

hydrogen ion is titrated at pH 3.5–7.3, only the second at pH 8.6–10.5. Calculation by Eqn. (1) for the above pH limits gave the following results:

pH	6.50	6.67	7.07	7.30	7.65	
$pK_1$	6.03	6.26	6.29	6.26	6.49	$(pK_1)_{av.} = 6.27 \pm 0.02$
pH	8.40	8.55	8.70	8.80	9.16	
$pK_2$	9.30	8.74	8.45	8.42	8.44	$(pK_2)_{av.} = 8.43 \pm 0.02$

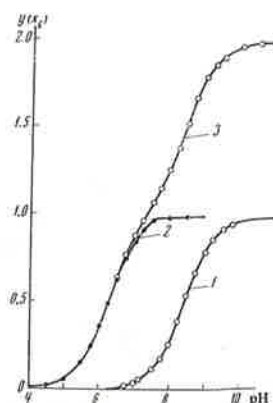


Figure 4. Variation of  $y(X_1)$ ,  $y(X_2)$ , and  $\sum_{i=1}^2 y(X_i)$  with the pH of the solution.

The increased value of  $pK_1$  at pH 7.65 is explained by the superposition at this pH of the titration of the second hydrogen.

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## Acid Dissociation Constants of Orthotelluric Acid

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The acid dissociation constants of orthotelluric acid have been determined by potentiometric titration and electrical conductivity methods:  $K_1 = (3.4 \pm 0.3) \times 10^{-8}$ ,  $K_2 = (4.6 \pm 0.2) \times 10^{-10}$ . The titration ranges of the hydrogen ions of the acid have been calculated.

To characterise orthotellurates thermodynamically the acid dissociation constants of orthotelluric acid must be known; however, the published data are contradictory (Table 1).

Jandert and Kienbaum<sup>4</sup> calculated the first acidity constant from the degree of dissociation. The values of the dissociation constant varied with the concentration of the solution, owing to polymerisation of the acid. Herbert and coworkers<sup>5</sup> calculated the values of  $K_1$  and  $K_2$  from the curve for the titration of  $H_6TeO_6$  by KOH solution by the equation:

$$[H^+]^2 = \frac{K_1 \cdot K_{H_6O}}{[H_5TeO_6^-]} + K_1 \cdot K_2$$

Table 1. Constants of telluric acid.

$K_1$	$K_2$	$t, ^\circ C$	Reference	$K_1$	$K_2$	$t, ^\circ C$	Reference
$2.29 \cdot 10^{-8}$	$6.46 \cdot 10^{-6}$	18	[1]	$pK_1 = 7.70$	$pK_2 = 10.95$	25	[5]
$1.6 \cdot 10^{-9}$	—	20		$6.8 \cdot 10^{-7}$	$4.1 \cdot 10^{-10}$		[6]
$6.8 \cdot 10^{-7}$	$4.1 \cdot 10^{-11}$	25		$1.6 \cdot 10^{-9}$	—		[7]
$2.29 \cdot 10^{-8}$	$6.46 \cdot 10^{-12}$		[2]	$2 \cdot 10^{-8}$	$9 \cdot 10^{-12}$		[7]
$2 \cdot 10^{-8}$	$5 \cdot 10^{-11}$		[3]		$K_2 = 3 \cdot 10^{-10}$		[7]
$2.51 \cdot 10^{-8}$	—						
$2.75 \cdot 10^{-7}$	—	25	[4]	$pK_a = 7.64$			[8]

They considered that

$$K_1 \cdot K_2 > \frac{K_1 \cdot K_{H_6O}}{[H_5TeO_6^-]}$$

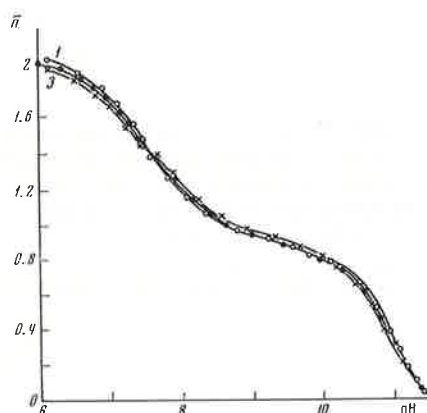
and neglected the first term of the equation in their calculations. According to these investigators<sup>4,5</sup>, solutions of telluric acid do not contain polymeric forms when  $[H_5TeO_6^-] \leq 10^{-3}$  M. Evidently at such tellurate ion concentrations the first term of the equation becomes commensurate with the second. From Table 1, clearly the values of  $K_1$  fluctuate from  $10^{-7}$  to  $10^{-9}$  and  $K_2$  from  $10^{-10}$  to  $10^{-12}$ .

The present paper deals with the determination of the acidity constants of telluric acid by potentiometric titration of sodium tellurate with hydrochloric acid and of telluric acid with sodium hydroxide.

#### Reagents and Method

Telluric acid was made by the oxidation of elemental tellurium with hydrogen peroxide and was recrystallised

thrice from doubly distilled water. KOH was freed from carbonate by a published method<sup>8</sup>. Sodium tellurate was made by the reaction of equivalent amounts of alkali and telluric acid. TeVI was determined by the dichromate method, and also iodometrically<sup>9</sup>. In the determination by the dichromate method TeVI was reduced to TeIV by boiling with HCl in the ratio 1 : 1 in a flask with reflux condenser. Both methods gave almost the same results. The potentiometric measurements were made on an LPU-01 apparatus with glass and silver chloride electrodes. The electrical conductivity was measured after the method described by Kryukov<sup>10</sup>, using an INO-ZM apparatus as null instrument, and a.c. of frequency 1000 Hz. In all the measurements the temperature was  $22^\circ \pm 0.2^\circ\text{C}$ .



**Figure 1.** Curve for the potentiometric titration of sodium tellurate solutions with hydrochloric acid. 1)  $[\text{Na}_2\text{H}_4\text{TeO}_6] = 1 \times 10^{-3}$  M; 2)  $[\text{Na}_2\text{H}_4\text{TeO}_6] = 5 \times 10^{-3}$  M; 3)  $[\text{Na}_2\text{H}_4\text{TeO}_6] = 5 \times 10^{-4}$  M.

## RESULTS AND DISCUSSION

Sodium tellurate was potentiometrically titrated with hydrochloric acid. The initial salt concentrations were  $1 \times 10^{-3}$  and  $5 \times 10^{-3}$  M. Fig. 1 shows the plot of  $\bar{n}$  against  $\lg [\text{H}^+]$  where  $\bar{n}$  is the Bjerrum function—the number of hydrogens associated with one tellurium atom<sup>11</sup>:

$$\bar{n} = \frac{H - h}{[\text{Te}^{\text{VI}}]}$$

$H$  the number of moles of acid introduced calculated for each titration point,  $h$  the equilibrium concentration of hydrogen ions, found potentiometrically from the pH, and  $[\text{Te}^{\text{VI}}]$  the total concentration of tellurium in the solution calculated for each titration point with allowance for the dilution.

From Fig. 1, clearly the plots of  $\bar{n}$  against  $\lg [\text{H}^+]$  almost agree at various concentrations of sodium tellurate in the solution, showing the absence of polymerisation at the chosen salt concentrations. The acidity constants were calculated by the equations:

$$K_1 = \frac{1}{\kappa_1}; \quad K_2 = \frac{1}{\kappa_2}$$

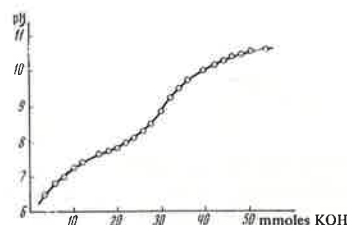
where  $\kappa_1$  and  $\kappa_2$  are the stepwise stability constants of orthotelluric acid in the first and second stages.

$$\kappa_1 = \frac{[\text{H}_6\text{TeO}_6]}{[\text{H}^+][\text{H}_5\text{TeO}_6^-]}; \quad \kappa_2 = \frac{[\text{H}_5\text{TeO}_6^-]}{[\text{H}^+][\text{H}_4\text{TeO}_6^{2-}]}; \quad p\kappa_1 = (\text{pH})_{\bar{n}=1.5}$$

$$p\kappa_2 = (\text{pH})_{\bar{n}=0.5}$$

$p\kappa_1$  and  $p\kappa_2$  were determined from the plot of  $\bar{n}$  against  $\lg [\text{H}^+]$ .

The stability constants found were used to calculate the first and second acidity constants of telluric acid;  $K_1 = (3.0 \pm 0.3) \times 10^{-8}$  and  $K_2 = (4.5 \pm 0.2) \times 10^{-10}$ . It is noteworthy that the pH of solutions of sodium and potassium tellurates varies with time. For sodium tellurate solutions which have stood for more than a week treatment of the potentiometric titration curves gives  $K_1 = (2.37 \pm 0.2) \times 10^{-7}$ . This is explained by the polymerisation of tellurate ions when the solution is kept. Since the pH of solutions of sodium tellurate varies with time, to check our constants we made a potentiometric titration of telluric acid with potassium hydroxide. The pH of telluric acid solutions does not change on standing. The concentrations of the telluric acid solutions titrated was  $1 \times 10^{-2}$  and  $1 \times 10^{-3}$  M (Fig. 2).



**Figure 2.** Curve for the potentiometric titration of telluric acid solution with NaOH.  $[\text{H}_6\text{TeO}_6] = 1 \times 10^{-3}$  M;  $V_{\text{H}_6\text{TeO}_6} = 25$  ml.  $[\text{KOH}] = 1.97 \times 10^{-3}$  M.

The acidity constants were calculated by formulae obtained from the conditions for the electrical neutrality of the solution<sup>12</sup>:

$$K_1 = \frac{h_2^2 \cdot a_2 (2c_1 - a_1) - h_1^2 \cdot a_1 (2c_2 - a_2)}{h_1 \cdot (a_1 - c_1) (2c_2 - h_2) - h_2 (a_2 - c_2) (2c_1 - a_1)}, \quad (1)$$

$$K_2 = \frac{h_2^2 \cdot h_1 \cdot a_2 (a_1 + c_1) - h_1^2 \cdot h_2 \cdot a_1 (a_2 + c_2)}{h_2^2 \cdot a_2 (2c_1 - a_1) - h_1^2 \cdot a_1 (2c_2 - a_2)}, \quad (2)$$

where  $h$  is the equilibrium concentration of hydrogen ions in the solution, and  $a$  and  $c$  are respectively the concentrations of alkali and acid calculated for each point of the titration with allowance for dilution. To solve equations of types (1) and (2) it is necessary to take two points on the titration curve with parameters  $h_1$ ,  $a_1$ ,  $c_1$ , and  $h_2$ ,  $a_2$ ,  $c_2$ .

To determine the range for the titration of the hydrogen of the acid the fundamental equation derived by Britton<sup>13</sup>, was used:

$$Z = -\bar{n}v + B\Sigma f(X_i)$$

where  $Z$  is the number of moles of titrant added to 1 litre solution titrated,  $\bar{n}$  the difference in the  $[\text{H}^+]$  and  $[\text{OH}^-]$  concentrations,  $\bar{n} = [\text{H}^+] - [\text{OH}^-]$ ,  $v$  the dilution of the solution, and  $B$  the initial concentration of the acid. The function  $\Sigma f(X_i)$  is obtained by summation of the functions  $f(X_1)$  and  $f(X_2)$  (for a dibasic acid), the latter being found

from values of  $X_1$  by the Table given by Britton<sup>13</sup>. The value of  $f(X_1)$  varies from 0 to 1 as  $X$  is changed from 0.5 to 4.  $X_1$  were calculated by the equation:

$$X_1 = \text{pH} - \lg \kappa_1,$$

where  $\kappa_1$  is the stability constant. The values of  $f(X_1)$  and  $f(X_2)$  are the number of titratable hydrogens. These data were used to construct graphs of the variation of  $Z/B$  with pH and of  $f(X_1)$  and  $f(X_2)$  on pH (Fig. 3), using  $K_1$  and  $K_2$  obtained in titrating sodium orthotellurate with hydrochloric acid. Table 2 gives the results for finding the range of titration of the hydrogen ions of orthotelluric acid from the experimental values of the pH and the values of  $\kappa_1$  and  $\kappa_2$ .

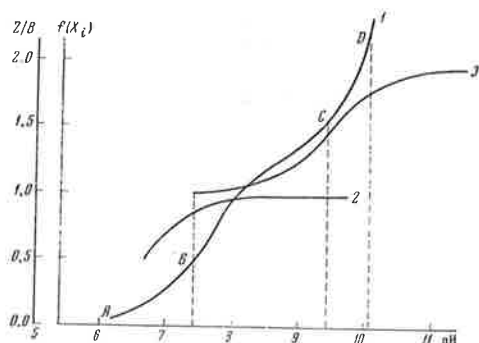


Figure 3. Curve for the potentiometric titration of telluric acid with alkali, with  $Z/B$  plotted against pH. 1) Experimental curve for the titration of telluric acid with alkali; 2) curve for the variation of  $f(X_1)$  with pH, calculated from the value  $K_1 = 3 \times 10^{-8}$ ; 3) curve for the dependence of  $f(X_2)$  on pH, calculated from the value  $K_2 = 4.5 \times 10^{-10}$ .

Table 2. Results to determine the range of titration of the first and second hydrogen ions of orthotelluric acid from the potentiometric titration curve.  $K_1 = 3 \times 10^{-8}$ ,  $\lg \kappa_1 = 7.52$ ;  $K_2 = 4.5 \times 10^{-10}$ ,  $\lg \kappa_2 = 9.35$ .

pH	$X_1$	$X_2$	$f(X_1)$	$f(X_2)$	pH	$X_1$	$X_2$	$f(X_1)$	$f(X_2)$
6.47	-1.05	-2.88	0.0818	1.0010	8.33	+0.81	-1.02	0.8659	1.0872
6.76	-0.76	-2.59	0.1481	1.0025	8.49	+0.97	-0.86	0.9032	1.1213
6.95	-0.57	-2.40	0.2121	1.0040	8.75	+1.23	-0.60	0.9444	1.2008
7.25	-0.27	-2.10	0.3494	1.0079	9.21	+1.69	-0.14	0.9800	1.4201
7.49	-0.03	-1.95	0.4827	1.0108	9.50	+1.98	+0.15	0.9896	1.5855
7.79	+0.27	-1.56	0.6506	1.0268	9.95	+2.43	+0.60	0.9968	1.7992
7.90	+0.38	-1.45	0.7058	1.0343	10.01	+2.48	+0.75	0.9970	1.8490
8.01	+0.49	-1.34	0.7555	1.0437					

Table 3 gives the results of the calculation of  $K_1$  and  $K_2$  by Eqns. (1) and (2) on different parts of the potentiometric titration curve. As Tables 2 and 3, and also Fig. 3, show, the calculation of  $K_2$  for  $\text{H}_6\text{TeO}_6$  from the potentiometric titration curve must be done in the pH range above 9.6, and that of  $K_1$  in the pH range from 6.5 to 7.3-7.4.

Calculations made for these pH ranges gave the following values for the acidity constants of telluric acid:

$$K_1 = (3.4 \pm 0.12) \times 10^{-8}; K_2 = (4.6 \pm 0.3) \times 10^{-10}.$$

Table 3. Values of  $K_1$  and  $K_2$  calculated from various parts of the potentiometric titration curve of orthotelluric acid against potassium hydroxide.

pH	$K_1$	$K_2$	Note
6.5-7.5	$(3.4 \pm 0.12) \cdot 10^{-8}$	$10^{-8} - 10^{-9}$	On those parts of the curve where the first and second hydrogens are titrated simultaneously, we give only the order of the constants obtained.
7.5-9.5	$10^{-8} - 10^{-9}$	$10^{-8} - 10^{-10}$	
9.6	$10^{-9} - 10^{-11}$	$(4.6 \pm 0.3) \cdot 10^{-10}$	

The electrical conductivity of solutions of telluric acid and sodium tellurate was measured (Table 4) and used to calculate the acidity constants.  $\lambda_\infty$  for telluric acid was determined by Kohlrausch's law starting from  $\lambda_\infty \text{Na}_2\text{H}_4\text{TeO}_6$ ;  $\lambda_\infty \text{HCl}$ ; and  $\lambda_\infty \text{NaCl}$

$$(\lambda_\infty)_{\text{H}_2\text{TeO}_6}^{25^\circ\text{C}} = (\lambda_\infty)_{\text{Na}_2\text{H}_4\text{TeO}_6}^{25^\circ\text{C}} - 2(\lambda_\infty)_{\text{NaCl}}^{25^\circ\text{C}} + 2(\lambda_\infty)_{\text{HCl}}^{25^\circ\text{C}} = 917 \Omega^{-1} \text{cm}^2 \text{g-equiv.}^{-1}.$$

Table 4. Measurement of the electrical conductivity of solutions of telluric acid.

$c_{\text{H}_2\text{TeO}_6}$ , M	$\kappa$	$\bar{\kappa}$	$\alpha = \lambda/\lambda_\infty$	$K_1$
0.5	$6.84 \cdot 10^{-4}$	1.374	$1.49 \cdot 10^{-3}$	$11 \cdot 10^{-7}$
0.25	$4.57 \cdot 10^{-4}$	1.836	$1.98 \cdot 10^{-3}$	$9.7 \cdot 10^{-7}$
0.125	$2.44 \cdot 10^{-4}$	1.952	$2.14 \cdot 10^{-3}$	$5.72 \cdot 10^{-7}$
0.0625	$1.33 \cdot 10^{-4}$	2.128	$2.32 \cdot 10^{-3}$	$3.34 \cdot 10^{-7}$
0.0312	$7.38 \cdot 10^{-5}$	2.372	$2.58 \cdot 10^{-3}$	$2.07 \cdot 10^{-7}$
0.0156	$4.28 \cdot 10^{-5}$	2.762	$2.90 \cdot 10^{-3}$	$1.31 \cdot 10^{-7}$

The dependence of  $\lambda_\infty \text{Na}_2\text{H}_4\text{TeO}_6$  on  $\lg c$  was extrapolated to infinite dilution and  $(\lambda_\infty)_{\text{Na}_2\text{H}_4\text{TeO}_6} = 286$ , so that the mobility of the tellurate ion is  $\lambda_{\text{H}_4\text{TeO}_6} = 206 \Omega^{-1} \text{cm}^2 \text{g-equiv.}^{-1}$ . The tellurate ion is hydrated in aqueous solutions  $[\text{TeO}_4^{2-} \cdot 2\text{H}_2\text{O}]$ . The acidity constants of telluric acid were calculated by the Ostwald dilution law. From Table 2, clearly, the acidity constants (the first acidity constant was determined by the electrical conductivity method) falls as the acid concentration is reduced. It has been shown<sup>14</sup> that isopolyacids exhibit a much greater acid function than do the monomeric forms. Jandert and Kienbaum<sup>4</sup> made a similar observation. The acidity constants calculated from the pH results via the degree of dissociation decrease with dilution of the solutions of orthotelluric acid. The variation of the acidity constants with the telluric acid concentration is undoubtedly connected with polymerisation. The acidity constants obtained from the electrical conductivity results were extrapolated to infinite dilution and gave  $K_1 = 3.0 \times 10^{-8}$ . Here good agreement was obtained with the results of the potentiometric titrations.

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## Preparation of Alkali Metal Oxodichloroaluminates

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The oxodichloroaluminates of sodium ( $\text{NaAlOCl}_2$ ), potassium ( $\text{KAlOCl}_2$ ), and caesium ( $\text{CsAlOCl}_2$ ) have been isolated by heating the tetrachloroaluminates with antimony(III) oxide. Chemical analysis, thermal analysis, and X-ray diffraction study have confirmed that the products isolated are individual chemical compounds. When heated, the oxodichloroaluminates decompose to aluminium oxide and the alkali metal chloride and tetrachloroaluminate. Study of the action of antimony(III) oxide on sodium and potassium tetrachlorogallates has shown that the oxodichlorogallates decompose at the temperature of the preparation.

Oxochloro-compounds of aluminium with the composition  $\text{MAL}_4\text{O}_4\text{Cl}_5$  were obtained by fusing aluminium oxide chloride with alkali metal chlorides<sup>1</sup>. Various oxochloro-compounds can be prepared by the reaction between the chlorides or chloro-complexes of various elements and the oxides of antimony or arsenic<sup>2-6</sup>. The aim of the present work was to prepare oxodichloroaluminates by the action of antimony(III) oxide on alkali metal tetrachloroaluminates and to establish the differences in the reactions of the chloro-complexes of aluminium and gallium with  $\text{Sb}_2\text{O}_3$ .

## EXPERIMENTAL

The tetrachloroaluminates and tetrachlorogallates required for the experiments were prepared by fusing together aluminium or gallium chlorides and the alkali metal chlorides in molybdenum glass ampoules, evacuated and sealed under a vacuum. Since gallium chloride is extremely hygroscopic, it was prepared directly before the experiment by chlorinating metallic gallium with gaseous chlorine in the vessels subsequently used for the preparation of the tetrachlorogallates. The ampoules containing the alkali metal tetrachloroaluminates and tetrachlorogallates were opened, and the melts ground, in a dry box.

To establish the optimal conditions for the preparation of the oxochloroaluminates, we carried out the differential thermal analysis (DTA) of a mixture of the reagents, taken in proportions corresponding to the stoichiometry of the reaction



where M = Na, K, or Cs. The mixtures were heated in a stream of argon.

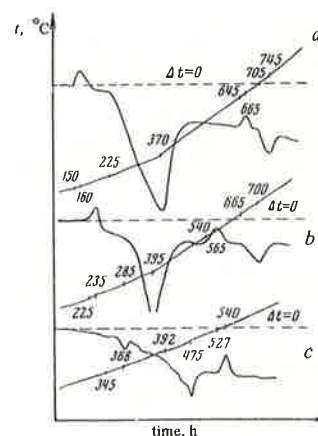


Figure 1. Heating curves for the reaction mixtures in a stream of argon: a)  $\text{NaAlCl}_4 - \text{Sb}_2\text{O}_3$ ; b)  $\text{KAlCl}_4 - \text{Sb}_2\text{O}_3$ ; c)  $\text{CsAlCl}_4 - \text{Sb}_2\text{O}_3$ .

The heating curve for the mixture of  $\text{NaAlCl}_4$  and  $\text{Sb}_2\text{O}_3$  (Fig. 1a) shows an exothermic effect at 150–160°C, corresponding to the fusion of sodium tetrachloroaluminate and the start of the reaction between the compounds. The formation of  $\text{NaAlOCl}_2$  is complete in the range 225–370°C. The endothermic effect at 225–370°C is due to the volatilisation of antimony(III) oxide. The reaction of potassium tetrachloroaluminate with  $\text{Sb}_2\text{O}_3$  takes place analogously. The exothermic effect at 225–235°C corresponds to the fusion of  $\text{KAlCl}_4$  and the start of the reaction, which is complete in the range 285–395°C (Fig. 1b).

The DTA of the mixture of  $\text{CsAlCl}_4$  and antimony(III) oxide showed that the formation of caesium oxodichloroaluminate begins above 400°C and is much slower than the reactions of the sodium or potassium compounds. The formation of caesium oxochloroaluminate is marked by an endothermic effect at 392–475°C (Fig. 1c). At a rate of