Change in the phase state in $LiNO_3-Fe_2O_3$ (1 : 2.5) mixture with change in the preparation conditions.

Preparation conditions		Lithium containing phases, mole %				Phase composition from X-ray diffraction study	Lattice parameter of spinel
t, °C	time, min	"free" Li₂O	Li₀.₅Fe₂.₅O₄ from measurements of σs	LiFeO₂	"free" LiNO₃		
450	5	9.3	2.4	1.52	80.7		
	15	12.4	2.5	7.5	47.6		
	30	16.5	2.6	16.3	0.3		
	45	16.1	2.9	16.5			
	60	15.6	3.3	16.6			
	90	15.2	3.9	16.8			
	120	14.9	4.5	16.2		α-Fe₂O₃ + LiFeO₂	
500	5	14.8	2.9	9.2	37.2		
	15	14.5	3.1	16.7	0.6	α-Fe₂O₃ + LiFeO₂	
	30	13.7	6.9	15.7	0.1		
	45	13.7	7.1	15.6	0.1		
	60	13.6	8.2	15.4			
	90	13.5	14.2	14.4			
	120	13.4	19.2	13.4		α-Fe₂O₃ + LiFeO₂	
550	5	13.0	3.1	16.5	0.5		
	15	11.8	8.8	15.7	0.1	α-Fe₂O₃ + LiFeO₂ + spinel (little)	
	30	9.8	83.7	1.34			
	45	9.3	85.5	1.0			
	60	9.0	90.7	0.26			
	90	8.5	91.1	0.1			
	120	8.3	91.3	0.1			
600	5	11.0	87.7	0.26		80% spinel + little α-Fe₂O₃	8.327
	15	6.1	94.0				
	30	5.15	95.0				
	45	4.60	95.0				
	60	4.20	95.2				
	90	4.08	95.8				
	120	3.6	96.6				
650	5	11.5	88.3	0.3		90% spinel	8.329
	15	4.9	94.5	0.2			
	30	3.9	94.9				
	45	3.84	95.3				
	60	3.72	96.7				
	90	3.60	98.3				
	120	3.50	98.4			95% spinel	8.329
700	5	8.3	90.3	0.3			
	15	5.33	94.0	0.3		100% spinel	8.325
	30	3.22	97.0				
	45	3.11	97.4				
	60	3.06	98.0				
	90	2.91	98.0				
	120	2.82	98.0			100% spinel	8.324
750	5	4.76	93.5	0.35			
	15	3.27	94.0	0.3		96% spinel	8.326
	30	2.16	94.6				
	45	2.16	97.0				
	60	1.96	98.0				
	90	1.87	98.0				
	120	1.83	98.3			100% spinel	8.327

of $Li_{0.5}Fe_{2.5}O_4$.   A review of all the results of the investigation shows that the primary reaction product is lithium orthoferrite

$$Li_2O_3 + Fe_2O_3 \rightarrow 2LiFeO_2$$
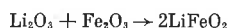
which disappears later as a result of the reaction

$$LiFeO_2 + 2Fe_2O_3 \rightarrow 2Li_{0.5}Fe_{2.5}O_4 .$$
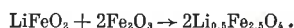
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Reaction of Sodium Tellurite and Potassium Tellurate with Sulphide Ions in Alkaline Solutions

T. N. Greiver and Yu. A. Zaitsev

Complex formation by tellurium(IV) and tellurium(VI) with monosulphide sulphur in alkaline solutions has been investigated. Stepwise complex formation has been found in the $TeO_3^{2-} - S^{2-} - OH^-$ and $TeO_4^{2-} - S^{2-} - OH^-$ systems. The stability constants of the complexes have been calculated by the Bjerrum method from the formation functions of the systems. The effect of the sulphide sulphur : tellurium ratio on the composition of the solutions has been examined. Thio-salts of tellurium(IV) with less than three ligands are unstable and disproportionate into tellurite and trithiotellurite ions. The most stable of the tellurium(VI) thio-salts are the oxomonothiotellurate and tetrathiotellurate.

Tellurium thio-salts are obtained on the dissolution of tellurium dioxide or disulphide in sodium monosulphide and of elemental tellurium and tellurides in polysulphide solutions[1-3]. There are reports of the existence of tellurium(IV) oxothio-salts, trithiotellurite, and tetrathiotellurate[1,4,5]. Despite the fact that these compounds are used in analytical chemistry[6], and in the technology of tellurium production[5,7,8], the composition of the tellurium thio-salts has been studied insufficiently and the stability constants of the compounds are unknown.

The present study aimed to investigate complex formation in the reaction of tellurium(IV) and tellurium(VI) oxosalts with sulphide ions in an alkaline medium. Chemical, spectrophotometric, and potentiometric methods were used.

"Chemically pure" grade reagents and T-AI grade tellurium of 99.99% purity were used for making up the solutions. Sodium sulphide nonahydrate was recrystallised twice. Potassium tellurate was made by oxidising an aqueous suspension of tellurium with hydrogen peroxide and then neutralising the solution with potassium hydroxide.
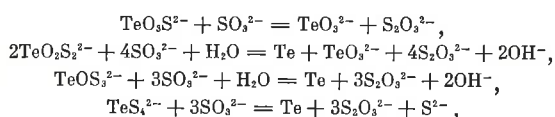
Sodium tellurite was made by oxidising tellurium with nitric acid, removing the latter, and then dissolving the tellurium dioxide in sodium hydroxide solution. NaOH or KOH (1 M) was introduced into all the solutions to suppress the hydrolysis.

The introduction of sodium sulphite into the solutions of the Te^{IV}–S^{2-} system at any S : Te ratio is accompanied by the precipitation of elemental tellurium. The molar ratio of tellurium to thiosulphate† in the reaction products is close to 2, which corresponds to the reaction:

$$TeO_3^{2-} + 2S^{2-} + 2SO_3^{2-} + 3H_2O = Te + 2S_2O_3^{2-} + 6OH^-.$$
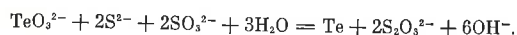
In the Te^{VI}–S^{2-} system at the molar ratio S : Te $\leqslant$ 1 the introduction of sulphite is not accompanied by precipitation. At the ratio S : Te = 2 half the tellurium is precipitated and the $S_2O_3^{2-}$: Te_{el} molar ratio in the products is close to 4. At the ratio S : Te $\geqslant$ 3 the tellurium is completely precipitated from the solution and the $S_2O_3^{2-}$: Te_{el} molar ratio in the reaction products is close to 3.

The observed quantitative relations are well described by the equations:

$$TeO_3S^{2-} + SO_3^{2-} = TeO_3^{2-} + S_2O_3^{2-},$$
$$2TeO_2S_2^{2-} + 4SO_3^{2-} + H_2O = Te + TeO_3^{2-} + 4S_2O_3^{2-} + 2OH^-,$$
$$TeOS_3^{2-} + 3SO_3^{2-} + H_2O = Te + 3S_2O_3^{2-} + 2OH^-,$$
$$TeS_4^{2-} + 3SO_3^{2-} = Te + 3S_2O_3^{2-} + S^{2-},$$

and show the formation (in addition to tetrathiotellurate) of stable oxothio-salts of Te^{VI} with less than three sulphur ligands.

The molar absorptivities of the solutions of our systems were measured on an SF-4 spectrophotometer. The solutions of the tellurium thio-salts exhibit an appreciable optical density in the blue–violet and ultraviolet ranges of the spectrum, increasing smoothly with decrease in the wavelength.

The change in the optical density of the solutions of the Te^{IV}–S^{2-} system as the S : Te ratio is increased from 0 to 3 obeys the Beer–Lambert law satisfactorily, which suggests the formation of a single stable ionic complex. A further increase in the S : Te ratio up to 6 is accompanied by a non-linear increase in the molar absorptivity, evidently owing to the formation of complexes with > 3 S^{2-} ligands.

Solutions of the Te^{VI}–S^{2-} system at the molar ratio S : Te $\leqslant$ 1 do not absorb in comparison with the standard (K_2TeO_4 at the same concentration) in the visible range and only slightly absorb in the ultraviolet. On increasing the ratio to S : Te > 1 a non-proportional increase in the intensity of the colour is observed up to the ratio S : Te $\simeq$ 6–10. These results show the formation in this system of a stable oxothio-complex with a single sulphur ligand in the inner sphere and suggest that in addition to the tetrathiotellurate ion several other sulphur-containing ions are formed when there is an excess of sulphide ion.

Potentiometric titration of alkaline solutions of Te^{IV} and Te^{VI} with sodium monosulphide solution, a tellurium indicator electrode and a saturated calomel half-cell as comparison electrode being used, allows only the formation of trithiotellurite and tetrathiotellurate to be fixed with confidence, these appearing as characteristic breaks on the titration curves.

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† Thiosulphate was determined iodometrically after binding the sulphite ion with formaldehyde and the precipitation of monosulphide sulphur with zinc acetate[9].

When a silver sulphide electrode was used as indicator electrode the data needed for calculating the stability constants of the tellurium thio-complexes formed were obtained. To avoid oxidation, closed vessels and a nitrogen atmosphere were used for the titration.
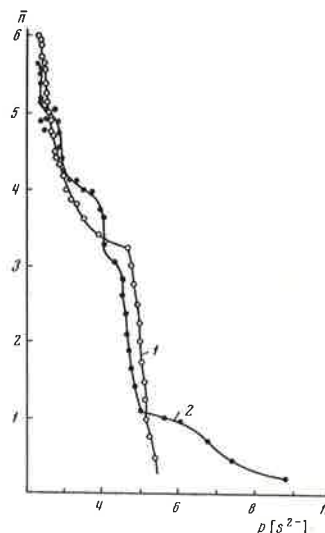

Figure 1. Formation functions of the thio-salts of tellurium in alkaline solution (18°C). *1*) Te^{IV} 0.0078 M, NaOH 1 M; *2*) Te^{VI} 0.0080 M; KOH 1 M.

The total concentration of free sulphide was determined from the calibration curve obtained by potentiometric titration at a silver electrode of 1 N sodium (potassium) hydroxide with sodium (or potassium) sulphide solution. These results were used to calculate the activity of the sulphide ion with allowance for the pH of the solution and the second dissociation constant of hydrogen sulphide. To check the reliability of the results we calculated the solubility product of silver sulphide:

$$\lg SP_{Ag_2S} = \frac{\varphi_{meas} - \varphi_0 + 0.029 \lg a_{S^{2-}}}{0.029},$$

where φ_0 is the normal potential of the silver electrode, and φ_{meas} the measured potential of the silver sulphide electrode referred to the hydrogen scale. The value found ($10^{-49.5}$) is close to the published value. The results were used to construct formation functions and calculate the stability constants of the tellurium thio-complexes.

Fig. 1 gives the formation functions of the complexes in these systems, that is, the variation of the mean coordination number $\bar{n} = c_{S \ bound}/c_{Te}$ with $p[S^{2-}]$. As the results show, in both systems there is stepwise complex formation. In each instance the maximal number of sulphur ligands in the inner sphere of the complex (n) is 6.

The results of the measurements were treated by the Bjerrum method[10,11]. Approximate values of the stepwise stability constants were found by the equation:

$$k_n = \frac{1}{[S^{2-}]_{\bar{n}=n-\frac{1}{2}}}.$$

and then more accurate values were obtained by the method of successive approximations. The maintenance of a constant high concentration of OH^- groups in the solutions makes it unnecessary for the activity of the OH^- ions to be included in the equation for the equilibrium constants. The activities of the other ions were replaced by their concentrations.

Tetrathiotellurite appears in appreciable quantities at the ratio $S:Te \simeq 2-2.5$ and becomes predominant at $S:Te = 5$. A large excess of sulphide is necessary for the formation of appreciable amounts of penta- and hexa-thiotellurite.

The bond with the first sulphur ion has characteristic high strength in the tellurium(VI) thio-salts. The intermediate di- and tri-thiotellurate ions are present in relatively small quantities at $S:Te \leqslant 3$ and partly disproportionate into monotellurate and tetrathiotellurate.

The composition found for the solutions of tellurium thio-salts agrees well with the above-mentioned peculiarities of the chemical behaviour and optical properties of the thio-compounds of tellurium in various oxidation states.

Exponents of the stability constants of the tellurium thio-complexes (18°C).

No. of sulphur ligands in the inner sphere of the complex	Tellurium(IV)		Tellurium(VI)	
	stepwise	cumulative	stepwise	cumulative
	pk_n	pk_n	pK_n	pk_n
1	−4.50	−4.50	−7.39	−7.39
2	−3.71	−8.21	−4.06	−11.45
3	−7.11	−15.32	−5.04	−16.49
4	−3.97	−19.29	−4.35	−20.84
5	−2.55	−21.84	−2.90	−23.74
6	−2.00	−23.84	−2.49	−26.23

It is notable that the formation constants of the first three thio-complexes of tellurite and first four of tellurate have been determined sufficiently reliably. For complexes of higher degree, the concentration of combined sulphide ion is determined as the difference between two relatively large quantities which makes the calculation considerably less accurate. The Table gives the values found.
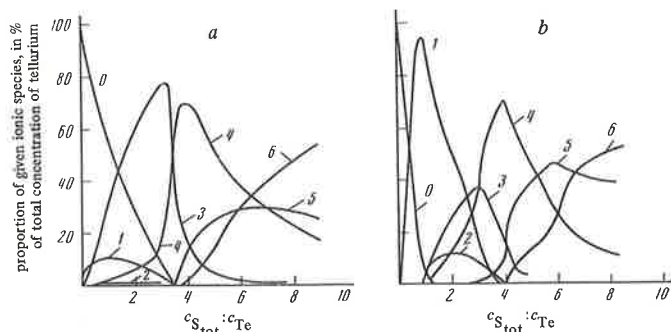

Figure 2. Ionic composition of solutions of the tellurium thio-salts. The numbers against the graphs correspond to the number of coordinated ligands. a) $TeO_3^{2-}-S^{2-}-OH^-$ system; b) $TeO_4^{2-}-S^{2-}-OH^-$ system.

The stability constants obtained were used to calculate the amounts of the various forms of tellurium ions in the solution (Fig. 2).

As the results show, the tellurium(IV) thio-complexes with $n = 1-2$ are unstable and disproportionate into tri-thiotellurate and oxo-salt.

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