by the partially hydrolysed chromium nitrate are absorbed by the unreacted WO_4^{2-} ions; the green solution formed after the addition of chromium nitrate when $Z < 0.833$ decomposes instantaneously with liberation of a green amorphous precipitate, which makes it impossible to measure the optical density in this region.

From $Z = 0.833$ ($H^+ : WO_4^{2-} = 5 : 6$), the solutions are more stable and it is possible to measure the optical density up to $Z = 2.0$. For $Z = 1.167$, which is characteristic of paratungstate-"A", the optical density and the stability are maximum. All the solutions with $Z \neq 1.167$ decompose fairly rapidly, the rate of decomposition being higher the more the acidity Z deviates from 1.167.

Fig. 3 shows that, when $Z = 1.167$, the interaction between the components takes place without a change in the acidity of the solution. The normal sodium tungstate solution acidified to $Z = 1.167$ (paratungstate-"A") shows the greatest capacity for complex formation with chromium(III).
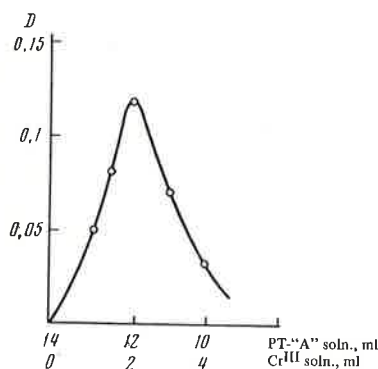

Figure 4. Isomolar series plot for solutions of paratungstate-"A" and chromium nitrate at 580 nm for an overall concentration of 0.04 M.

The investigation has shown that the most active form of tungsten-containing anions is paratungstate-"A". Therefore subsequently we studied the interaction of lithium paratungstate-"A" with chromium nitrate. The composition of the complex was determined by the isomolar series method. A series of solutions with overall concentrations of 0.01, 0.02, and 0.04 M were prepared. The initial paratungstate-"A" and chromium nitrate solutions were introduced into 50 ml volumetric flasks. Then the solution was made up to the mark and the optical density was measured 5 min after preparation. The results of the study of the isomolar series leads to the conclusion that a tungstochromate complex with the ratio Cr : W = 1 : 6 is formed in solution (Fig. 4). In series with Cr : W = 1 : 3.6 and 1 : 2.5 and with smaller amounts of tungsten, a turbidity or a precipitate is observed immediately after mixing the solutions. The introduction of alkali after adding the reactants is known to stabilise the heteropolycomplex. Therefore we attempted to extend the range of homogeneity of the solutions by adding alkali. However, the addition of a very small amount of alkali to solutions with Cr : W = 1 : 3.6, 1 : 2.5, 1 : 1.8, 1 : 1.3, and 1 : 1 only increased the amount of precipitate.

Additional evidence that the complex formed is not a member of the 12-series was provided by a study of the ultraviolet spectra. While all the heteropolytungstates of the 12-series, metatungstate, and metatungstic acid as well as boiled solutions of tungstate with acidities ranging from 0.5 to 3.0 give rise to an absorption maximum at about 260 nm after heating, heteropolytungstates of the 6-series as well as the solutions investigated here do not show a maximum of this kind down to 220 nm.

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The Role of Tellurium(VI) in the Formation of Heteropolyacids

E.Sh.Ganelina and L.A.Bubnova

The role of tellurium(VI) in the formation of heteropolyacids (HPAC) and the conditions governing their existence have been investigated. The optimum pH for the existence of the tellurium(VI) heteropolyanion (HPA) in solution is in the range 2.2–3.2. The formation in solution of tellurium(VI) heteropolyacids saturated with tungsten to different extents has been demonstrated spectrophotometrically. A mechanism is suggested for the formation of the tellurium(VI) heteropolyacids. The initial complex formation stage involves the formation of a Te^{VI}-4W complex by the replacement of hydroxy-groups in the $[TeO_2(OH)_4]^{2-}$ anion by tungstic acid molecules. The formation of heteropolyacids saturated with tungsten to different extents proceeds via further saturation with tungsten of the Te^{VI}-4W heteropolyacids. The degree of formation and the stability constant of the Te^{VI}-4W complex, $(2.9 \pm 1.3) \times 10^{18}$, have been calculated from the photometric measurements. A hypothesis is put forward concerning the composition of the first and second coordination spheres of the Te^{VI}-W heteropolyanions.

The role of tellurium(VI) in the formation of heteropolyacids has already been investigated[1-3]. It has been stated[2] that a heteropolyacid exists with the molar ratio

$W(Mo):Te^{VI} = 6$, the optimum pH for its formation being in the range 8.0—7.5.

This study deals with the possibility of the formation and the conditions governing the existence of heteropoly-acids saturated with tungsten to different extents; an attempt was made to elucidate the mechanism of the formation of tellurium(VI) heteropolyacids of different compositions. The spectrophotometric method, usually employed[4-6] in the study of heteropolyacids and used[7] to elucidate the mechanism of the formation of tellurium(IV) heteropolyacids, was chosen for the solution of the problem formulated. It has been shown[7] that the formation of the tellurium(IV) heteropolyacids begins with the formation of the $Te^{IV}-2W$ heteropolyacid, which must be regarded as the central unit in the complex formation process. The formation in solution of heteropolyacids saturated with tungsten to a greater extent entails the enrichment of the $Te^{IV}-2W$ heteropolyacids with tungsten.

Here we investigated the stability of the tellurium(VI) heteropolyacids in the pH range 1.5—6.5. A mixture of solutions of orthotelluric acid and sodium tungstate (with molar ratios $W:Te = 1-20$) was acidified with 0.052 M nitric acid solution. The overall concentration of tellurium was constant for systems of all compositions at 1.68×10^{-4} M.
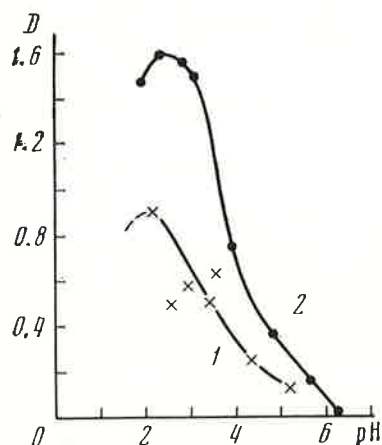

Figure 1. Variation of the optical densities of the $H_6TeO_6-Na_2WO_4-HNO_3-H_2O$ system with pH at 320 nm: 1) $W:Te = 6$; 2) $W:Te = 12$.

Fig. 1 presents curves illustrating the variation of the optical densities of the solutions with pH for systems with $W:Te = 6$ (curve 1) and $W:Te = 12$ (curve 2). Fig. 1 shows that the optimum pH for the existence of the hetero-polyacids in solution is in the range 2.2—3.2. We reached a similar conclusion in the study of systems of other compositions. Therefore the subsequent spectrophoto-metric investigation by the method involving a variable concentration of one of components and by the isomolar series method was performed at pH 3.

The $H_6TeO_6-Na_2WO_4-HNO_3-H_2O$ system with a constant tellurium(VI) concentration (1.68×10^{-4} M) and a variable concentration of tungsten was studied. Orthotelluric acid solution (1 ml of 8.4×10^{-3} M solution) and specified

amounts of aqueous sodium tungstate (at the same concen-tration) such that the $W:Te$ molar ratio varied from 2 to 20 were placed in 50 ml volumetric flasks. The mixture of solutions was acidified with a calculated amount of 0.052 M HNO_3 to pH 3. The amount of nitric acid was calculated as before[7]. The pH of the solutions was mea-sured with an LPU-01 pH-meter. The optical density measurements were carried out on an SF-4A spectrophoto-meter with an optical pathlength $l = 1$ cm and a UFS-2 filter in the wavelength range 320—370 nm. Water was used as the reference liquid. The clearest dependence of the optical density on the $W:Te^{VI}$ molar ratio was obtained for $\lambda = 320$ nm. Fig. 2 shows that at pH 3 tellurium^{VI} heteropolyacids of different compositions exist.
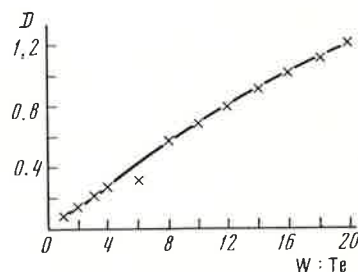

Figure 2. Variation of the optical densities of the solutions with tungsten concentration at the constant tellurium concentration $[Te] = 1.68 \times 10^{-4}$ M and 320 nm.

The system was also studied by the isomolar series method. The mixtures were prepared by mixing solutions of orthotelluric acid, sodium tungstate, and nitric acid at the same concentrations and in the same sequence as in the preceding experiments. The results of the measure-ments are presented in Fig. 3, which shows (curves 1—3) that the formation of heteropolyacids of different composi-tions in solution begins with the molar ratio $W:Te^{VI} = 4$. The isomolar series curves for tellurium(IV) have an inflection corresponding to the molar ratio $W:Te^{IV} = 2.$[7] The minimum degree of condensation of tungsten in the formation of the tellurium(IV) heteropolyacids was calcula-ted by the method proposed by Vorob'ev et al.[8] and was found to be 2.[7] Comparison of the isomolar series curves and the results of the calculation for the tellurium(IV) heteropolyacids also led to a conclusion concerning the minimum condensation of tungsten for tellurium(VI) heteropolyacids. It was found to be 4. The formation of the $Te^{VI}-4W$ anions may be represented as follows:

$$H_2[TeO_2(OH)_4] + 4H_2WO_4 \rightarrow H_6TeO_6 \cdot 4H_2WO_4.$$

We compared the mechanisms of the formation of tellurium(IV) and tellurium(VI) heteropolyacids based on the tellurite $[TeO_2(OH)_2]^{2-}$ and orthotellurate $[TeO_2(OH)_4]^{2-}$ (Biryukov and Ganelina[9]) ions and concluded that the formation of the heteropolyanions is associated primarily with the substitution of the hydroxy-groups in the tellurite and orthotellurate anions by tungstic acid molecules.

Thus the central unit produced on formation of the orthotelluric acid—sodium tungstate complex at pH 3 is the $Te^{VI}-4W$ heteropolyacid, which should be regarded as

the basis for the formation of heteropolyanions containing more tungsten.

The stability of the central $Te^{VI}-4W$ group was estimated. The experimental results were treated as before[10]. Table 1 presents the calculated degrees of binding in the complex, degrees of complex formation, and the stability constants of the $Te^{VI}-4W$ heteropoly-acids[11].

$$\beta = \frac{[complex]}{[Te]_{eq}\,[WO_4^{2-}]_{eq}^4} \quad (\beta = \text{stability constant});$$

$$\Phi = \frac{c_{Te}}{[Te]_{eq}} \quad (\Phi = \text{degree of binding in the complex})$$

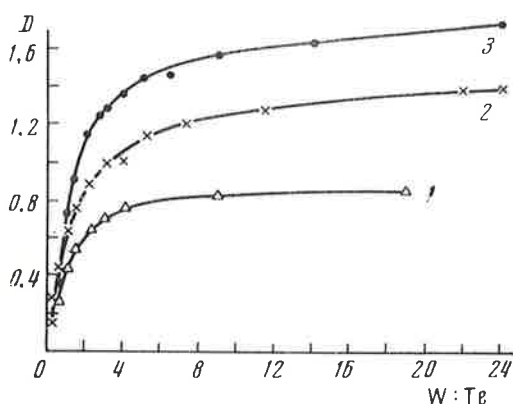$$\alpha = \frac{[complex]}{c_{Te}} \quad (\alpha = \text{degree of complex formation}).$$

Figure 3. Isomolar series curves for the $H_6TeO_6-Na_2WO_4-HNO_3-H_2O$ system at 350 nm:
1) $\Sigma[Te + W] = 3.36 \times 10^{-3}$ M;
2) $\Sigma[Te + W] = 4.20 \times 10^{-3}$ M;
3) $\Sigma[Te + W] = 5.04 \times 10^{-3}$ M.

The equilibrium concentrations of tellurium and tungsten were calculated from the following relations:

$$[Te]_{bound} = \frac{D_x}{D_0}[Te]_{tot},$$

$$[Te]_{eq} = [Te]_{tot} - [Te]_{bound} = [Te]_{tot}\frac{D_0 - D_x}{D_0},$$

$$[W]_{bound} = 4[Te]_{bound}.$$

where D_0 is the optical density of the solution corresponding to the complete binding of tellurium in the heteropoly-anion and D_x are the optical densities of the test solutions.

The stability constant of the $Te^{VI}-4W$ complex is $(2.9 \pm 1.3) \times 10^{18}$, i.e. the data in Table 1 show that the $Te^{VI}-4W$ central HPA cell is stable in solution.

An attempt was made to elucidate the mechanism of the further saturation of the $Te^{VI}-4W$ heteropolyacid by tungsten. The method proposed by Barbanel'[12] based

on the analysis of differential spectra, was chosen for this purpose. The $\Delta D - \lambda$ curves remain unchanged when only one complex is present, ΔD being the optical density of the solution measured relative to that of the reference liquid. When the non-complexed ion and two or more complexes are formed, $\gamma = \Delta D_{\lambda_1}/\Delta D_{\lambda_2} \neq$ const. This method is designed to determine the region of existence of complexes in the continuous series ML_1, ML_2, ..., ML_n. The linear relation between the experimental quantity $f^{n_2-n_1}$ and $[L]^{n_2-n_1}$, where $f = (\Delta L^{n_2-n_1}/\Delta\gamma)^{1/2}$, L is the ligand, and $n_2 - n_1$ is the number of ligands species added on passing from a lower to a higher complex, may serve as a criterion of the simultaneous presence in the solution of the complexes ML_1 and ML_2.

Table 1. Data used in the calculation of the stability constants of the $Te^{VI}-4W$ heteropolyanion ($c_{Te} = 1.68 \times 10^{-4}$ M, $D_0 = 0.165$).

D_{350}	$10^4\,W_{tot}$	$10^4\,[W]_{bound}$	$10^4\,[W]_{eq}$	$[Te]_{bound} = 10^4 \times [complex]$	$10^4\,[Te]_{free}$	Φ	α	$10^{-18}\beta$
0.095	2.55	2.31	0.24	0.58	1.12	1.51	0.32	2.3
0.112	2.97	2.74	0.23	0.68	1.02	1.66	0.40	2.7
0.129	3.40	3.15	0.25	0.79	0.91	1.86	0.46	3.2
0.150	3.82	3.60	0.22	0.90	0.80	2.12	0.52	3.6
0.165	4.25	4.00	0.25	1.00	0.70	2.42	0.56	4.00

Mean $(2.9 + 1.3) \cdot 10^{18}$

Table 2. Data used in the calculations of the function f for different W : Te ratios.

Molar ratio W : Te	$\gamma_1 = \frac{\Delta D_{320}}{\Delta D_{350}}$	$\gamma_2 = \frac{\Delta D_{320}}{\Delta D_{340}}$	$\gamma_3 = \frac{\Delta D_{340}}{\Delta D_{350}}$	$\Delta n_1 = 2$		$\Delta n_2 = 4$	
				$f_1 = \sqrt{\frac{\Delta L^2}{\Delta\gamma_1}}\cdot10^4$	$f_2 = \sqrt{\frac{\Delta L^2}{\Delta\gamma_3}}\cdot10^4$	$f_3 = \sqrt{\frac{\Delta L^4}{\Delta\gamma_1}}\cdot10^7$	$f_4 = \sqrt{\frac{\Delta L^4}{\Delta\gamma_2}}\cdot10^7$
2:1	1.28	1.54	1.79				
4:1	1.25	1.49	1.69	6.65	7.28	2.17	2.61
6:1	1.28	1.53	1.75	6.52	6.95	2.12	2.20
8:1	1.25	1.50	1.70	6.52	7.28	2.12	2.61
10:1	1.29	1.52	1.75	6.79	6.79	2.21	2.21
12:1	1.31	1.54	1.77	6.79	6.79	2.21	2.21
14:1	1.26	1.52	1.74	6.39	6.95	2.13	2.20
16:1	1.27	1.52	1.73	6.52	7.11	2.12	2.31
18:1	1.32	1.59	1.79	6.27	7.28	2.04	2.61
20:1	1.34	1.59	1.82	6.52	6.79	2.21	2.21

In the present study, we recorded the differential spectra in the wavelength range $320-370$ nm for the $H_6TeO_6-Na_2WO_4-HNO_3-H_2O$ system at pH 3. The W : Te ratio in the system was varied from 2 to 20. The reference solution was prepared as follows: 1 ml of 9.4×10^{-3} M orthotelluric acid and water were placed in a 50 ml volumetric flask, the solution being acidified with nitric acid to pH 3. The values of γ obtained varied from 1.29 to 1.75 for the system with the ratio W : Te = 6. Therefore the results of the spectrophotometric measurements were treated as in Barbanel''s work[12].

Table 2 presents the results of the calculation of γ and the function f. The values of γ were calculated as the ratio $\Delta D_{\lambda_1}/\Delta D_{\lambda_2}$, where $\lambda_2 - \lambda_1 = 10$ nm. We investigated a system with a constant tellurium concentration of 1.68×10^{-4}, that of tungsten being varied from 3.36×10^{-4} to 3.36×10^{-3} M. In the calculations of the function $f = (d\gamma/dL^{\Delta n})^{-1/2}$, the change in ligand concentration $\Delta[L]$ was constant and equal to 3.36×10^{-4} M. Table 2 presents the results of the calculation by Barbanel''s method[12] for the system with W : Te = 2.20, a constant value of $\Delta[L]$ and $\Delta n = 2.4$, Δn being the change in the number of tungsten groups in the heteropolyacid.

Examination of columns 5–8 in Table 2 shows that the functions f remain almost constant on passing from system to system. The virtual constancy of f for solutions of all compositions (with various W : Te molar ratios) is evidence that the change from one heteropolyacid composition to another does not take place abruptly and does not entail an alteration of structure, the change being gradual and involving the same structural cell. This conclusion confirms the mechanism of the formation of the tellurium-(VI) heteropolyacids and accounts for their wide variety.

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Polarographic Behaviour of Molybdovanadogermanic Acid and Its Reduction Products in Aqueous and Alcoholic Solutions

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The conditions governing the formation of the blue complex have been investigated by the potentiometric titration of molybdovanadogermanic acid in sulphuric acid solution with a solution of ascorbic acid. Blue compounds consisting of molybdogermanate complexes containing not more than three molybdenum(V) atoms have been isolated by the ether adduct method.

The properties of the yellow and blue complexes in aqueous and alcoholic solutions have been investigated polarographically with 1 M sulphuric acid solution as the supporting electrolyte. An alcoholic solution of molybdovanadogermanic acid has been electrolysed at a controlled potential and the electrolysis products have been determined. The number of electrons involved in the reduction of the yellow complex has been estimated by polarographic microcoulometry. A mechanism is proposed for the reduction of the molybdovanadogermanate complex at the dropping mercury electrode.

The molybdovanadogermanic acid $GeO_2.10MoO_3.V_2O_5. .nH_2O$ (Ge−Mo−V) was obtained for the first time by Ivanov-Emin[1] in the form of yellow-orange octahedral crystals. Other methods for the preparation of the Ge−Mo−V complex have been described in the literature[2,3]. The properties of the compound have been investigated spectrophotometrically[4] and potentiometrically[5]. A reduced form of the Ge−Mo−V acid has been obtained in solution and some of its properties have been studied[4,6].

The study of the properties of the Ge−Mo−V complex and of its reduced form in non-aqueous solvents is of undoubted interest. Our aim was to isolate the blue form of the Ge−Mo−V acid in a crystalline state and to investigate the properties of the yellow and blue complexes polarographically in aqueous and alcoholic solutions. The Ge−Mo−V acid was obtained by the ether adduct method[2]. As a check, the product was analysed for germanium, molybdenum, and vanadium by standard methods[2].

The conditions governing the formation of the Ge−Mo−V acid "blue" were investigated by the potentiometric titration of the heteropolycomplex with a solution of ascorbic acid in the presence of 1 N sulphuric acid. A curve with a distinct jump was obtained. Points corresponding to the beginning middle and end of the titration jump were noted on the curve. In subsequent experiments, equal volumes of solutions of the Ge−Mo−V acid were put in three beakers and to each was added a specified volume of ascorbic acid solution corresponding to one of the points noted above. The mixtures were immediately passed through a column filled with KU-2 cation-exchange resin in the H^+-form. The conditions for the separation of the components were found in preliminary experiments on mixtures of solutions of vanadyl sulphate with those of molybdovanadogermanic acid and the "blue". The vanadyl ions were absorbed on the cation exchanger, while the blue complex passed through the column. The vanadyl ions were eluted with 4 M sulphuric acid solution and were determined by titration with potassium permanganate solution. The vanadium content in the test solution were found to be 24.5, 35.0, and 40.3% of the amount present in