and the literature values of the force constants for the CrO_4^{2-}, CrO_3X^-, and $Cr_2O_7^{2-}$ ions. The results of the calculations are presented in Table 4.

Table 3. The force constants of the $CrIO_6^-$ and $Cr_2O_7^{2-}$ ions (mdyn $Å^{-1}$).

Ion	$K_1(Cr-O)$	$K_2(Cr-O_b)$	K_d	K'
$Cr_2O_7^{2-}$	6.07	3.27	0.42	0.25
$CrIO_6^-$	5.87	4.41	0.74	0.13

Table 4. The bond force constants and orders in the complexes investigated.

Complex	Force constants, mdyn A^{-1}		Bond orders	
	$K_1(Cr-O)$	$K_2(Cr-O_b)$	$N(Cr-O)$	$N(Cr-O_b)$
K_2CrO_4	5.5		1.5	
$KCrO_3F$	6.2		1.6	
$KCrO_3Cl$	6.3		1.6	
$K_2Cr_2O_7$	6.1	4.2	1.6	1.2
$KCrIO_6$	6.2	5.2	1.6	1.5

Tables 3 and 4 show that the substitution of one of the oxygen atoms in the CrO_4^{2-} ion by a halogen leads to a sharp increase of the Cr–O force constant and bond order in the CrO_3 group. A similar increase of the Cr–O force constant and bond order is observed when one of the oxygen atoms in the chromate ion is substituted by complex oxygen-containing groups, which is evidence of a high rigidity of the Cr–O bond in the CrO_3 group. The closeness of the force constants and orders of the terminal bonds in the CrO_3F^-, CrO_3Cl^-, $Cr_2O_7^{2-}$, and $CrIO_6^-$ ions is consistent with the similarity of the interatomic distances in the CrO_3 groups, determined by X-ray diffraction analysis ($R_{Cr-O} = 1.58-1.63$ Å). In contrast to the terminal groups, the bond in the Cr–O–I bridge is stronger than in the Cr–O–Cr bridge (Table 4), approaching in its characteristics the Cr–O bonds in the CrO_4^{2-} ion. As stated above, such strengthening of the Cr–O bond in the Cr–O–I bridge compared with the Cr–O–Cr bridge can be explained by a redistribution of electron density at the I^V and Cr^{VI} atoms due to the difference between their electronegativities.

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Faculty of Chemistry,   Received 14th September 1972
Zhdanov Leningrad
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The State of Tellurium(IV) in Perchloric Acid Solutions

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The regions where monomeric and polynuclear tellurium(IV) compounds predominate in perchloric acid solutions have been found by comparative dialysis, electrodialysis, and spectrophotometric methods and the stability constants of tellurium(IV) hydroxo-complexes have been determined.

The ions of polyvalent elements in acid solutions are known to be capable of forming hydrolytic polynuclear compounds and hydroxo-complexes of different compositions which to a large extent determine the reactivities of these elements. Moreover, information about a specific standard state of the elements in solutions is necessary for the investigation of the mechanism of the formation and stability of their complexes with various ligands. The most convenient standard systems are perchlorate solutions, since complexes are not formed with ClO_4^- ions or can be neglected. Nevertheless the state of tellurium(IV) in perchlorate solutions has been hardly investigated. Only the dissociation constants of tellurous acid[1] and the first dissociation constant of the hydroxo-complex[2] $TeO(OH)_2$ are known.

This paper describes a study of the state of tellurium(IV) ions in the acidity range from pH 2 to 5 N $HClO_4$ and with $[Te^{IV}]$ ranging from 2×10^{-4} to 1×10^{-1} g-atom litre^{-1}. The experiments were performed at 20°C. At $[HClO_4] < 0.5\ N$, a constant ionic strength of 0.5 was maintained by the addition of $NaClO_4$; at $[HClO_4] > 0.5\ N$ the ionic strength of the solution was virtually equal to that of perchloric acid. The acidity of the solution was determined by titration with alkali or with the aid of a LPU-01 pH-meter using a glass electrode; the absorption spectra were recorded on an SF-4A spectrophotometer.

The initial tellurous acid solution was prepared by dissolving TeO_2 in perchloric acid and that of cobalt perchlorate was made by dissolving cobalt hydroxide in perchloric acid. The concentrations of tellurium in the test solutions were determined photometrically by the reaction with lead dichloride and those of cobalt by the reaction with the nitroso R-salt.

Table 1. Determination of the relative dialysis coefficient D_{Te} and the average polymerisation factor F for tellurium at different concentrations of the latter* {$[Co^{2+}]_1$ = const. = 2.2 × 10⁻⁵ g-atom litre⁻¹}.

[HClO₄], M	[Te]₁ = 5×10⁻³ g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P	[Te]₁ = 1×10⁻² g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P	[Te]₁ = 1×10⁻¹ g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P
0.01	2.90	2.66	0.620	1.17	8.00	3.80	0.460	2.07	—	—	—	—
0.10	4.20	3.06	0.606	1.19	8.05	3.60	0.484	2.06	—	—	—	—
0.50	3.96	2.78	0.550	1.44	7.60	3.04	0.550	1.44	8.50	1.20	0.154	18.5
1.00	2.00	1.70	0.540	1.49	7.68	2.90	0.583	1.30	14.0	1.72	0.278	13.9
3.0	3.60	2.60	0.594	1.25	7.29	2.70	0.594	1.25	15.0	1.66	0.198	11.2
5.0	3.95	2.38	0.610	1.17	8.00	2.90	0.605	1.17	19.0	1.50	0.279	1.96

[HClO₄], M	[Te]₁ = 2×10⁻⁴ g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P	[Te]₁ = 5×10⁻⁴ g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P	[Te]₁ = 2×10⁻³ g-atom litre⁻¹ $[Te]_2$	$[Co]_2$	D_{Te}	P
0.01	0.158	2.66	0.660	1.02	0.50	3.60	0.640	1.02	1.80	3.02	0.645	1.06
0.10	0.166	2.80	0.660	1.02	0.40	2.70	0.664	1.01	1.68	2.86	0.647	1.05
0.50	0.160	2.66	0.664	1.00	0.35	2.30	0.661	1.00	2.00	3.36	0.653	1.00
1.00	0.125	2.12	0.651	1.03	0.30	2.00	0.664	1.00	2.00	3.38	0.660	1.02
3.0	0.130	2.26	0.664	1.00	0.41	2.80	0.663	1.02	1.60	2.66	0.664	1.00
5.0	0.134	2.20	0.664	1.00	0.44	2.93	0.665	1.00	1.24	2.10	0.651	1.02

(In the sub-tables above, the "10⁻⁴ g-atom litre⁻¹ in dialysate" columns give $[Te]_2$ and $[Co]_2$.)

*$D_{Te} = [Co]_1[Te]_2 P/[Co_2][Te]_1 = (D_{Te(mas.)}/D_{Te})^2$. The subscripts 1 and 2 refer to the inner and outer dialyser vessels respectively.

Comparative Dialysis

The method was used to determine the regions where monomeric and polynuclear tellurium species predominate. The experiments were performed in dialysers with cellophane membranes; the relative dialysis coefficient D_{Te} and the average polymerisation factor F were calculated by a method described in the literature[3]. Co^{2+} served as the reference ion; in each series of experiments in the test solutions constant $HClO_4$ and Co^{2+} concentrations were maintained and only the tellurium concentration was varied, which ensured that the state of the reference ion (cobalt) remained unaltered. The duration of dialysis was 2.5 h. During this period, not more than 10% of the total amount of tellurium and cobalt taken initially diffused to the outer vessel, which ruled out the possibility of distortion of the results by the large difference between the concentration gradients of the test and reference ions.

The results of the experiments are presented in Table 1, which shows that polynuclear compounds ($P > 1$) are formed only when $[Te^{IV}] > 5 \times 10^{-3}$ g-atom litre⁻¹, a decrease of the H⁺ concentration and an increase of the tellurium(IV) concentration promote their formation. Particularly high polymerisation factors are observed when $[Te^{IV}] = 0.1$ g-atom litre⁻¹. Fig.1 shows the regions where monomeric and polynuclear tellurium species predominate as a function of $[HClO_4]$ and $[Te^{IV}]$.

Comparative Electrodialysis

The method was used to determine the average charge of the monomeric cationic tellurium species. The experiments were performed in a five-compartment electrodialyser with cellophane membranes using Co^{2+} as the reference ion. At pH < 2 both tellurium and cobalt ions migrated to the cathode only. The average charge of the tellurium cations was calculated by a method already described[4] assuming that $Z_{Co} = +2$. The tellurium and cobalt concentrations in the test solutions were 2 × 10⁻³ and 2.2 × 10⁻³ g-atom litre⁻¹ respectively. The experiments were carried out at a current of about 20 mA maintaining the condition $E\tau \simeq 2000$ volt min. The results are presented in Table 2 and show that, with increase of $HClO_4$ concentration, the average charge of the tellurium
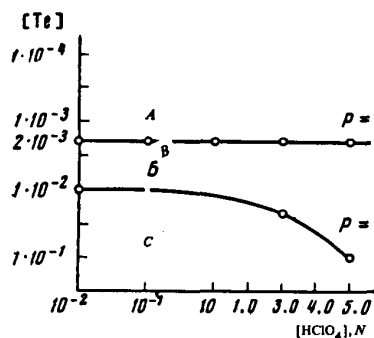

Figure 1. Diagram relating the predominance of monomeric and polynuclear tellurium(IV) species to the concentrations [Te] and [HClO₄]; P is the average polymerisation factor: zone A—monomers; zone B—mixture of monomers and dimers; zone C—polynuclear compounds with $P > 2$.

Table 2. Experimental and calculated data for the determination of the charge $\bar{Z}$ of the tellurium cations and of the average number $\bar{n}$ of OH⁻ ions bound to tellurium*.

[HClO₄], N	-lg [OH⁻]	E, V	τ, min	10⁴[Co], g-atom litre⁻¹ n_{st}	ϵ_{st}	10⁴[Te], g-atom litre⁻¹ n_x	ϵ_x	$\bar{Z}$	$\bar{n}$
0.003	11.48	16—17	125	1.80	3.06	0.30	0.30	0	4.0
0.020	12.30	15—16	133	2.74	3.60	3.00	3.33	0.6	3.4
0.10	13.00	13—14	143	2.80	3.06	4.65	4.80	0.7	3.3
0.50	13.70	7.0—7.5	263	2.00	4.20	2.05	2.52	0.8	3.2
1.00	14.00	5.5—6.5	333	4.07	4.30	3.20	3.30	1.6	2.4
1.50	14.17	5.5—6.0	360	2.60	2.72	4.15	4.30	1.9	2.1
2.00	14.30	4.8—5.0	370	2.60	3.60	2.15	3.10	2.1	1.9
2.50	14.40	4.8—5.0	424	2.66	3.06	3.30	4.15	3.1	0.9
3.00	14.48	4.6—5.0	435	2.60	2.80	3.10	3.58	4.0	0

*$\bar{Z} = 2n_{st}(\epsilon_x - n_x)/n_x(\epsilon_{st} - n_{st})$, where ϵ_{st} and ϵ_x are the concentrations of cobalt and tellurium in the catholyte after electrodialysis during a period τ (min.) and n_{st} and n_x are the corresponding concentrations when no electric current is passed ("blank" experiment).

ions changes from 0 to +4, i.e. the transition $H_2TeO_3 \to$ $\to Te^{4+}$ takes place. The last column of Table 2 lists the average values of $\bar{n} = OH^-$: Te^{IV} calculated from the relation $\bar{n} = 4-\bar{Z}$. Using the data in Table 2, $\bar{n}$ was plotted against $-lg[OH^-]$. Fig. 2 shows that the formation curve for tellurium(IV) hydroxo-complexes is not symmetrical, which precludes an accurate calculation of the stability constants by Bjerrum's method. On the other hand, the shape of the curves has certain characteristic features which yield information about the mechanism of the formation of the hydroxo-complexes.

The extremely sharp rise of the curve in the region where $\bar{n} = 0-2$ suggests that, for the given acidity of the medium, the hydroxo-complexes are formed via the mechanism

$$Te^{4+}+2OH^- \rightleftharpoons Te(OH)_2^{2+} \qquad (1)$$

or

$$Te^{4+}+2OH^- \rightleftharpoons TeO^{2+}+H_2O\uparrow \qquad (2)$$
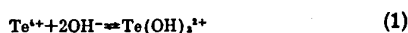
Preference should probably be given to mechanism (1), since Zr^{4+} and Hf^{4+} ions, whose ionic radii are close to that of Te^{4+},[1] have been shown to form the hydroxo-complexes $M(OH)_n^{4-n}$.[5-8] In the range $\bar{n} = 2-4$ two steps appear on the curve in Fig. 2, indicating further stepwise addition of two OH^- ions:

$$Te(OH)_2^{2+}+OH^- \rightleftharpoons Te(OH)_3^+ \qquad (3)$$
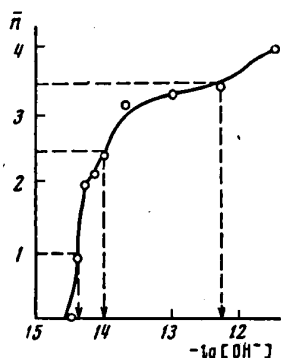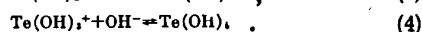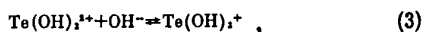$$Te(OH)_3^+ + OH^- \rightleftharpoons Te(OH)_4 \qquad (4)$$

Figure 2. Formation curve for tellurium(IV) hydroxo-complexes.

Approximate stepwise stability constants of the tellurium(IV) hydroxo-complexes formed by reactions (1), (3), and (4) can be calculated from the concentrations of OH^- ions at which $\bar{n} = 1.0$, 2.5, and 3.5:

$$\beta_{1,2} = \frac{[Te(OH)_2^{2+}]}{[Te^{4+}][OH^-]^2} = \frac{1}{(4\cdot10^{-14})^2} = 6.3\cdot10^{26} \quad (I \cong 2.5),$$

$$\beta_3 = \frac{[Te(OH)_3^+]}{[Te(OH)_2^{2+}][OH^-]} = \frac{1}{1\cdot10^{-14}} = 1.0\cdot10^{14} \quad (I \cong 1.0),$$

$$\beta_4 = \frac{[Te(OH)_4]}{[Te(OH)_3^+][OH^-]} = \frac{1}{6\cdot10^{-13}} = 1.7\cdot10^{12} \quad (I \cong 0.5).$$

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†In order to simplify the formulation, the water molecules in the inner coordination sphere of tellurium are not indicated.

In an earlier study[2] it was found by the solubility method that $\beta_4 = (2.1 \pm 0.6) \times 10^{12}$, which agrees with the value obtained here.

Fig. 3 shows the proportions of the tellurium(IV) species in perchlorate solutions under the conditions where the monomeric species predominate. The dissociation constants of tellurous acid employed in the calculation[1] had been adjusted to $I = 0.5$. It follows from Fig. 3 that the isoelectric point of tellurous acid, corresponding to the maximum accumulation of $H_2TeO_3.nH_2O$ molecules, is at pH 2.3. In a more acid medium the cationic forms of tellurium predominate; Te^{4+} ions are formed in appreciable amounts only when $[HClO_4] > 2-3$ N.

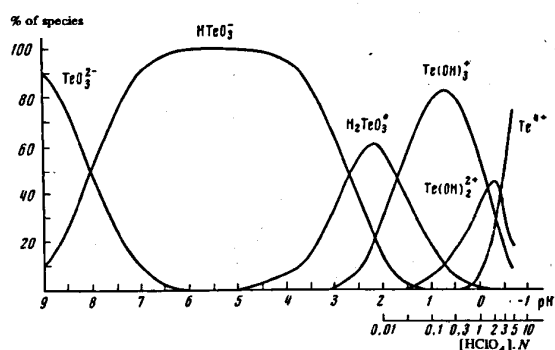**Figure 3.** Diagram illustrating the state of tellurium(IV) in perchlorate solutions; $[Te^{IV}] < 2 \times 10^{-3}$ g-atom litre^{-1}; $I > 0.5$.
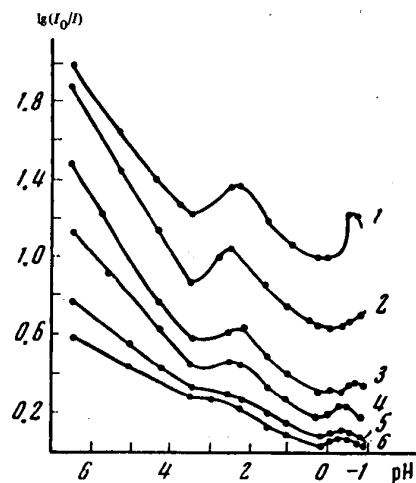

Figure 4. Variation of the optical densities of the tellurium(IV) perchlorate solutions with the acidity of the medium (HClO$_4$); λ (nm); 1) 215; 2) 220; 3) 225; 4) 230; 5) 235; 6) 240; $[Te^{IV}] = 2 \times 10^{-3}$ g-atom litre^{-1}; $l = 1$ cm.

Additional experiments on the absorption of tellurium by AV-17 anion-exchange resin and KU-2 cation-exchange resin showed that, in accordance with the diagram in

Fig. 3, when the pH is changed from 7 to 0 the degree of sorption by the anion exchanger decreases and that by the cation exchanger increases. However, when $[HClO_4] >$ 2–3 N the degree of sorption by the cation exchanger falls sharply. Under the same conditions, Ti^{4+} and Th^{4+} cations are almost completely sorbed by KU-2 cation-exchange resin[9]. Therefore at high $HClO_4$ concentrations tellurium perchlorate complexes are probably formed, reducing the positive charge of tellurium, which facilitates its displacement from the resin phase by hydrogen ions.

Spectrophotometry

The absorption spectra recorded for different acidities of the medium under the conditions where monomeric tellurium species predominate show absorption bands at $\lambda < 260$ nm without characteristic maxima; with decrease of the wavelength, the optical density of the solution increases continuously.

Fig. 4 presents the variation of the optical density of tellurium(IV) perchlorate solutions with the acidity of the medium at different wavelengths. The shape of the curves in general reflects the diagram in Fig. 3. The increase of the optical density when the pH is raised from 3 to 5 is due to the formation of $HTeO_3^-$ ions. The maxima on the curves at 215–230 nm (Fig. 4) and pH ~ 2 correspond to the formation of molecular species derived from tellurous acid; the maxima on the curves in the range 230–240 nm at pH ~ –0.2 may be attributed to the formation of $Te(OH)_2^{2+}$. Finally the increase of the optical density on the curves at 220 and 215 nm at pH < -0.4 is evidently related to the formation of Te^{4+} ions.

The Compositions of Certain Sulphur-containing Potassium Polyphosphates

B.A.Beremzhanov, Yu.A.Pokrovskaya, D.Z.Serazetdinov, and E.V.Poletaev

When potassium sulphate is fused with phosphoric acid in molar proportions ranging from 1:2 to 2:1 at temperatures in the range 400–1000°C, water-soluble potassium polyphosphates are formed. They retain the X-ray diffraction pattern of the Kurrol salt but have different infrared spectra. The possible influence of SO_4^{2-} ions on the structure of the polyphosphate chains is discussed.

The formation of heteroatomic compounds of polymeric phosphates and certain polyanions (Cr, As, W, Si, and S) is regarded as possible in view of their structural similarity—the identical tetrahedral coordination of oxygen and similar E–O bond lengths. There are data concerning the preparation of arsenatophosphates, silicatophosphates, and sulphatophosphates [1,2]. These compounds are of undoubted interest from the standpoint of the chemistry of inorganic polymers but they have been very little investigated.

This paper deals with a study of the products of the reaction of potassium sulphate with phosphoric acid at temperatures in the range 400–1000°C which may be expected to result in the formation of sulphatophosphates, since, according to Shaver's data[3], the latter are formed independently of the type of starting materials provided that the ratio $K_2O : (P_2O_5 + SO_3) < 1$ holds.

X-Ray diffraction data for compositions in the $K_2SO_4-H_3PO_4$ system.

Molar ratio $K_2SO_4:H_3PO_4$ in initial mixture	M.p.,°C	Duration of fusion, min	Phase composition of solidified melt according to X-ray diffraction data	Refractive index of vitreous component
1:2	400—600	15—120	Double salt $KHSO_4.KH_2PO_4$ + glass	1.468—1.471
	700—1000	15—120	Potassium polyphosphate + glass	1.471
1:1	400—600	15—120	$KHSO_4.KH_2PO_4$ + glass	1.471
	700	80—120	Potassium polyphosphate + glass	1.471
	800—1000	15—120	Potassium sulphate + glass	1.489
1.5:1	400—600	15—120	Double salt + glass	1.471
	700	15—120	Potassium polyphosphate + glass	1.471
	800—1000	15—120	Potassium sulphate + glass	1.489
2:1	400—600	15—220	Double salt + glass	1.471
	700—1000	15—120	Potassium sulphate + glass	1.489

The products were studied by X-ray diffraction (photographic recording, $NiK\alpha,\beta$ radiation) and infrared spectroscopy (UR-10 spectrophotometer). The Table presents data for the phase compositions of the solidified melts obtained in the $K_2SO_4-H_3PO_4$ system for different process parameters (ratio of starting materials, temperature, duration of fusion). It is seen that the powder diffraction patterns reveal three crystalline phases: the double salt $KHSO_4.KH_2PO_4$, potassium polyphosphate, and potassium sulphate. It is interesting to note that in each composition not more than one crystalline phase is formed : potassium

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