THE OXIDES AND OXYACIDS OF TELLURIUM

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I. INTRODUCTION

Tellurium, like sulfur and selenium, readily forms oxides which can be hydrolyzed to produce oxyacids. The more metallic nature of tellurium and its amphoteric behavior are reflected in the chemistry of the oxides and oxyacids.

Considerable data are available on the most stable oxide, tellurium dioxide. However, much less is known of the other oxides, TeO, TeO_3, and Te_2O_5. The pentoxide was discovered only recently as one of the products of the thermal decomposition of orthotelluric acid, H_6TeO_6 (116).

Of the oxyacids, H_2TeO_3, H_6TeO_6, and H_2TeO_5, orthotelluric acid is of particular interest in view of the marked difference in its structural and ionization properties from those of the corresponding sulfur and selenium acids and of its tendency to polymerize to form metatelluric acid, $(H_2TeO_4)_n$.

This work presents for the first time a critical review of the preparation and properties of the oxides and oxyacids of tellurium, together with relevant electrochemical data.

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II. TELLURIUM MONOXIDE, TeO

A. EXISTENCE

The first attempts by Berzelius (92) to prepare tellurium monoxide from tellurium and tellurium dioxide and by the action of dry sodium carbonate on tellurium dichloride were unsuccessful. Later, Divers and Shimosé (92) reported the preparation of the monoxide by heating $TeSO_3$ to 180–230°. This work was confirmed by Doolan and Partington (25), who showed the red $TeSO_3$ to be stable to 180°, at which temperature it slowly became black. On heating to 225°, they obtained a gray powder which looked like powdered tellurium, but which was less dense and gave the correct analysis for TeO (theoretical: Te, 88.85%; found: Te, 87.84%). Damiens (23) concluded that the material described by Divers and Shimosé was actually a mixture of tellurium and tellurium dioxide. More recently, Glemser and Poscher (50) attempted the preparation of the monoxide by (a) heating Te + TeO_2; (b) thermal decomposition of $TeSO_3$; and (c) oxidation of Te with NO_2. Although the chemical analyses of the products of (b) and (c) gave the values expected for TeO (theoretical: Te, 88.85%; found: Te, 88.89 and 89.23%, respectively), X-ray analysis of all three products showed only a mixture of tellurium and tellurium dioxide. Consequently, the existence of tellurium monoxide in the solid phase is doubtful.

B. VAPOR PHASE SPECTRA

Although it seems fairly well established that tellurium monoxide has not yet been formed in the solid phase, there is considerable evidence for its existence in the vapor. Both the emission and absorption spectra of this molecule have been recorded. Shin-Piaw (123) obtained the absorption spectrum of TeO by simply heating the compound in an open porcelain tube, in an electric furnace. Above 1000°, if the vapor density is sufficiently low, the absorption spectrum of the diatomic molecule TeO appeared, superimposed on the spectrum of tellurium dioxide. The emission spectrum of tellurium monoxide has been obtained using three different discharge techniques, giving generally similar results. Shin-Piaw (122) passed an electric discharge between platinum electrodes in a heated tube containing tellurium vapor and oxygen, and obtained a spectrum, in the region 3190–3820 A, which consisted of 30 bands. From this, the fundamental frequencies of 796.1 cm^{-1} in the ground state and 372.9 cm^{-1} in the excited state were obtained, and a dissociation energy of 5.70 ev was calculated for the ground state. However, Shin-Piaw (124) reported elsewhere dissociation energies of 0.4 (normal) and 2.7 ev (excited). Purbrick (113) used an electrodeless quartz discharge tube containing tellurium, oxygen, and argon and found essentially the same spectrum in the 3075–3825-A region, plus an additional band system in the region 3825–4875 A. Dissociation energies of 3.03 ev for the ground state and 0.92 ev for the excited state of the 3075–3825-A band system were calculated using the equation $D_e = \omega_e^2/4X_e\omega_e$. A high voltage dc arc between tellurium electrodes in air, or between zinc rods fed with tellurium powder, has been used to obtain the emission spectrum of TeO (58). This study produced three band systems in the region 2600–6200 A, with fundamental frequencies of 408.8, 370.1, and 524.6 cm^{-1} (Purbrick's values for the first two systems are 409.5 and 373.6 cm^{-1}, respectively). Herzberg (61) gives values of 370.1 and 796.0 cm^{-1} for fundamental frequencies, ω_e, of the excited and normal states, respectively, and the corresponding values of $\omega_e X_e$ are 5.10 and 3.50. Dissociation energies of 2.728 and 3.453 ev are given depending on whether the dissociation products of the A state are in $^1D + {}^3P_2$ or $^3P_0 + {}^3P_2$. Gaydon (43) compared the observed dissociation energy (D_0 = 2.725 ev) with the value calculated using the Birge–Spooner linear extrapolation ($D_{\text{lin}} = \omega_e^2/4\omega_e X_e - {}^1/_2\omega_e$ = 5.76 ev for TeO) and values of ω_e and $\omega_e X_e$ from Herzberg. A semi-empirical δ-function model of chemical binding has been used to calculate the bond properties of diatomic molecules (86). The calculated dissociation energies D_0 = 77.0 kcal/mole (3.34 ev) and D_e = 78.1 kcal/mole (3.39 ev) compare with observed D_0 values of 62.9 and 79.5 kcal/mole (2.73 and 3.45 ev, respectively), and the calculated value of ω_e = 824 cm^{-1} corresponds to the observed value of 796 cm^{-1}. The calculated value of $\omega_e X_e$ of 4.47 is significantly higher than the value of 3.50 reported by Herzberg. Using the formula $\omega = 2.065 \times 10^{-3}(Z_1 - Z_2)^{1/4}\mu^{1/2}r_e^{-0.92}$ (cm^{-1}) for the fundamental frequency, Guggenheimer (52) obtained ω for TeO of 768 cm^{-1} using the value of 1.82 A for r_e. Although Barrow and Hurst (8) also report a value of r_0 = 1.828 A, Lippincott and Dayhoff (86) record a value of r_e = 1.74 A. When this value is substituted in the equation used by Guggenheimer, a value of ω = 800 cm^{-1} is obtained, in good agreement with the experimental value of 796 cm^{-1}. A summary of bond lengths, fundamental frequencies, and dissociation energies of tellurium monoxide is given in Table I.

Although the observed spectra of TeO reported by various authors are in fairly good agreement, with the more recent work giving more bands and possibly better resolution and accuracy, there is considerable disagreement concerning the treatment of these data and the derivation of values from the spectra. The fundamental frequency for the normal state is almost certainly 796 cm^{-1}, and for the excited state probably in the region 370–374 cm^{-1}. The value reported by Kelly and King (74), *viz.*, 789 cm^{-1}, is probably a misprint, since Herzberg is cited as a reference. The

TABLE I

BOND LENGTHS, FUNDAMENTAL FREQUENCIES, AND DISSOCIATION ENERGIES OF TeO

	Fundamental frequency		Dissociation energy, ev				
			Normal		Excited		
Bond length, A	Obsd[a]	Calcd	Obsd	Calcd	Obsd	Calcd	Ref
			0.4		2.7		124
	796.1 (n)		5.70				122
	372.9 (e)						
				5.76	2.725		43
	796 (n)				2.728		61
	370.1 (e)				3.453		
1.74	796	824		3.39	2.727	3.34	84
					3.45		
	370.1 (e)						58
1.82	796.1	768					52
	373.6 (e)				3.03		111
					0.93		
1.828							8
	789						74
		800					This work[b]
1.823							12

[a] n = normal state; e = excited state. [b] Calculation of ω using $\omega = 2.065 \times 10^{-3}(Z_1 - Z_2)^{1/4} \mu^{1/2} r_e^{-0.92}$ with r_e = 1.74 A.

reported values of some of the dissociation constants are interrelated. It appears that Shin-Piaw's original value for the dissociation constant of tellurium monoxide in the excited state, 2.7 ev, was recalculated by Gaydon to 2.725 ev, corrected by Herzberg to 2.728 ev, and converted to 62.9 kcal/mole (2.727 ev) by Lippincott and Dayhoff (86).

C. THERMOCHEMICAL DATA

There are very few thermochemical data available on tellurium monoxide, and, because of the instability of the oxide, the thermochemical values have been calculated from spectroscopic data. Table II lists the heat and free energy of formation of gaseous TeO reported by Coughlin (22) for the reaction

$$Te + {}^1/{}_2O_2 \longrightarrow TeO$$

Phase changes for the element occur at 723 (melting point) and 1360°K (boiling point).

TABLE II

HEAT AND FREE ENERGY OF FORMATION OF TeO(g)

T, °K	ΔH, kcal/mole	$\Delta F°$, kcal/mole
298.16	+43.0 ± 10.0	+36.5 ± 10.5

Using Herzberg's data (61), Kelly and King (74) calculated values of $S_T° = 40.80$, $S_r° = 14.80$, $S_v° = 0.22$, and $S_{298}° = 55.8 \pm 0.5$ eu. From these same data, Kelly (73) tabulated the values of $H_T - H_{298.15}$ and $S_T - S_{298.15}$ which are recorded in Table III. The formula calculated from these values was

$$H_T - H_{298.15} = 8.44T + 0.16 \times 10^{-3}T^2 + 0.83 \times 10^{-5}/T - 2809$$

and was accurate to 0.3% in the range 298 to 2000°K. The heat capacity equation was obtained by differentiation

$$C_p = 8.44 + 0.32 \times 10^{-3}T - 0.83 \times 10^{-5}/T^2$$

The accuracy of these values must depend on the accuracy of the spectroscopic data from which they were derived, but they must be considered the best values, since there are no others available for comparison.

TABLE III

HEAT CONTENT AND ENTROPY OF TeO(g)

T, °K	$H_T - H_{298.15}$, kcal/mole	$S_T - S_{298.15}$, cal/deg mole	T, °K	$H_T - H_{298.15}$, kcal/mole	$S_T - S_{298.15}$, cal/deg mole
400	.795	2.29	1000	5.895	10.03
500	1.610	4.11	1200	7.650	11.63
600	2.445	5.63	1400	9.410	12.99
700	3.295	6.94	1600	11.180	14.17
800	4.155	8.09	1800	12.955	15.22
900	5.020	9.11	2000	14.730	16.15

III. TELLURIUM TRIOXIDE, TeO_3

Tellurium trioxide is reported to exist in two forms. The common, readily prepared α form is a bright yellow, amorphous powder with a density of 5.075 (95). It is insoluble in cold water and soluble in strong alkali. The more obscure β form is reported to be a gray, microcrystalline material of density 6.21 which is soluble in molten potassium hydroxide, but insoluble in hot water, acid, or alkali solutions (100).

A. PREPARATION AND PHYSICAL PROPERTIES, α-TeO$_3$

Although tellurium trioxide cannot be prepared by the oxidation of tellurium dioxide, it is readily prepared by the thermal decomposition of orthotelluric acid, H_6TeO_6, in air at 300–320° according to the reaction

$$H_6TeO_6 \xrightarrow{300°} 3H_2O + TeO_3$$

This reaction is reversible in boiling water with about 33% of the tellurium trioxide being dissolved in a large excess of water after boiling for 6 days (95). On heating above 400°, TeO_3 decomposes into Te_2O_5, and finally to the stable dioxide, TeO_2 (116). Tellurium trioxide formed by sintering electrolytic mud with soda is unstable and starts to decompose at 350°, with decomposition being complete at 600°, or in the presence of soda, at 700° (128). An attempt was made to measure the decomposition pressure of the reaction

$$2TeO_3 \longrightarrow 2TeO_2 + O_2$$

using a Knudsen cell, but without success mainly because the rate of evolution of oxygen at low temperatures was too slow to allow the attainment of equilibrium in the cell (109). Using a simple static method, it was found that oxygen was given off at temperatures as low as 280°. Thus, in the decomposition of orthotelluric acid, oxygen will be lost from the tellurium trioxide formed even as the last of the water is being driven from the orthotelluric acid. At a temperature of 450°, the decomposition pressure is greater than 1 atm, but the rate of evolution of oxygen is still very low. Because of this low rate of oxygen evolution, which was explained as being due to the low rate of diffusion of oxygen through the layer of tellurium dioxide formed on the surface of the tellurium trioxide particles, the apparent rate of decomposition of tellurium trioxide was dependent on the mode of preparation and the particle size as well as the temperature of decomposition. The reverse reaction

$$2TeO_2 + O_2 \longrightarrow 2TeO_3$$

did not proceed to a measurable extent at the temperatures employed.

There seems to be no structural data on tellurium trioxide except the density (95) and the fact that it is amorphous and does not give an X-ray powder pattern. Although Dutta and Gupta (28) claim to have photographed the absorption spectrum of TeO_3 vapor and compared it with the spectra of N_2O_5 and MoO_3, the fact that they report a melting point of 795° for tellurium trioxide, while other authors report decomposition at about 450° (109) and complete decomposition at 600° (127), casts some doubt on the actual species, the spectrum of which was obtained. A comparison of the general curve given by Dutta and Gupta with the spectral data on tellurium dioxide reported by Shin-Piaw (123) indicates that the spectrum obtained by Dutta and Gupta is probably that of tellurium dioxide rather than tellurium trioxide, since the absorption regions are broad and the differences between the observed values relatively small.

B. PREPARATION AND PHYSICAL PROPERTIES, β-TeO_3

Gray, microcrystalline, β-TeO_3 is said to be formed by heating orthotelluric acid to 320° for 12–15 hr with a trace of sulfuric acid in a sealed tube (34). Although β-TeO_3 is said to give an X-ray powder pattern, the actual data are not reported (96). Attempts to produce β-TeO_3 by the following methods were unsuccessful (116): (a) heating H_6TeO_6 in a sealed tube at 310° for 12–15 hr; (b) heating H_6TeO_6 with concentrated H_2SO_4 (ratios 1:1, 1:2, 1:3) in a sealed tube at 310°; or (c) heating α-TeO_3 in a sealed tube at 310°.

Attempts in this laboratory to prepare β-TeO_3 from orthotelluric acid were similarly unsuccessful. Small samples of orthotelluric acid were sealed in glass tubes, with and without a trace of sulfuric acid, in air and under vacuum. After heating for 15 hr at 300–310°, the samples in air had formed a milky liquid, possibly allotelluric acid (see section VIIA), while the evacuated samples had formed yellow α-TeO_3. After 6 days at 300°, all four samples contained yellow α-TeO_3 with no trace of the gray β form. However, on dissolving one of the samples (no H_2SO_4, evacuated) in concentrated potassium hydroxide, a residue of gray-yellow material remained. After washing with water, Debye–Scherrer X-ray analysis indicated that it was probably a mixture of orthotelluric acid and tellurium dioxide. Heating tellurium trioxide for extended periods increased the number of tellurium dioxide lines present in the X-ray pattern (116). Thus these results and those obtained in this laboratory could explain the X-ray pattern obtained by Montignie (96) but do not explain the density of 6.21 (*cf.* α-TeO_3, 5.07; Te_2O_5, 4.14; TeO_2, 5.75 (rhombic) or 6.07 (tetragonal); H_6TeO_6, 3.2) or the very close analysis obtained (theoretical for TeO_3: Te, 72.7%; found: 72.6%).

C. CHEMICAL PROPERTIES

Tellurium trioxide is an oxidizing agent, and, on boiling with concentrated hydrochloric acid, chlorine is liberated (95, 100). On heating with tellurium trioxide, sulfur, selenium, phosphorus, and carbon are oxidized, and a vigorous reaction occurs with easily oxidizable metals like zinc, aluminum, cerium, manganese, and cadmium, and a less vigorous reaction with iron and bismuth. Sulfides are oxidized to sulfur dioxide, and thus from Cu_2S, PbS, MoS_3, or Bi_2S_3, the sulfates or oxides can be formed. Tellurium trioxide does not react with ammonia at 310°, and hydrogen at 350° only reduces it to tellurium dioxide.

In the cold, hydrazine, semicarbazide, and hydrogen sulfide reduce tellurium trioxide to elemental tellurium, as do molten oxalic acid, potassium cyanide, and potassium thiocyanate. A cold, concentrated sodium sulfide solution reacts only slightly, and, on boiling, tellurium separates. Dilute sulfuric acid gives a mixture of tellurium and sulfur, while sodium thiosulfate, hypophosphorous acid, or a mixture of white phosphorus and water also reduce tellurium trioxide to the element. There is no perceptible reaction between tellurium trioxide and stannous chloride (in acid or alkali), selenium dioxide, or sugar.

Many reagents, such as ammonium salts, potassium borate, citric and acetic acids, iodates, periodates, and alkali tungstates, which react with tellurium dioxide, do not react with tellurium trioxide.

IV. TELLURIUM PENTOXIDE, Te_2O_5

The previously unreported compound Te_2O_5 has been prepared during a thermogravimetric analysis of the decomposition of orthotelluric acid (116). It was formed by heating H_6TeO_6 or α-TeO_3 at 406° for 25 hr, and is stable at room temperature.

Tellurium pentoxide dissolves readily in 30% KOH with effervescence indicative of decomposition. The existence of both tellurium(IV) and -(VI) in the solution was determined chromatographically. The oxygen given off during the disproportionation reduced the amount of tellurium(VI) found in the solution to only 10% of the total.

The density of tellurium pentoxide was found to be 4.14 g/cm^3, and the compound is paramagnetic. The *d* values found using a Debye–Scherrer camera are clearly different from those of tellurium dioxide, and are given in Table IV.

TABLE IV

d VALUES OF Te_2O_5

d	Intensity
3.39	4
3.08	3
2.48	1
2.07	1

V. TELLURIUM DIOXIDE, TeO_2

The most stable oxide of tellurium, TeO_2, occurs naturally as the mineral tellurite or paratellurite with two different crystal structures. It can be prepared by a variety of methods as a white crystalline material which, with the addition of impurities, will solidify in the glassy form. The solid is very slightly soluble in water, more soluble in aqueous sodium hydroxide solution. Tellurium dioxide reacts readily with a wide variety of compounds, forms basic addition compounds, and complexes with organic ions such as citrate and tartrate. Solid tellurium dioxide melts at 732.6°, and its vapor pressure has been studied by a number of authors.

A. PREPARATION

Tellurium dioxide can be prepared by a number of methods. These include the combustion of elemental tellurium in air, the action of nitric or sulfuric acids on tellurium (92), the thermal decomposition of orthotelluric acid or its anhydride, tellurium trioxide, (95), the oxidation of tellurium dichloride by liquid N_2O_4 (6), and the oxidation of tellurium in water or sodium hydroxide solution with oxygen at 60 atm at 150° (135). A convenient method is afforded by the action of nitric acid on tellurium whereby a basic tellurium nitrate is formed which is then thermally decomposed into tellurium dioxide in about 85% yield (88).

Tellurium dioxide is formed from the reduction of telluric acid by tellurium or by osmium at faint red heat ("au rouge naissant") (97). The reaction of vanadium pentoxide with tellurium, instead of forming a vanadium telluride, produces tellurium dioxide (99). Tellurium dioxide can also be precipitated from a potassium hydroxide solution of copper electrolysis sludge by neutralization with sulfuric acid (59). Sponge copper residue, after removal of selenium and containing Na_2TeO_4, TeO_3, or $2CuO \cdot TeO_2$, can be reduced to tellurium dioxide by sulfur (134).

B. CHEMICAL PROPERTIES

Attempts have been made to reduce tellurium dioxide with elemental tellurium to form the monoxide, but without success (50). Moreover, it has been shown that in the Te–TeO_2 system, there is no mutual solubility in either the solid or liquid state up to 800° (14). X-Ray diagrams showed only two pure components, tellurium and tellurium dioxide.

In the presence of water vapor above 600°, tellurium dioxide forms a gaseous hydroxide according to the equation

$$TeO_2 + H_2O \leftrightharpoons TeO(OH)_2$$

(47–49). However, at room temperature the dioxide is only sparingly soluble in water (Table V).

Although tellurium dioxide cannot be oxidized in air to form the trioxide or by nitric acid to tellurium(VI), potassium permanganate will oxidize it to orthotelluric acid (91). Lead dioxide will oxidize tellurium dioxide at 170° to form lead tellurate almost quantitatively if the two solids are sufficiently well mixed (90). A mixture of calcium hydroxide and sodium carbonate (mole ratio 0.5:1.0) will oxidize tellurium dioxide quantitatively in 5 hr at 575°, while a fivefold excess of calcium hydroxide and a temperature of 975° are necessary when no sodium carbonate is used (89). Tellurium dioxide reacts with sodium and potassium carbonates to form normal tellurates and ditellurates, and when heated with ammonium hydroxide, small crystals having the empirical formula $NH_3 \cdot 5TeO_2 \cdot 5H_2O$ were formed (83).

Tellurium dioxide is easily reduced to the metal by phenylhydrazine or hydrazine hydrochloride, and this reaction is used as a method of analysis for tellurium (54, 55). Aluminum, zinc, cadmium, and cerium react vigorously with tellurium dioxide to form tellurium and the oxide of the metal. Silver and bismuth react less vigorously, and mercury does not react at all. The oxides of silver and lead (litharge) react with tellurium dioxide to form tellurides, while bismuth oxide is reduced to elemental bismuth suspended in molten tellurium dioxide. Oxides of nickel and cobalt form tellurites, while molybdenum trioxide forms a telluromolybdate which decomposes into an alloy, soluble only in aqua regia. Chromium sesquioxide does not react with tellurium dioxide but forms a solid solution.

Sulfides of zinc, mercury, lead, antimony, and bismuth liberate sulfur dioxide and tellurium, while the reaction of molybdenum sulfide, MoS_3, with tellurium dioxide is said to form a blue oxide. Ferrous sulfate in acid solution is oxidized by tellurium dioxide to ferric sulfate and tellurium. Ferric chloride undergoes a double decomposition with tellurium dioxide, forming tellurium tetrachloride and ferric oxide. Potassium iodide, in the presence of hydrochloric acid, liberates iodine on reaction with tellurium dioxide, while ammonium thiocyanate, either molten or in a boiling, concentration solution, reduces the dioxide to elemental tellurium. Molten copper thiocyanate forms a copper–tellurium alloy. Tellurium dioxide displaces ammonia from ammonium salts at elevated temperatures, and even at room temperature in some cases. In the case of ammonium chloride, tellurium tetrachloride is formed.

Tellurium dioxide is reduced to tellurium by white phosphorus in boiling water, stannous chromate in alkali medium, aluminum in the presence of potassium hydroxide, zinc in hydrochloric acid, molten oxalic acid, and hot cuprous oxide. With hot ammonium nitrate solution, tellurium dioxide precipitates metallic silver, and boiling Fehling's solution is decolorized with the partial formation of cuprous oxide. Potassium ferricyanide is reduced to the ferrocyanide, but tellurium dioxide will not reduce bivalent copper salts (98). Tellurium dioxide reacts with vanadium pentoxide to form a solid solution with a lower oxide of vanadium.

The reaction of tellurium dioxide with silver sulfide to produce insoluble silver telluride is given as an explanation of the low extraction of tellurium from roasted, water-leached, silver-bearing slimes (107).

Selenium dichloride, Se_2Cl_2, reacts with tellurium dioxide to form tellurium tetrachloride according to the equation (82)

$$TeO_2 + 4Se_2Cl_2 \longrightarrow TeCl_4 + 2SeOCl_2 + 6Se$$

A similar reaction with selenium tetrafluoride at 80° produces tellurium tetrafluoride and selenium oxyfluoride (16).

$$TeO_2 + 2SeF_4 \longrightarrow TeF_4 + 2SeOF_2$$

With nitryl fluoride, NO_2F, tellurium dioxide reacts to form the white solid, nitronium pentafluorotellurite, $(NO_2)TeF_5$, but nitryl fluoride does not react with tellurium trioxide (7).

Tellurium dioxide forms basic addition compounds, $2TeO_2 \cdot SO_3$, $2TeO_2 \cdot HNO_3$, $2TeO_2 \cdot HClO_4$, and $2TeO_2 \cdot HIO_4$, and based on its insolubility in concentrated sulfuric acid or oleum, polymeric insoluble sulfates such as $TeO(OH)(SO_4H)$ or $Te_2O_3(OH)(SO_4H)$ (which can be written as $TeO_2 \cdot H_2SO_4$ and $2TeO_2 \cdot H_2SO_4$, respectively) were postulated (36). Tellurium dioxide is said to form the addition compounds $2TeO_2 \cdot 3HCl$, $TeO_2 \cdot 3HCl$, and $TeO_2 \cdot HCl$, below room temperature (24, 81). By passing hydrogen chloride gas over tellurium dioxide at a given temperature Parker and Robinson (102) obtained a white solid and a yellow liquid of indefinite composition. However, no evidence was found for the formation of a definite addition compound of TeO_2 and HCl in the range 0–150°. From the data given, the experiments do not appear to eliminate the possibility of formation of the complex $TeO_2 \cdot 2HCl$. However, its existence is unlikely.

In the system TeO_2–H_2O–$CuSO_4$ (aq), which is of importance in the industrial production of metallic tellurium from electrolytic sludge, it was found that crystalline tellurium dioxide does not react with a solution of copper sulfate. However, tellurous acid does, forming a green solid of variable composition, $xTeO_2 \cdot yCuTeO_3 \cdot zCuSO_4$ (where $x > y > z$) (142). Melting copper sulfate with tellurium dioxide produced the complex salt $Cu_2[CuTeO_3(SO_4)_2]$ (143).

Although tellurium dioxide is effective as a Friedel–Crafts catalyst and as an oxidizing agent for organic compounds, it is not as good as selenium dioxide owing partially to its low solubility in the usual solvents for these reactions (35).

C. SOLUBILITY

The solubility of tellurium dioxide in various aqueous salt solutions has been studied by a number of authors, and a summary of the available data is given in Table V. All values have been converted to approximately the same units, moles/l. or moles/kg, where possible.

Cheng (17) found a minimum solubility at 25° in water of pH 4.5 of 0.1 mg of TeO_2 per 100 ml (6.3×10^{-6} mole/l.). This value increased sharply with heating especially above 40°, and the mean differential heat of solution from a log M *vs.* $1/T$ plot was found to be 6670 cal/mole for the range 8–80°. Ethanol decreases the solubility of tellurium dioxide drastically, while a variety of ammonium salts generally cause only a slight increase in solubility. The exception is ammonium citrate which causes a 400-fold increase in the solubility of tellurium dioxide, indicating formation of a tellurium–citrate complex.

Although tellurium dioxide is reported to be insoluble in concentrated sulfuric acid and oleum (36), Mellor (92) gives definite solubility values for 20, 30, and 50% aqueous sulfuric acid, but states that

TABLE V

SOLUBILITY OF TeO_2 IN VARIOUS MEDIA

Temp, °C	Medium	Concn	Concn of TeO_2	Ref
18	H_2O	pH 6.5	3.75×10^{-5} mole/l.	64
25	H_2O	pH 4.5	6.3×10^{-6} mole/l.	17
25	NH_4ClO_4	2 moles/l., pH 4.5	1.4×10^{-5} mole/l.	17
25	NH_4NO_3	2 moles/l., pH 4.5	1.5×10^{-5} mole/l.	17
25	NH_4Cl	2 moles/l., pH 4.5	1.3×10^{-5} mole/l.	17
25	$(NH_4)_2SO_4$	0.4 mole/l., pH 4.5	1.5×10^{-5} mole/l.	17
25	(NH_4) citrate	1.0 mole/l., pH 4.5	2.4×10^{-3} mole/l.	17
25	Ethanol	...	$\ll 6 \times 10^{-7}$ mole/l. (graph)	17
...	H_2SO_4	100%	Insoluble	36
...	$H_2SO_4 \cdot SO_3$	...	Insoluble	36
...	H_2SO_4	20%	0.05 mole/l.^{a} (0.7%)	92
...	H_2SO_4	30%	0.065 mole/l.^{a} (0.85%)	92
...	H_2SO_4	50%	0.383 mole/l.^{a} (4.4%)	92
25	$HClO_4$	0.7370 *M*	5.20×10^{-3} mole/1000 g	92
25	$HClO_4$	0.2924 *M*	1.96×10^{-3} mole/1000 g	92
25	$HClO_4$	0.1028 *M*	0.74×10^{-3} mole/1000 g	92
30	$HClO_4$	6 *M*	0.05 *M*	57
...	HCl	Concentrated	Soluble	57
...	HCl	6 *M*	Soluble	57
Hot	$NaBO_2$	Concentrated	Soluble	98
Hot	NaF	Concentrated	Soluble	98
Hot	NH_4F	Concentrated	Soluble	98
18	HCl	0.1 mole/l.	0.57×10^{-3} mole/l.	72
18	HCl	0.22 mole/l.	1.2×10^{-3} mole/l.	72
18	HCl	0.46 mole/l.	3.7×10^{-3} mole/l.	72
18	HCl	0.92 mole/l.	9.1×10^{-3} mole/l.	72
25	HCl	1 *N*, pH 3.8	1.02×10^{-2} mole/l.	64
25	HNO_3	43.72%	0.28 mole/l. (3.56%)	139
70	HNO_3	48.60%	0.24 mole/l. (3.15%)	139
70	Na_2O	15.22%	2.93 moles/l. (40.75%)	78
0	HF	Anhydrous	19% by weight	112
10	HF	22.6 g/100 g H_2O soln	63 g/100 g soln	112

^{a} Appears to be supersaturated. Questionable values.

these are probably supersaturated solutions, since crystallization occurs on standing.

In a study of the exchange between tellurium(IV) and tellurium(VI) as TeO_2 and H_6TeO_6, Hanson and Hoering (57) found that in concentrated and 6 *N* hydrochloric acid, tellurium(VI) was rapidly converted to tellurium(IV), thus implying solubility of tellurium dioxide in hydrochloric acid. No exchange was found in a solution of 6 *N* $HClO_4$ in which the tellurium dioxide concentration was 0.05 mole/l. (not necessarily saturated). Mellor also quotes values for perchloric acid solution, which indicate that Hanson and Hoering's solution was probably far from saturated with respect to tellurium dioxide.

Hot, aqueous solutions of sodium borate and sodium and ammonium fluorides are reported to dissolve tellurium dioxide, but no quantitative data are given (98).

Kasarnowsky (72) reports a series of solubility values for various concentrations of hydrochloric acid at 18°, which agree well with the value of the minimum solubility of tellurium dioxide in 1 *N* HCl at the isoelectric point of pH 3.8 (64).

In nitric acid solution, the formation of basic tellurium nitrates increases the solubility to the highest value for any acid solution (139), except the 50% sulfuric acid solution quoted by Mellor, which is questionable.

The formation of tellurates in the system Na_2O–TeO_2–H_2O is responsible for the maximum solubility of almost 3 moles/l. of tellurium dioxide in a 15.22% solution of Na_2O in water at 70° (79). This solubility decreases again as the concentration of sodium hydroxide increases, and the maximum occurs when there is a very slight molar excess of tellurium dioxide over sodium oxide. The solubility is somewhat less at 25° (78).

The solubility of tellurium dioxide in aqueous and anhydrous hydrogen fluoride was studied by Prideaux and Millott (111, 112).

A summary of the solubility of tellurium dioxide in various media is given in Table V.

D. SPECTRA

The emission spectrum of tellurium dioxide was first mentioned by Howell and Rochester (63), but no details are given. The absorption spectrum of tellurium dioxide vapor in a heated, open porcelain tube has been compared with the spectra of sulfur dioxide

TABLE VI

EQUATIONS FOR VAPOR PRESSURE OF TeO_2

Equation	Temperature range, °C	Ref
$\log P(\text{mm}) = -12{,}000/T + 10.947$ (Eq 1)	573–733	129
$\log P(\text{mm}) = -11{,}300/T + 10.247$ (Eq 2)	733–938	129
$\log P(\text{mm}) = -13{,}169/T + 12.257$ (Eq 3)	457–704	144
$\log P(\text{mm}) = -13{,}292.9/T + 12.4185$ (Eq 4)	600–733	109
$\log P(\text{mm}) = -13{,}222/T + 12.3284$ (Eq 5)	450–733	109
$\log P(\text{mm}) = -12{,}650/T + 11.66$ (Eq 6)	640–720	48

and selenium dioxide (123). A complete analysis is not given, but two periodicities of 650 and 210 cm^{-1}, corresponding to the normal and excited states, were noted. Duchesne and Rosen (26) related all the bands in the electronic spectrum of tellurium dioxide vapor to only one valence symmetric frequency in each state, $V_1'' = 815$ cm^{-1} and $V_1' = 650$ cm^{-1}. In a later paper (27), objections were raised toward the analysis by Spin-Piaw, although the spectral data obtained agree quite well. Corrected values of $V_1'' = 810$ cm^{-1} and $V_1' = 670$ cm^{-1} are also given. Walsh (140) has noted that the only strong upper-state frequency for tellurium dioxide is at 650 cm^{-1} due to symmetric stretching, while the ground-state frequency is 815 cm^{-1}.

A study of the infrared and Raman spectra of the crystalline (tetragonal) and glassy tellurium dioxide indicates that the glassy and crystalline states have similar structures, *i.e.*, tetrahedral (18). From the selection rules, the symmetry group is considered to be D_4, and partial assignments of absorption bands have been made on this basis.

E. THERMOCHEMICAL DATA

The melting point of white, tetragonal tellurium dioxide, determined by extrapolation of the heating curves, was found to be 732.6 ± 1° (1005.8°K) (126), and confirmed visually to be 733 ± 1° in a quartz capillary tube (129). The vapor pressure of tellurium dioxide has been measured by both effusion and dynamic methods, by different authors, leading to similar vapor pressure equations and generally similar values for the heat of sublimation. A Knudsen cell was used for vapor pressure measurements of solid tellurium dioxide, while the dynamic method was used at temperatures above the melting point (129). The experimentally determined vapor pressure equations, with their ranges of validity, are given in chronological order in Table VI.

Equation 4 was calculated by Prescher and Schroedter (109) from their own data, and Eq 5 was calculated using these data plus those of other investigators (129, 137, 144). Glemser's more recent data simply confirm the previous results (48). Since all these data are in good agreement, the best vapor pressure equation for tellurium dioxide is probably Eq 5.

The heats of sublimation calculated from the vapor pressure equations are given in Table VII.

TABLE VII

HEAT OF SUBLIMATION OF TeO_2 (kcal/mole)

Equation (Table VI)	ΔH_s	Temp, °C	Ref
1	54.9	573–733	129
3	60.1 ± 0.6	581	144
4	60.8 ± 3	600–733	109
5	60.5	450–733	109
6	57.8	640–720	48
. . .	57.5	631.6	137

Soulen's value from Eq 1 seems to be in error, although it is based mainly on the data of Uyeno combined with two confirmatory values of his own below the melting point. The average of the other values is 59.3 kcal/mole, and the best estimate of the heat of sublimation of tellurium dioxide is probably 59 ± 2 kcal/mole.

The heat of fusion of tellurium dioxide has been measured calorimetrically and estimated from the vapor pressure data of the solid and the liquid. The values are given in Table VIII.

TABLE VIII

HEAT OF FUSION OF TeO_2 (kcal/mole)

ΔH_f	Method	Ref
3.2 ± 0.5	Vapor pressure	129
7.3	Calorimeter	109
6.95 ± 0.1	Calorimeter	94
6.0 ± 2	Vapor pressure	94

The calorimetric data are in fairly good agreement and compare favorably with the value calculated by Mezaki and Margrave (94) from three sets of vapor pressure data. The extremely low value of 3.2 kcal/mole (129) is due to an error in estimating the heat of sublimation, although the value of the heat of vaporization is probably correct. The heat of fusion, calculated from the best value of the heat of sublimation, 59 kcal/mole, and the value of 51.7 kcal/mole (129) for the heat of vaporization, is 7.3 kcal/mole, which is also the value found calorimetrically by Prescher and Schroedter (109). The best value of the heat of fusion of tellurium dioxide is thus 7.0 ± 0.5 kcal/mole. The only experimentally determined value of the heat of vaporization of tellurium dioxide is 51.7 kcal/mole (129) for the range 733–938°. The heat of vaporization calculated from the heats of sublimation and fusion is 52 kcal/mole, confirming the above value.

Using calorimetry, Mezaki and Margrave (94) measured the heat capacity of tellurium dioxide and calculated the equation

$$C_p = 15.58 + 3.48 \times 10^{-3}T - 1.20 \times 10^5/T^2$$

which is valid in the range 193–687°. At 300°K, the heat capacity of tellurium dioxide was 15.28 cal mole^{-1} deg^{-1}. In the range of liquid tellurium dioxide from 745 to 873°

$$C_p = 26.92 + 0.52 \times 10^{-3}T$$

A similar equation

$$C_p = 15.667 + 333666 \times 10^{-3}T$$

was obtained (110) for the range 25–733° from which a value of 16.68 cal mole^{-1} deg^{-1} was calculated for 25°, and using the more accurate equation

$$C_p = 19.655 - 8.706 \times 10^{-4}T - 3.97537 \times 10^5/T^2$$

a value of 14.92 cal mole^{-1} deg^{-1} was calculated for 25° (110). A value of the molar heat capacity of 15.89 cal mole^{-1} deg^{-1} at 25° was calculated from an empirical formula relating entropy and heat capacity (44). The best value of the heat capacity of tellurium dioxide at 25° is probably 16 ± 1 cal mole^{-1} deg^{-1}.

From an approximate fitting of the high temperature heat content with a Debye equation, Mezaki and Margrave (94) estimated the entropy of tellurium dioxide, $S°_{298} = 14 \pm 2$ eu, while an estimated value of 16.8 ± 1 eu is reported by Kubaschewski and Evans (77). A value of 17.57 cal mole^{-1} deg^{-1} has been reported for the entropy of tellurium dioxide at 25° from electrochemical data (44). Since the difference between the reported values of the entropy is quite large, the thermochemical value of 14 ± 2 eu is probably more correct than the electrochemical value.

For the reaction

$$Te(s) + 2H_2O(l) \rightarrow TeO_2(s) + 2H_2(g)$$

the value of −77.807 kcal/mole was calculated for the heat of formation of tellurium dioxide, and a value of −64.668 kcal/mole for the free energy of formation in the range 25–45° (44). For the same reaction, Schumann (121) found values of $\Delta F_{298} = -64.32$ kcal/mole and $\Delta H_{298} = -77.7$ kcal/mole. A value for $\Delta H°_{298}$ (tetragonal) of −90.6 ± 0.3 kcal/mole has been given (41). From the heat of combustion of tellurium in a bomb calorimeter, the heat of formation of tellurium dioxide was found to be −76.9 ± 1.2 kcal/mole (120).

The values of the heat and free energy of formation calculated by Coughlin (22) are given in Table IX. Phase changes occur at 723°K (melting point of Te) and at 1006°K (melting point of TeO_2), and the estimated heat of fusion is 6.1 kcal/mole.

On the basis of the preceding discussion, the thermochemical values for tellurium dioxide listed in Table X can be recommended.

TABLE IX

HEAT AND FREE ENERGY OF FORMATION OF TeO_2

T, °K	ΔH, kcal/mole	ΔF, kcal/mole
298.16	−77.70 ± 1.0	−64.60 ± 0.70
400	−77.4	−60.2
500	−77.1	−55.9
600	−76.8	−51.7
700	−76.4	−47.6
723	−76.3	−46.6
723	−80.5	−46.6
800	−80.2	−43.0
900	−79.8	−38.4
1000	−79.3	−33.8
1006	−79.2	−33.6
1006	−73.1	−33.6
1100	−72.4	−29.9
1200	−71.5	−26.1
1300	−70.7	−22.3

TABLE X

RECOMMENDED THERMOCHEMICAL VALUES FOR TeO_2

Melting point	732.6 ± 0.1° = 1005.8°K
Vapor pressure equation	$\log P(\text{mm}) = -13{,}222/T + 12.3284$ (450–733°)
Heat of sublimation	59 ± 2 kcal/mole
Heat of fusion	7.0 ± 0.5 kcal/mole
Heat of vaporization	51.7 kcal/mole
Molar heat capacity at 25°	16 ± 1 cal mole^{-1} deg^{-1}
Entropy at 25°	14 ± 2 eu
Heat of formation	$Te(s) + O_2(g) \rightarrow TeO_2(s)$ $\Delta H_{298} = -77.75$ kcal/mole
Free energy of formation	$Te(s) + O_2(g) \rightarrow TeO_2(s)$ $\Delta F_{298} = -64.5$ kcal/mole

F. CRYSTAL STRUCTURE

Tellurium dioxide occurs in two definite crystal forms, the rhombic form, which is found in the naturally occurring mineral tellurite, and the tetragonal form, which is produced by any artificial method of preparation of the compound. Tellurium dioxide also solidifies as a transparent glass when impurities (1–10%) are added.

1. Rhombic Form

The structure of a tellurite single crystal was determined by oscillation (Mo Kα) and Weissenberg (Co Kα) photographs and a diffractometer (ionization spectrometer, Mo Kα) (68). It was found that V_R^{15}–P_{cab} was the only possible space group for the crystal, and each unit cell contains eight molecules of tellurium dioxide. The unit cell dimensions and other data are given in Table XI.

The X-Ray Powder File, Card 9-433, gives different cell dimensions (Table XI) which demand a different space group: D_{2H}^{15}–P_{bca}. The reported density of 5,75 g/cm^3 compares well with the value of 5.76 g/cm^3 found experimentally by Clarke (20). The density value of 5.90 g/cm^3 reported by Ito and Sawada (68) is high and casts some doubt on the cell parameters. More recent work (9) confirms the Powder File space group, D_{2H}^{15}–P_{cab}, but does not resolve the discrepancy

TABLE XI

STRUCTURAL DATA FOR TELLURIUM DIOXIDE

TeO_2 (Tellurite)

	Ito and Sawada (68)	Powder File (9-433)	Beyer, *et al.* (9)	Clarke (20)
Density	5.90, 5.86[a]	5.75	5.799[a]	5.76
Unit cell *a*	5.50	5.607	5.44	
b	11.75	12.034	12.02	
c	5.59	5.463	5.59	
a:*b*:*c*	0.468:1:0.4747[a]	0.454:1:0.466	0.453:1:0.465[a]	
Space group	V_H^{15}–(P_{cab})	D_{2H}^{15}–(P_{bca})	D_{2H}^{15}–(P_{cab})	
Z	8	8		
	Rhombic	Orthorhombic		

TeO_2 (Paratellurite)

	Zlomanov, *et al.* (144)	Leciejewicz (80)	Stehlik and Balak (133)	Powder File (11-693)
Density	6.07[a]	6.04[a]	6.07	6.017
Unit cell *a*	4.796	4.796	4.796	4.810
c	7.588	7.626	7.594	7.613
c/a	1.582[a]	1.590	1.583	1.583
Space group		D_4^4–$P4_12_12$ or D_4^8–$P4_32_12$		
Z	...	4	4	4
	...	Tetragonal	Tetragonal	Tetragonal

[a] Value calculated from data given.

in the density, since the value calculated from the unit cell dimensions is 5.799 g/cm³, while the average of the other determinations is 5.79 g/cm³.

2. Tetragonal Form

Stehlik and Balak (132, 133) studied tellurium dioxide by the rotating crystal method using Cu Kα radiation and found that all artificially prepared samples had the same lattice structure. A study of the thermal properties showed no change in the tetragonal form up to the melting point (144). The unit cell dimensions and other data are given in Table XI.

The unit cell dimensions given in the X-Ray Powder File, Card 11-693, are slightly larger than those reported by Stehlik and Balak, but the *c/a* value, 1.583, is identical. Using Cu radiation, the same value of *a* as that of Stehlik and Balak was found, but the value for *c* was smaller (144). Leciejewicz (80), using thermal neutrons, again found the same value of *a* but a considerably larger value of *c*. All authors agree, however, that the unit cell contains four molecules of tellurium dioxide and the space group is either D_4^4–$P4_12_12$ or D_4^8–$P4_32_12$. There appears to be evidence for covalent chains of Te–Te linkages.

Angles between various crystallographic planes of tetragonal crystals, including tellurium dioxide, have been computed, the *c/a* value for tellurium dioxide being 1.5833 (40).

The density values of tetragonal tellurium dioxide range from 6.017 g/cm³, with both the average and most probable value being 6.04 g/cm³.

3. Glassy Form

Brady (11) studied the structure of tellurium dioxide glass on an X-ray diffractometer using Mo Kα radiation and a scintillation counter. The sample contained 1.84% Li_2O by weight so that a glass would form. It was concluded that there were crystallites of approximately unit cell dimensions in the glass, and the unit cell was octahedral, containing eight molecules of tellurium dioxide. Since the octahedral unit cells are edge sharing in crystalline tellurium dioxide, the addition of an impurity such as lithium oxide facilitates glass formation by supplying oxygen atoms which permit a change to corner-linked octahedra and a more or less random structure built up of octahedral unit cells. Brady's conclusion that the unit cells of the crystal are unchanged on glass formation is confirmed by Cheremisinov and Zlomanov (18) who found, however, that all artificially prepared tellurium dioxide samples were tetragonal, and from infrared and Raman evidence showed that the glass had the same symmetry as the tetragonal crystal, *i.e.*, elementary cell containing four molecules of tellurium dioxide with D_4 symmetry.

Although the assumption (18) that tetragonal crystalline tellurium dioxide forms a glass containing tetragonal crystallites is reasonable, the technique is not as convincing as the X-ray data. However, Brady's argument is based on an octahedral starting material which was shown by Cheremisinov and Zlomanov's X-ray work to be correct. If Brady's data could be reinterpreted in terms of tetragonal crystalline tellurium dioxide, then the structure of glass tellurium dioxide would be resolved.

VI. TELLUROUS ACID, H_2TeO_3

White, amorphous tellurous acid can be prepared by the displacement reaction of potassium tellurite with nitric acid at 0° (34)

$$K_2TeO_3 + 2HNO_3 \longrightarrow H_2TeO_3 + 2KNO_3$$

An aqueous solution of a fused equimolar mixture of potassium carbonate and tellurium dioxide will slowly precipitate tellurous acid on exposure to the air (83). At higher temperatures, the precipitate dissolves, the tellurous acid displacing carbonic acid. Tellurous acid must be stored in water since in the dry state it loses water, and on heating above room temperature, it readily loses water to form tellurium dioxide. The solubility in water is very slight, about 3×10^{-6} mole/l. at 18° (34, 64). This is a factor of 10 less than the value of 3.75×10^{-5} mole/l. reported for tellurium dioxide in pure water.

The formation of tellurous acid has been considered the likely product of the anodic oxidation of tellurium in alkaline solutions (5)

$$Te + 4OH^- \longrightarrow H_2TeO_3 + H_2O + 4e$$

Although tellurous acid cannot be obtained in the dry state, the salts of potassium, sodium, magnesium, cadmium, nickel, cobalt, and lead can be obtained in the dry state as definite hydrates, while the silver salt is anhydrous (83).

Chiang and Cooper (19) obtained crystalline potassium tellurite dihydrate, $K_2TeO_3 \cdot 2H_2O$, and disodium tellurate dihydrate, $Na_2H_4TeO_6 \cdot 2H_2O$, as well as the anhydrous compounds.

The first and second dissociation constants of tellurous acid were found from conductivity and neutralization curves to be 2.7×10^{-3} and 1.8×10^{-8}, respectively (10). Issa and Awad (64) report that tellurium dioxide is amphoteric with an isoelectric point at pH 3.8. Thus tellurous acid has an acid dissociation constant of $1.4–4.3 \times 10^{-6}$ and a basic dissociation constant of 3.1×10^{-11}. The value of K_a' differs from Blanc's value of 2.7×10^{-3} (10), but for a polybasic acid, K_a' represents the mean value of all the dissociation constants, unless the first is the predominating one. Using another means of calculation, Issa and Awad obtained a more definite value of 2.51×10^{-6} for K_a', in agreement with the range obtained from their solubility measurements. These values are summarized in Table XIV, along with values for telluric acid.

In 3 N HCl solution, tellurous acid is reduced by finely divided silver at room temperature to silver telluride. This reaction can be used as an analytical method for tellurium(IV) (60).

VII. ORTHOTELLURIC ACID, H_6TeO_6

A. PREPARATION AND PHYSICAL PROPERTIES

Colorless crystals of orthotelluric acid can be prepared by a number of methods, starting from either elemental tellurium or tellurium dioxide. Fehér (34) gives the oxidation of tellurium with $HClO_3$ as the most convenient method (93), with oxidation of tellurium dioxide with potassium permanganate, reaction of tellurium or tellurium dioxide with 30% H_2O_2 or with chromic oxide as less convenient methods. However, if tellurium dioxide is readily available, its oxidation by means of potassium permanganate (91) is a convenient and rapid method of preparing orthotelluric acid. Orthotelluric acid can also be prepared by the action of nitric acid on calcium tellurate, which is formed by heating calcium hydroxide with tellurium dioxide in the presence of sodium carbonate (89).

When orthotelluric acid is crystallized from water below 10°, it forms the hexahydrate, $H_2TeO_4 \cdot 6H_2O$ (101). In measuring the solubility of $H_2TeO_4 \cdot 6H_2O$ from 0 to 15°, and of $H_2TeO_4 \cdot 2H_2O$ from 10 to 110°, Mylius (101) found that the solubility of the hexahydrate changed more rapidly with temperature than the dihydrate, being higher at 15°, about the same at 10°, and much lower than expected at 0°. The solubility of the dihydrate, $H_2TeO_4 \cdot 2H_2O$, is 3.15 moles of H_2TeO_4/100 moles of H_2O at 10°, and 14.5 moles at 100°.

The formula for orthotelluric acid may be written as H_6TeO_6, $Te(OH)_6$, or $H_2TeO_4 \cdot 2H_2O$, but Fouasson (38) has stated that the acid does not lose water below 120°, and thus in the formula $H_2TeO_4 \cdot 2H_2O$, the $2H_2O$ is water of constitution, not of crystallization, and the more correct form is $Te(OH)_6$ or H_6TeO_6. The correctness of this formulation is supported by the formation of $Te(OMe)_6$, Hg_3TeO_6, Zn_3TeO_6, and Cu_3TeO_6 (69, 106). The inactivity of orthotelluric acid was also considered evidence of the formulation $Te(OH)_6$ (71). From osmotic data in the presence of alcohols, the existence of six hydroxyl groups in the molecule of telluric acid was confirmed (130, 131), and further evidence of the hexa activity of orthotelluric acid was supplied by Fouasson (37), who measured the conductivity of telluric acid solution as it was titrated with sodium hydroxide. Breaks in the curve were found corresponding to $NaOH/H_6TeO_6$ ratios of 1, 2, 4, and 6, indicating formation of the salts NaH_5TeO_6, $Na_2H_4TeO_6$, $Na_4H_2TeO_6$, and Na_6TeO_6. The existence of $H_2Na_4TeO_6$ has been questioned by Hessaby and Souchay (62), who were unable to prepare the compound.

Although Karve (71) recognized the existence of three forms of telluric acid, Patry (104) concluded that there were only two different acids, orthotelluric acid, H_6TeO_6, and metatelluric acid, $(H_2TeO_4)_n$, which in concentrated solution (as when dissolved in the water of constitution by heating orthotelluric acid in a sealed tube) has been called allotelluric acid. The molecular weight of orthotelluric acid, H_6TeO_6, was found to be 230 ± 5 (calcd 229.66) by cryoscopic measurements (115), indicating that there is very little polymerization in dilute solution.

From measurements of the ionization constants of telluric acid, Antikainen (1) concluded that mainly dimeric polyacids are formed in telluric acid solution, but the concentration is too small to be observed in cryoscopic or diffusion measurements. In a further study, Antikainen (3) produced formation constants for the dimer and trimer of $K_2 = 1.45 \times 10^{-7}$ and $K_3 = 1.23 \times 10^{-7}$, respectively. Ghosh and Dhar (45) assumed that aqueous telluric acid exists in three equilibrium forms—simple molecules in solution, polymerized molecules in solution, and a colloidal sol. There was no change in the pH, viscosity, or conductivity of the sol with time. Polymerized telluric acid solutions up to 0.4 M have been prepared by ion-exchange methods (42). Depolymerization occurs on aging, on dilution, or on the addition of polyhydroxy organic compounds, the latter due to complex formation.

In a sealed tube, orthotelluric acid melts at 136°, forming a syrupy mass of so-called allotelluric acid which is very soluble in water (69, 101), and which has been shown to be a highly polymerized species (42). In an open tube, orthotelluric acid loses water at about 120°, to form H_2TeO_4 which is soluble only with difficulty and is assumed to be a polymer $(H_2TeO_4)_n$. Mylius (101) found a value of $n = 2.9$ in solution from freezing point depression measurements, while Jander and Kienbaum (69) found a value of 2.8 to 3 from dialysis experiments. Patry (104) measured the molecular weight of $[TeO_4(C_2H_5)_2]_n$ in ether and chloroform solution and found $n = 11 \pm 1$. The same value was assumed for the acid $(H_2TeO_4)_n$ in agreement with the value determined conductometrically ($n = 10$). The low value of 3.2 obtained cryoscopically was said to be due to ionization.

The ultraviolet absorption of tellurate ions at longer wavelength than telluric acid in solution allows the titration of telluric acid by ammonia to be followed spectrophotometrically (250–280 mμ) with an accuracy of better than 1% (84).

The thermal decomposition of orthotelluric acid proceeds in four steps as water and oxygen are lost forming tellurium dioxide as the final product (116).

$$H_6TeO_6 \xrightarrow{-H_2O} (H_2TeO_4)_n \xrightarrow{-H_2O} TeO_3 \xrightarrow{-O_2} Te_2O_5 \xrightarrow{-O_2} TeO_2$$

B. CHEMICAL PROPERTIES

Telluric acid is easily reduced by phenylhydrazine, forming a bright yellow precipitate which could not be isolated and which readily decomposed into elemental tellurium (55). Elemental tellurium is also one of the products of the reaction of telluric acid with iron, aluminum amalgam, magnesium, zinc, cadmium, or the sulfides of nickel, cobalt, copper, and zinc. Tellurium and osmium reduce the acid only to tellurium dioxide, and no reaction occurs with silver or gold (97).

Telluric acid is said to increase greatly the stability of potassium permangate in alkaline solution, but there is no indication of the actual role played by telluric acid (65).

The known reactivity of tellurate ions toward polyhydroxy organic compounds such as ethylene glycol, glycerol, fructose, and mannitol has been investigated in more detail in recent years (30, 31, 70). This is a condensation reaction in which telluric acid masks the coordinating organic ligand toward oxidizing agents such as periodic acid (70). The formation constants of some 20 polyoltellurate complexes have been determined (30).

C. SPECTRA

The Raman spectra of crystals of orthotelluric acid and an aqueous solution of the acid were reported independently by Venkateswaran (138) and Gupta (53). Essentially the same lines were observed in both cases, but at slightly different frequencies. More recently, new Raman lines were reported for solid orthotelluric acid in potassium bromide (69). These Raman data, the infrared data on orthotelluric acid, and infrared and Raman data on $(H_2TeO_4)_n$ and tellurium dioxide are given in Table XII, along with the assignments made by Siebert (125).

From the Raman spectrum of orthotelluric acid, Gupta (53) concluded that the configuration of the molecule is octahedral. The appearance of six bands in the infrared spectrum near 650 cm^{-1} is indicative of a symmetry which is not strictly octahedral (125). Bent Te–O–H groups would reduce the over-all symmetry of the molecule and allow six bands in the 650-cm^{-1} region to be infrared-active. Thus the configuration would be distorted octahedral.

The similarity of the TeO stretching and deformation vibrations in $(H_2TeO_4)_n$ and those of H_6TeO_6 leads to the conclusion that tellurium must also be six coordinated in the polymeric acid (125), and consequently Te–O–Te bonds must be formed. If four coordination occurred, the stretching vibration would be at a higher frequency. In the case of the polymeric acid, the infrared bands are broadened, as expected for an amorphous material.

As would be expected, some of the TeO stretching bands in the tellurium dioxide spectrum correspond closely to some of the lower frequency bands in the infrared spectrum of orthotelluric acid.

D. CRYSTAL STRUCTURE

Orthotelluric acid is reported to exist in two crystalline modifications, cubic and monoclinic, although only one paper reports the monoclinic modification. The X-Ray Powder File (Card 1-0329) states that the data index well for the cubic phase except for a single line, although cell dimensions of two cubic phases and the monoclinic form are given.

TABLE XII

INFRARED AND RAMAN DATA ON TELLURIC ACID AND TeO_2[a]

Assignment (125)	H_6TeO_6 (solid)				H_6TeO_6 (soln)		$(H_2TeO_4)_n$		TeO_2 (crystals)	
	Infrared (125)	R (138)	R (69)	R (53)	R (138)	R (53)	Infrared (138)	R (69)	Infrared (18)	R (18)
	...	...	...	...	...	345mbr	...	...	...	343
	...	365w	362m	...	357wbr	...	...	...	...	365
	...	...	385m	...	...	...	...	...	...	392s
	...	...	...	...	...	...	...	...	...	409
δ(TeO)	411w	...	418m	...	...	...	450mbr	490m	...	495
	605vs	...	...	...	...	619w	600sbr	...	...	590
	650vs	...	...	630w	624vwbr	...	...	...	...	...
γ(TeO)	658vs	657vw	...	655s	647vs	644vs	...	655m	648vs	648s
	675vs	670vs	665vs	...	...	...	...	...	...	667
	708s	...	...	...	...	...	720vs	690m	714vs	717
	730s	...	...	...	...	...	800vs	...	760m	766
	...	...	...	...	...	...	1085mbr	...	...	...
	1125m	...	...	...	...	...	...	...	...	...
δ(TeOH)	1190m	...	...	...	...	...	...	...	...	...
	1222s	...	...	...	...	...	...	...	...	...
δ(H_2O)	...	...	...	...	...	...	1618w	...	...	...
	2200w	...	...	...	...	...	...	...	...	...
2δ(TeOH)	2280m	...	...	...	...	...	...	...	...	...
	2370m	...	...	...	...	...	2360m	...	...	...
γ(TeOH)	3100vs	3121wbr	3100mbr	3050mbr	...	...	3200vsbr	...	...	...
γ(H_2O)							3360vsbr	...	...	...

[a] w, weak; m, medium; s, strong; vs, very strong; br, broad.

1. Monoclinic Form

Gossner and Kraus (51) report the existence of the two crystal structures of orthotelluric acid. From X-ray data on the monoclinic form, a unit cell with $a = 5.54$, $b = 9.30$, and $c = 9.74$ A, and $\beta = 104°\ 30'$ was found. The space group was $C_2{}^5R$, and the unit cell contained four molecules of orthotelluric acid. Two of the values reported in the X-Ray Powder File for monoclinic orthotelluric acid (card 1-0329) are slightly different, not in agreement with the reference cited. The crystal data are all given in Table XIII.

2. Cubic Form

The structure of cubic crystalline orthotelluric acid was first determined by Kirkpatrick and Pauling (76) using Mo Kα radiation. The value of the unit cell edge was found to be 15.48 A, and Z, the number of molecules per unit cell, was found to be 32. The calculated density of 3.26 is slightly higher than the experimental value of 2.999 (21) for orthotelluric acid. The space group of $Te(OH)_6$ was $O_H{}^8$. A slightly larger unit cell with $A_0 = 15.68 \pm 0.01$ A was found by Passerini and Rollier (103) using Cu Kα and Fe Kβ radiation. Using $Z = 32$, a density of 3.158 was found with the space group $O_H{}^8$. Although Gossner and Kraus (51) found a cubic cell with $A_0 = 7.83$ A and $Z = 4$, Pauling (105) reaffirmed the value of $Z = 32$, supported by additional rotation photographs. A summary of the crystal data is given in Table XIII.

It seems well established that the crystal structure of cubic orthotelluric acid as determined by Kirkpatrick and Pauling is correct, although the value of the cell edge probably is between 15.48 and 15.68 A. In a

TABLE XIII

CRYSTAL STRUCTURE OF H_6TeO_6

Monoclinic	Ref 51	X-Ray File (1-0329)
Unit cell a	5.54	9.74
b	9.30	9.30
c	9.74	5.70
β	104° 30'	91.0°
Z	4	...
Space group	$C_{2H}{}^5$	...

	Ref 76	Ref 103	Powder File (1-0329)	Ref 51	Ref 21
Unit cell a	15.48	15.68 ± 0.01	15.51, 7.85	7.83	
Z	32	32	32	4	
Space group	$O_H{}^8$	$O_H{}^8$	$O_H{}^8$	$O_H{}^5$	
Density	3.26, 3.29[a]	3.158, 3.20[a]	3.27[a]	3.18[a]	2.99

[a] Calculated from data given.

TABLE XIV

DISSOCIATION CONSTANTS OF TELLUROUS AND TELLURIC ACIDS

	K_1	K_2	K_3	Ref
	H_2TeO_3			
	$K_a = 1.4 - 4.3 \times 10^{-6}$			64
	Combined K_1 and K_2	2.51×10^{-6}		64
	2.7×10^{-3}	1.8×10^{-8}		10
Recommended values	3×10^{-3}	2×10^{-8}		
	H_6TeO_6			
	2.0×10^{-8}	1.12×10^{-11}		30
	2.0×10^{-8}	9.2×10^{-12}	$\sim 3 \times 10^{-15}$	29
	$pK_{1,0} = 8.180 - 2.36 \times 10^{-2}T$			4
	2.448×10^{-8}	...		1
	$\sim 10^{-6}$ to 10^{-9}	10^{-11}		6
	1.15×10^{-8}	4.7×10^{-11}		38
	6.8×10^{-7}	4.1×10^{-11}		10
	1.6×10^{-9}	...		115
Recommended values	2.0×10^{-8}	1×10^{-11}	$\sim 3 \times 10^{-15}$	
	$(H_2TeO_4)_n$			
	3.55×10^{-8}	...	...	87
	2.82×10^{-8}	...		37
	2.09×10^{-8}	6.46×10^{-12}		13
Recommended values (same as for H_6TeO_6)	2.0×10^{-8}	1×10^{-11}		

recent paper (116) the power pattern for H_6TeO_6 is shown, but no numerical data are given. It is stated that the material is monoclinic, in agreement with Gossner. However, calculation of the d spacing from the available diagram (116) shows that these values agree almost as well with the cubic as with the monoclinic data which were recalculated from Gossner's cell parameters and reflecting crystal planes. The formulas used for calculating the d spacings were taken from D'Eye and Wait (33). A sample of orthotelluric acid prepared in this laboratory gave a powder pattern which agreed very well with the data in both the X-ray Powder Index and the values calculated from Gossner's data for the cubic structure. From this it may be concluded that the monoclinic form may exist, but the cubic form is more easily obtained. Rosicky, Loub, and Pavel (116) may have had a mixture of the monoclinic and cubic forms.

E. DISSOCIATION CONSTANTS

Although most authors agree that the correct formula for orthotelluric acid is H_6TeO_6 or $Te(OH)_6$, in general only the first two dissociation constants have been measured. A value of about 3×10^{-15} has been reported for K_3, the third dissociation constant, estimated spectrophotometrically (29). The values of the first and second dissociation constants for orthotelluric acid have been determined from conductivity measurements (10, 115), from conductometric and pH measurements (39), potentiometric titrations (87), neutralization curves (10, glass electrode measurements (13), and optical density measurements (29). The values, which range from 1.6×10^{-9} to 6×10^{-7} for K_1, and from 9.2×10^{-12} to 4.7×10^{-11} for K_2, are listed chronologically in Table XIV. The best value of K_1 is probably 2×10^{-8}, determined from optical density *vs.* pH data (29), and confirmed by measuring pH values at the neutralization and half-neutralization points (30). The values of K_2 of 9.2×10^{-12} (29) and 1.12×10^{-11} (30) are in fairly good agreement and are probably correct. The latter value applies to a 5.22×10^{-3} M telluric acid solution at 25°. Measurements of K_1 and K_2 obtained at higher concentrations or at 61° gave significantly higher results, probably because of polymerization.

A similar effect was reported by Antikainen (4), and in the range 0 to 50° the first ionization constant of telluric acid is given by $pK_{1,0} = 8.180 - 2.36 \times 10^{-2}T$. From this equation, the heat of ionization is given by $\Delta H = 5.44 \times 10^{-2}RT^2$, which is 9.25 kcal/mole at 20°. The variation in the ionization constant is attributed to increased polymerization at higher temperatures.

A value of 3.55×10^{-8} was reported for the first dissociation constant of H_2TeO_4 (87) and compared with a previously reported value of 2.82×10^{-8} (37). The formula used was H_2TeO_4 because only two dissociations were detected. Britton and Robinson (13) also reported dissociation constants for H_2TeO_4. The similarity between the dissociation constants reported for H_6TeO_6 and H_2TeO_4 seem to indicate that the same acid, H_6TeO_6, was the object of measurement in all cases.

In neutral salt solutions, *e.g.*, KCl, NaCl, $NaNO_3$, etc., the first ionization constant for telluric acid was found to be greatly decreased. The increased acid strength allowed telluric acid to be titrated with sodium hydroxide using phenolphthalein as an indicator (2).

From photometric and pH data evidence has been provided for the existence of polytellurates in solutions of telluric acid (29). By analogy with the boric acid system, the polytellurate ions appear to be mononegative, and on this basis it was calculated that a trimer is the only polymer in the region 0.4–1.1 *M* (29). Below 0.4 *M*, dimers are more important, and above 1.0 *M*, higher polymers can be formed. No evidence of dehydration of the various tellurate ions was found, and the coordination number of tellurium was 6 in all cases.

VIII. METATELLURIC ACID $(H_2TeO_4)_n$

Metatelluric acid is said to exist as a difficultly soluble polymer and is formed by heating orthotelluric acid in an open tube. The value of *n* seems to depend on the type of measurement used, and values of 3, 10, and 11 have been found. This material is discussed more fully in section VII.

IX. PEROXOMONOTELLURIC ACID, H_2TeO_5

Potassium tellurate dihydrate, $K_2TeO_4 \cdot 2H_2O$, is oxidized quantitatively in 2 days at 10° by hydrogen peroxide to give potassium peroxomonotellurate, $K_2TeO_5 \cdot 2H_2O$, according to the equation

$$K_2TeO_4 \cdot 2H_2O + H_2O_2 \longrightarrow K_2TeO_5 \cdot 2H_2O + H_2O$$

The salt is converted to the acid by passage through an ion-exchange column of Lewatite S-100 resin. The acid solution will quantitatively oxidize iodide to iodine (118).

X. PENTAFLUOROORTHOTELLURIC ACID, $HOTeF_5$

Pentafluoroorthotelluric acid, $HOTeF_5$, has been prepared by heating barium tellurate and HSO_3F (mole ratio 1:10) for 3 hr at 160° and distilling the resulting mixture of volatile tellurium compounds (32). Pentafluoroorthotelluric acid is a colorless, glass-crystalline solid which is a mobile, strongly refractive liquid above 40°. The compound hydrolyzes in aqueous solution to give telluric and hydrofluoric acids with the result that it has not been possible to precipitate from such solutions compounds having the anion $OTeF_5^-$.

XI. POLAROGRAPHY OF TELLURIUM(IV) AND TELLURIUM(VI)

Although tellurium dioxide is only slightly soluble in neutral or acid medium, the solubility is greatly increased by the presence of citrate or tartrate, and it is freely soluble in ammoniacal or alkaline medium. Such media have been used to study the polarographic behavior of tellurium(IV). The polarographic reduction of tellurium(IV) proceeds directly to the element or to the −2 state, but there is no evidence for the formation of the +2 state in solution (85). During the reduction of tellurium(IV), a maximum occurs beyond which the current returns to its former value. During the maximum, a brown precipitate forms as a cloud around the dropping mercury electrode. In the region before this maximum, tellurium(IV) is reduced to elemental tellurium (56), and at the voltage at which the maximum occurs, the reduction continues to the telluride, which then reacts with the tellurite ions, forming brown, colloidal elemental tellurium.

$$TeO_3^{-2} + 2Te^{-2} + 3H_2O \rightarrow 6OH^- + 3Te$$

The main waves were found to precede the maximum at pH values between 0.4 and 3, but they do not correspond to stepwise reduction of tellurium(IV) (85). In sodium hydroxide solution, there is a single wave with a half-wave potential close to the standard potential of the couple $Te + 2e \rightarrow Te^{-2}$ (−1.21 v for 1m*M* Te). Values of the cathodic inflections for the reduction of tellurite ions in hydrochloric acid or sulfuric acid solution were reported to be −0.41, −0.78, and −1.2 v *vs.* saturated calomel electrode (46). The second inflection which takes place at tellurium(IV) concentrations of 5×10^{-5} *M* was considered to correspond to the reduction to H_2Te.

The polarographic reduction of tellurium(VI) appears to proceed directly from Te^{+6} to Te^{-2} in one wave at all pH values (119). The reaction

$$3Te^{-2} + Te^{+6} \longrightarrow 4Te$$

appears to be too slow to occur in the diffusion layer surrounding the mercury electrode, as in the case with tellurium(IV), but it does take place as indicated by the appearance of elemental tellurium. The reduction of telluric acid is said to be better represented by

$$H_6TeO_6 + 6e \longrightarrow Te + 6OH^-$$

since the corresponding reduction to Te^{-2} is considered improbable (66).

In the electrolyte solution of 0.5 *M* NH_4Cl, 0.5 *M* NH_4OH, 0.1 *M* Na_2SO_3, and 0–0.01% gelatin, the polarographic reduction of tellurium(VI) is reported to produce the complete waves of tellurium(IV) and tellurium(VI) (15). Since the polarographic waves formed depend largely on the conditions and electrolyte used, these factors may explain the apparent difference between the results of Schmidt and Stackelberg and those of Bykov. In neither case is the formation of the +2 state mentioned.

XII. ELECTROLYTIC BEHAVIOR OF TELLURIUM

A. ELECTROLYSIS OF TELLURIUM(IV)

The electrolysis of tellurium dioxide in alkaline medium to produce tellurium is of industrial importance (141). The over-all reactions are

$$TeO_2 + 2NaOH \longrightarrow Na_2TeO_3 + H_2O$$

and

$$Na_2TeO_3 + H_2O + 4e \longrightarrow Te + O_2 + 2NaOH$$

The anodes are iron, with stainless steel cathodes. A current density of 10–20 amp/ft^2 is used in an electrolyte at 100°F (38°) containing about 19 g/l. of sodium hydroxide and about 150 g/l. of tellurium. The conditions do not appear to be critical, since Soshnikova and Ezernitskaya (127) report that the best results are obtained using a current density of 60 amp/m^2 in an electrolyte containing 60–80 g/l. of sodium hydroxide and 100–200 g/l. of tellurium at 40–45°.

B. TELLURIUM ELECTRODE POTENTIALS

From Tafel lines obtained using samples of massive tellurium after anodic or cathodic polarization, it was concluded that the evolution of hydrogen was governed by an electrochemical mechanism (75). In another study, tellurium electrodes which were prepared from the powdered metal by electrodeposition or by vacuum sublimation, produced potentials, in oxygen-free buffer solutions, which coincided with the thermodynamic potential for the Te–TeO_2 system (67). Massive electrodes gave a higher potential corresponding to $^2/_{15}$ of the electrode surface being covered with oxygen bubbles.

There is some discrepancy in the values of the Te–TeO_2 or Te–H_2TeO_3 potentials, and the values which have been reported are summarized in Table XV.

TABLE XV

ELECTRODE POTENTIALS[a] OF TELLURIUM ELECTRODES

Potential, v		
Acid soln	Basic soln (pH 14)	Ref
0.530 (pH 1.5)		67
$E = 0.593 - 0.0469(\text{pH})$	−0.063	114
$E = 0.603 - 0.058(\text{pH})$	−0.21	136
0.529		117
$E° = 0.521 - 0.0591(\text{pH})$	−0.306	108
$E° = 0.604 - 0.0591(\text{pH})$	−0.223	108
$E° = 0.620 - 0.060(\text{pH})$	−0.220	5
0.559(pH 0)		121

[a] The above electrode potentials are the Gibbs–Stockholm potentials and are opposite in sign to the Latimer "oxidation potentials." The recommended values are those of Pourbaix (108).

The emf of the cell, Te(s)|TeO_2(s) buffer solution|| saturated calomel electrode, was measured at 25° and various pH values (114). The relationship $E = 0.349 - 0.0469(\text{pH})$ was obtained for the range of pH 2.2 to 8.0. When related to the standard hydrogen electrode, the intercept becomes 0.593 v compared with the value of 0.529 v in an acid solution (presumably pH 0) at 25° for the electrode potential of the reaction (117)

$$Te + 2H_2O \longrightarrow TeO_2 + 4H^+ + 4e$$

In the cell, Te(s)|TeO_2(s), $HClO_4$||H_2(g), at 25°, the reduction potential of tellurium was found to be −0.559 v (121). In an oxygen-saturated buffer using massive tellurium electrodes, the relationship $E = 0.603 - 0.058(\text{pH})$ in the range of pH 0–9 was found (136).

The results of thermochemical calculations are reported by Pourbaix (108) with a value of $E° = 0.521 - 0.0591(\text{pH})$ for anhydrous TeO_2 and $E° = 0.604 - 0.0591(\text{pH})$ for TeO_2 hydrate (H_2TeO_3). From a plot of pH *vs.* the reversible potential of a tellurium anode in sodium hydroxide solution, Awad (5) obtained an experimental value of $E_B = -0.220$ v at pH 14. This value was compared with $E_B = -0.300$ v for the Te–TeO_2 system and a laboriously calculated value of $E_B = -0.240$ v for Te–H_2TeO_3. From Pourbaix's relation for H_2TeO_3, $E_B = -0.223$ v at pH 14. Thus Awad concluded that the net anode reaction of tellurium in sodium hydroxide solution is

$$Te + 4OH^- \longrightarrow H_2TeO_3 + H_2O + 4e$$

and his experimental results agree well with the thermochemical data.

The differences between the values obtained by various authors are explained by the fact that different buffer solutions were used, and the electrodes were prepared differently. The most accurate data, however, are the values calculated from thermochemical data by Pourbaix.

C. TELLURIUM AS A HYDROGEN ELECTRODE

Tomicek and Poupe (136) measured the potential of a tellurium electrode against a saturated calomel electrode and compared it with a standard hydrogen electrode. A monotonic change in the potential with pH was found which was not quite linear, depending on the pretreatment of the tellurium electrode.

Kasarnowsky (72) noted that the potential of a tellurium electrode varied with the hydrogen ion concentration of the solution in which it was immersed. The resulting relationship, $E_1 - E_2 = 0.058 \log [H^+]_1/[H^+]_2$ for potassium chloride solutions in a nitrogen atmosphere, implied a linear pH–potential relationship.

Studies on various types of tellurium electrodes (massive, powdered, electrodeposited, or sublimed) in the presence and absence of oxygen have led to widely varying results, but all gave linear pH–potential relationships (67). For electrodeposited tellurium on platinum in the absence of air, the theoretical value of the Te–TeO_2 couple of $E = 0.530 - 0.059(\text{pH})$ is approached. The overvoltage, which occurred in most cases, was presumed to be due to an oxygen film covering part of the electrode surface.

Ricketts and Tresselt (114) obtained the relationship $E = 0.593 - 0.0469(\text{pH})$ using polished tellurium rods scratched with emery paper in a buffer solution saturated with tellurium dioxide. The presence of oxygen increased the emf of the cell.

Awad (5) studied the changes in potential of tellurium anodes in sodium hydroxide solutions at pH 11.75 to 14 as a function of current density. From the stationary potentials at low current densities, the relationship $E =$

$0.620 - 0.060(\text{pH})$ was found to be valid. The anode reaction in sodium hydroxide solution was assumed to be

$$\text{Te} + 4\text{OH}^- \longrightarrow \text{H}_2\text{TeO}_3 + \text{H}_2\text{O} + 4\text{e}^-$$

The lack of agreement of potential–pH relationships of metal–metal oxide electrodes among various authors is well known. Although it seems definitely established that a linear potential–pH relationship exists, the actual values of the slope and intercept depend on many factors, some of which may be still unknown or unsuspected. The use of a tellurium electrode as a hydrogen ion indicator for a given set of measurements in similar solutions might be feasible once the electrode was calibrated, and if a definite procedure was established for the preparation of the electrode. However, these stringent requirements overshadow the convenience of using a tellurium electrode, except in very special cases. Consequently, its use as a hydrogen ion indicator will probably continue to be very limited.

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