggested^{8,9}. This reaction,



($n = 1$ or 2), analogous to that with *o*-diphenols⁵, should occur in neutral or basic solutions; in acidic media, reaction (A) can be expected to prevail over reaction (D).

As to reactions of oligo alcohols with Mo(VI), reaction of dimolybdate with alcoholic sugars has been reported^{23,17}, actually proceeding without participation of hydrogen ions, but observed only with alcoholic sugars with a minimum of four alcohol groups. With alcohols containing less than four alcohol groups, such as glycerol, the reaction of Mo(VI) does not take place in aqueous solutions. That the equilibrium (D) does not establish in aqueous tartrate solutions is evidenced by potentiometric titrations for $c_{\text{T}} > c_{\text{M}}$, as the scatter of the K_{A} values calculated from Eq. (2) would be considerably higher if the equilibrium (D) also established in the solutions.

The stability constant of the $\text{MoO}_2(\text{TH}_{-1})_2^{4-}$ complex is

$$\beta = [\text{MoO}_2(\text{TH}_{-1})_2^{4-}] / [\text{MoO}_2^{2+}] [\text{TH}_{-1}^{3-}]^2 ; \quad (9)$$

constants of this type have been published^{8,24}. The knowledge of the $K(\text{MoO}_4^{2-} + 4 \text{H}^+ = \text{MoO}_2^{2+})$ and $K(\text{T}^{2-} = \text{TH}_{-1}^{3-} + \text{H}^+)$ values is prerequisite for converting K_{A} to β . However, the MoO_2^{2+} and TH_{-1}^{3-} species do not form in dilute aqueous solutions, they appear in measurable concentrations only at $\text{pH} < 1$ or $\text{pH} > 13$. The values of the two constants required for the conversion of K_{A} to β have been, in

fact, published^{6,25}, but we do not consider them reliable enough in view of the difficulties in measuring pH in extremely acidic or extremely basic solutions. For this reason, conversion of the equilibrium constants determined to the stability constants²⁶ was rejected.

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