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Argonne National Laboratory

LABORATORY INVESTIGATIONS IN SUPPORT OF FLUID-BED FLUORIDE VOLATILITY PROCESSES

Part X. A Literature Survey on the Properties of Tellurium, Its Oxygen and Fluorine Compounds

by

D. R. Vissers and M. J. Steindler

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Chemical Engineering Division

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- Part I (ANL-6742) - The Fluorination of Uranium Dioxide-Plutonium Dioxide Solid Solutions
- Part II (ANL-6753) - The Properties of Plutonium Hexafluoride
- Part III (ANL-6762) - Separation of Gaseous Mixtures of Uranium Hexafluoride and Plutonium Hexafluoride by Thermal Decomposition
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ABSTRACT

The results of a literature survey of the properties of tellurium, its oxides, fluorides, and oxyfluorides have been assembled. The pertinent data for the physical and chemical properties as well as the behavior of tellurium in processing of nuclear fuels by fluoride volatility methods are included. An appendix containing tabulated vapor pressures and abstracts of all pertinent references is furnished.

1.0 INTRODUCTION

Fission-product tellurium is transformed into a volatile compound in the processing of reactor fuels by the various fluoride volatility methods. The volatile compound, believed to be the hexafluoride, is relatively stable and inert; consequently, it is difficult to remove from the off-gases of the fluoride volatility process. The presence of tellurium in the off-gases becomes an increasingly serious problem as the cooling time of the fuel is shortened. The purpose of this survey is to present in one reference all the pertinent information, both scientific and technological, available on the subject of off-gas problems of tellurium. This report is, therefore, oriented toward the fluoride compounds of tellurium, but also includes information on tellurium and tellurium-oxygen compounds.

2.0 PREPARATION OF TELLURIUM

Tellurium in ores is commonly found associated with sulfides and selenides, forming the corresponding and often isomorphous telluride, of iron, copper, lead, bismuth, and silver. Tellurides of gold and silver are quite common. Native tellurium is also found.

The principal commercial source of tellurium is the anode sludge from the electrolytic refining of copper. The sludge is normally oxidized and leached with a caustic solution, and the liquor is then neutralized to

pH 6-6.2 with sulfuric acid to precipitate impure tellurous acid as "tellurium mud." Elemental tellurium is recovered from the "mud" by one of three methods:¹ (1) direct reduction by heating with flour (carbonaceous) under a cover of borax; (2) acid dissolution of the "mud," followed by reduction with sulfur dioxide or zinc; (3) dissolution of the mud in caustic soda and electrolysis of the solution between stainless steel electrodes, followed by melting of the cathode deposit of tellurium. The latter method is the most satisfactory. The metal may be further purified by sublimation and by various other means.²

2.1 Properties of Tellurium

2.1.1 General Properties

The element tellurium (atomic number 52; atomic weight 127.60) has eight stable isotopes with mass numbers between 120 to 130. Tellurium is in group VIA of the periodic table and has an electronic configuration of 2-8-18-18-6, where the outer six electrons are $5s^2 5p^4$. Tellurium shows oxidation states of -2, 0, +2, +4, and +6. The availability of 4f orbitals for hybridization enables four- and six-valent tellurium compounds to form complexes with various electron donor compounds.^{3,4}

Elemental tellurium is found in both the amorphous and hexagonal crystalline form. The crystal lattice parameters are $a_0 = 4.44$ and $c_0 = 5.912$ Å. The crystal density is 6.24 g/cm^3 . Tellurium has a covalent radius of 1.35 Å and an atomic radius of 1.60 Å. The six-valent tellurium has an ionic radius of 0.56 Å. The Pauling electronegativity of tellurium is 2.1 eV.

The principal fission-product isotopes of tellurium are $\text{Te}^{127\text{m}}$ and $\text{Te}^{129\text{m}}$, which have reported fission yields* of 0.035-0.056 and 0.34-0.35%, respectively. A complete list of the tellurium fission products is shown in Table 1.^{5,6}

2.1.2 Melting Point, Boiling Point, and Vapor Pressure

Simek and Stehlik⁷ report the melting point of tellurium to be 452°C ; Guertler and Pirani⁸ found it to be 450°C . Brooks⁹ estimated the boiling point of tellurium from vapor pressure studies to be $989.3 \pm 3.8^\circ\text{C}$; Machol and Westrum¹⁰ by extrapolation to the boiling point from their vapor pressure studies of liquid tellurium found it to be 994°C .

The vapor pressure of crystalline tellurium between 208 and 427°C is given by¹¹

$$\log_{10} P_{\text{mm}} = 9.753 - (7,599.758/T), \quad (1)$$

*Thermal-neutron fission of U^{235} .

where T is in °K. Vapor pressure equations for crystalline tellurium have also been developed by other investigators.¹²

TABLE 1. Tellurium Fission Products^{5,6}

Isotope	Fission Yield ^a (percent)	Mode of Decay	Daughter Product	Half-life	Specific Activity (day/sec-g)	γ max (MeV)	β max (MeV)
Te ¹²²	0.013	Stable	-	-	-	-	-
Te ¹²⁴	0.02	Stable	-	-	-	-	-
Te ^{125m}	0.003	I.T. ^b	Te ¹²⁵	58 days	6.66×10^{14}	0.1097	-
Te ¹²⁵	0.023	Stable	-	-	-	-	-
Te ¹²⁶	0.10	Stable	-	-	-	-	-
Te ^{127m}	0.035, 0.056	I.T.	Te ¹²⁷	105 days	3.62×10^{14}	0.089	0.67
Te ¹²⁷	0.25	β^- , γ	I ¹²⁷	9.4 hr	9.71×10^{16}	0.418	0.69
Te ¹²⁸	0.50	Stable	-	-	-	-	-
Te ^{129m}	0.35, 0.34	I.T.	Te ¹²⁹	33.5 days	1.12×10^{15}	0.106	1.53
Te ¹²⁹	1.0	β^- , γ	I ¹²⁹	72 min	7.49×10^{17}	1.10	1.45
Te ¹³⁰	2.0	-	-	$\sim 10^{21}$ yr	$\sim 1.02 \times 10^{-7}$	-	-
Te ^{131m}	0.44	I.T.	Te ¹³¹	30 hr	2.95×10^{16}	1.63	2.51
Te ¹³¹	2.9	β^- , γ	I ¹³¹	24.8 min	2.14×10^{18}	1.14	2.14
Te ¹³²	4.7, 4.4	β^- , γ	I ¹³²	77.7 hr	1.13×10^{16}	0.225	0.22
Te ^{133m}	4.9, 4.6	I.T.	Te ¹³³	63 min	8.2×10^{17}	1.0	2.4
Te ¹³³	6.0	β^- , γ	I ¹³³	2 min	2.6×10^{19}	1.0	2.4
Te ¹³⁴	6.9, 6.7	β^- , γ	I ¹³⁴	44 min	1.18×10^{18}	0.262	-
Te ¹³⁵	4.2	β^- , γ	I ¹³⁵	~ 1 min	5.1×10^{19}	-	-

^aThermal-neutron fission of U²³⁵; yields listed are total yields of mass chains and independent fission, where the sum of the total yield is 200% for binary fission.
^bIsomeric transition.

The vapor pressure of liquid tellurium between 515 and 808°C is described by⁹

$$\log_{10} P_{\text{mm}} = 7.5999 - (5960/T). \quad (2)$$

Machol and Westrum also developed a vapor pressure equation for liquid tellurium.¹⁰

2.1.3 Toxicity

At the 27th Annual Meeting of the American Conference of Governmental Industrial Hygienists,¹³ a maximum safe concentration of airborne tellurium was given as 0.1 mg/m³. Studies carried out by Sandratskaya¹⁴ on tellurium and tellurium oxide set the maximum permissible concentration of airborne tellurium at 0.01 mg/m³ for assured safety. Hammond¹⁵ states that workmen exposed to tellurium in airborne concentrations as small as 0.01 mg/m³ or less develop "tellurium breath," which has a garlic odor. A safe maximum concentration of airborne tellurium thus is probably <0.01 mg/m³.

2.2 Chemical Reactions of Tellurium

2.2.1 Reactions with Fluorine

Prideaux¹⁶ found that gaseous fluorine and powdered tellurium metal react at room temperature with the evolution of heat to form the volatile hexafluoride. Campbell and Robinson¹⁷ report that at temperatures of approximately 150°C pure tellurium hexafluoride is formed when tellurium is reacted with fluorine; at approximately 60°C some ditellurium decafluoride, Te_2F_{10} , is formed, and at 0°C the principal product of the fluorination is tellurium tetrafluoride. English and Dale¹⁸ reported that ditellurium decafluoride was formed in 20% yield when fluorine was reacted with powdered tellurium metal in the presence of calcium fluoride.

2.2.2 Reactions with Chlorine, Bromine, and Iodine

When heated slightly, tellurium reacts with chlorine, bromine, and iodine to form the respective tetrahalide.¹⁹⁻²¹

2.2.3 Other Halogenation Reactions

Liquid iodine monochloride reacts with finely powdered tellurium metal to form tellurium tetrachloride.²² Sulfur monochloride and thionyl chloride²³ also react with tellurium metal powder to form tellurium tetrachloride. Bromine trifluoride and chlorine trifluoride react with finely divided tellurium to form tellurium hexafluoride^{24,25} at 25 and 0°C, respectively.

2.2.4 Reduction of Tellurium Halides by Metallic Tellurium

Powdered tellurium metal reacts with tellurium hexafluoride at 200°C in an alumina tube to yield tellurium tetrafluoride.^{26,27} When heated with the tetrachloride or reacted with the tetrabromide at -80°C, powdered metallic tellurium forms the corresponding tellurium dihalide.^{28,29}

2.2.5 Reactions with Oxygen and Sulfur

Finely powdered, crystalline tellurium burns in oxygen to form tellurium dioxide.³⁰ Molten sulfur dissolves powdered tellurium metal to form the sulfide TeS .

2.3 Thermochemical Properties of Tellurium

2.3.1 Heats of Evaporation, Sublimation, and Fusion

Heats of evaporation and sublimation evaluated from the vapor pressure equations for liquid and crystalline tellurium are

$$\Delta H_{\text{vap}} = 27.26 \pm 0.07,^9 \quad 33.8 - 0.009t(^{\circ}\text{C}),^{10} \quad 28.3 \pm 0.5^{12} \text{ kcal mole}^{-1}; (3)$$

$$\Delta H_{\text{sub}} = 37.76^{11} \text{ kcal mole}^{-1}. (4)$$

The heat of fusion of tellurium calculated from these values is approximately 7 kcal mole^{-1} . This value corresponds to $11.9 \text{ kcal mole}^{-1}$ as given by Rossini.³¹

2.3.2 Entropy and Heat Capacity

The entropy of crystalline tellurium has been reported as 11.88 ± 0.10 and $12.85 \pm 0.50 \text{ cal deg}^{-1} \text{ mole}^{-1}$ by Slansky-Coulter³² and Anderson,³³ respectively.

The heat capacity for tellurium metal is given in the following:³⁴

C_p (cal deg ⁻¹ g ⁻¹)	Temperature (°C)
0.0533	250
0.0540	300
0.0551	350
0.0565	400

2.3.3 Dissociation Energy

The dissociation energy of $\text{Te}_2(\text{g})$ is 53 kcal/mole ;¹⁵ the bond length is $2.59 \pm 0.02 \text{ \AA}$.

3.0 TELLURIUM OXIDE PREPARATIONS

Three oxides of tellurium have been reported in the literature: TeO , TeO_2 , and TeO_3 . Tellurium dioxide is the most common and the most chemically stable. It has been reported to occur in nature in Transylvania, Colorado, and South Dakota, in the mineral called tellurite.

3.0.1 Preparation of Tellurium Monoxide

Tellurium monoxide may be prepared in the gaseous state by reacting vaporized tellurium with oxygen in an electrodeless, quartz discharge tube equipped with a high-frequency (18 Mc) oscillator.³⁵ Divers and Shimose³⁶ as well as Doolan and Partington³⁷ reported that tellurium monoxide is formed by the thermal decomposition of TeSO_3 according to the following equation:

Glemser and Porscher,³⁸ however, report that tellurium monoxide is not stable in the solid phase and dispute the results obtained by Divers-Shimose and Doolan-Partington. The existence of tellurium monoxide in the solid state is, consequently, in question.

3.0.2 Preparation of Tellurium Dioxide

Tellurium dioxide may be prepared by burning tellurium in oxygen,³⁰ or by the oxidation of metallic tellurium with nitric acid followed by ignition at 300°C.³⁹ Ignition of the nitrate or sulfate of tellurium results in the formation of the dioxide.

3.0.3 Preparation of Tellurium Trioxide

Tellurium trioxide is prepared by the thermodehydration of orthotelluric acid (H_6TeO_6) at 300-360°C. The last traces of water are difficult to remove. Tellurium trioxide obtained in this way is orange-yellow, and the granules retain the form of the crystals of the orthotelluric acid from which they were derived. The trioxide is decomposed at low red heat to oxygen and tellurium dioxide. The trioxide has been reported in trace quantities by the anodic oxidation of tellurium in an alkaline media.⁴⁰

3.1 Properties of Tellurium Oxides

3.1.1 Structure and Density

Crystalline tellurium dioxide exists in three different systems. Two of the systems are tetragonal: $a_0 = 4.79$ and 4.805 , and $c_0 = 3.77$ and 7.609 Å, respectively. The third crystalline system is an orthorhombic system with $a_0 = 11.75$, $b_0 = 5.50$, and $c_0 = 5.59$ Å. Systematically prepared tellurium dioxide normally is formed in the tetragonal system which contains a long c axis and has a density of 5.67 g/cc at 0°C. The orthorhombic crystal has a density of 5.90 g/cc at 0°C. Tellurium trioxide exhibits both an α and β form with densities of 5.075 and 6.21 g/cc, respectively.

3.1.2 Melting Point, Boiling Point, and Vapor Pressure of Tellurium Dioxide

The melting point of tellurium dioxide is 733°C.⁴¹ It is reported to decompose below the boiling point.⁴¹ The Handbook of Chemistry and Physics¹⁵ quotes a boiling point of 1245°C.

The vapor pressure of tellurium dioxide over the temperature ranges from 573 to 733°C and from 733 to 938°C are described by the following equations:⁴²

$$\log_{10} P_{\text{mm}} = 8.067 - (12,000/T)(573 \text{ to } 733^\circ\text{C}); \quad (6)$$

$$\log_{10} P_{\text{mm}} = 7.367 - (11,300/T)(733 \text{ to } 938^\circ\text{C}), \quad (7)$$

where T is in $^\circ\text{K}$. Equations describing the vapor pressure of tellurium dioxide over the temperature range from 457 to 704°C ⁴³ and 600 to 733°C ⁴⁴ have also been reported.

3.1.3 Toxicity

Sandratskaya¹⁴ determined the maximum permissible concentration of airborne tellurium and tellurium dioxide as 0.01 mg/m^3 .

3.1.4 Absorption Spectra

Tellurium monoxide may not exist as a stable solid, but its existence in the gas phase has been well established.⁴⁵ Rotational structure in the electronic absorption spectrum of TeO shows a band at $31,301 \text{ cm}^{-1}$ which is characterized by the simple 2-branch structure expected for a $0^+ - 0^+$ transition. R and P branches of the most abundant molecules, TeO^{130} , TeO^{128} , and TeO^{126} are well resolved. The analysis indicates an internuclear distance of $1.828 \text{ \AA}$. The emission spectrum of tellurium monoxide has been investigated by Shin-Piaw,⁴⁶ R. L. Purbrick,³⁵ and Rosen.⁴⁷ Rosen summarizes some unpublished work performed with Migeotti.

The absorption spectra of the tellurium dioxide was investigated between 3000 and $4500 \text{ \AA}$.⁴⁸ The bands of the system have all been correlated with a single valence symmetrical frequency in each state, with $\nu'' = 815 \text{ cm}^{-1}$ and $\nu' = 650 \text{ cm}^{-1}$. Fainter bands toward $3000 \text{ \AA}$ are arranged in several series with $\nu \approx 200 \text{ cm}^{-1}$.

3.2 Chemical Reactions of Tellurium Dioxide

3.2.1 Introduction

The chemical reactions of tellurium monoxide are not discussed in this section of the report since its existence as a stable solid has not been definitely established, and little is known of the chemical reactions of gaseous tellurium monoxide.

3.2.2 Reduction of Tellurium Dioxide

Tellurium dioxide is reduced to the metallic state when reacted with powdered aluminum, zinc, cadmium, and cerium metals, or when reacted with the sulfides of lead, zinc, mercury, antimony, or bismuth.⁴⁹ Carbon monoxide⁵⁰ and hydrogen⁵¹ also reduce the tellurium dioxide to the metallic state, as does a simple hot gas flame.⁵¹

Pure tellurium metal is prepared by dissolving purified tellurium dioxide in hydrochloric acid and reducing it with sulfur dioxide⁵² or stannous chloride.⁵³

3.2.3 Oxidation of Tellurium Dioxide

Tellurium dioxide is oxidized to telluric acid by boiling the oxide in a chromium trioxide solution,⁵⁴ a potassium permanganate-sulfuric acid system,⁵⁵ a sulfuric acid-potassium dichromate system,⁵⁶ an alkaline potassium permanganate solution,⁵⁷ or a peroxide solution.⁵⁸

3.2.4 Halogenation of Tellurium Dioxide

Sulfur monochloride²³ and selenium monochloride⁵⁹ react at room temperature with tellurium dioxide to form tellurium tetrachloride. Tellurium dioxide when heated in a stream of thionyl chloride²³ or anhydrous hydrogen chloride⁶⁰ is converted to the tetrachloride.

Tellurium dioxide reacts with selenium tetrafluoride smoothly and quantitatively at 80°C to form tellurium tetrafluoride.⁶¹ Fluorine reacts with tellurium dioxide to form tellurium hexafluoride, ditellurium decafluoride, and tellurium oxyfluorides.^{17,18,62} These fluorination reactions will be discussed more thoroughly in the section on tellurium fluorides. Bromine pentafluoride and chlorine trifluoride also fluorinate tellurium dioxide to the hexafluoride.

3.3 Chemical Properties of Tellurium Trioxide

Tellurium trioxide is a fairly strong oxidizing agent; it oxidizes hot concentrated hydrochloric acid with the liberation of chlorine while being reduced to the tetravalent state. Hot concentrated solutions of potassium hydroxide or carbonate slowly converts the trioxide to the potassium acid tellurate, $K_2H_4TeO_6$. Tellurium trioxide is quite insoluble in cold water, and cold nitric and cold hydrochloric acids. It dissolves slowly in hot water to form orthotelluric acid, H_6TeO_6 .

3.4 Thermochemical Properties of Tellurium Dioxide

3.4.1 Free Energy, Heat, and Entropy of Formation

$$\Delta F_{298}^\circ = -64.32;^{63} \quad -64.60^{31} \text{ kcal/mole}; \quad (8)$$

$$\Delta H_{298}^\circ = -77.7;^{31} \quad -90.0^{64} \text{ kcal/mole}; \quad (9)$$

$$\Delta S_{298}^\circ = 16.99 \text{ e.u.}^{31} \quad (10)$$

3.4.2 Heat of Fusion, Sublimation, and Evaporation

$$\Delta H_{\text{sub}} = 57.5,^{65} \quad 60.1 \pm 0.6,^{43} \quad 54.9^{42} \text{ kcal/mole}; \quad (11)$$

$$\Delta H_{\text{vap}} = 51.7 \text{ kcal/mole};^{42} \quad (12)$$

$$\Delta H_{\text{fus}} = 3.2,^{42} \quad 7.3,^{66} \quad 6.95^{67} \text{ kcal/mole}. \quad (13)$$

4.0 PREPARATION OF TELLURIUM HEXAFLUORIDE

4.0.1 Reaction of Tellurium with Fluorine¹⁶⁻¹⁸

Prideaux,¹⁶ Yost,⁶² and Moissan⁷⁰ found that fluorine gas reacts with powdered tellurium metal, producing incandescence below room temperature. Each of these investigators identified only one reaction product, tellurium hexafluoride, but all described the formation of a white solid which Prideaux analyzed as 52.3 to 66.9% tellurium and which was probably impure tellurium tetrafluoride. Campbell and Robinson¹⁷ made a comprehensive study of the effect of temperature on the reaction of tellurium metal powder with elemental fluorine gas. The results of the study showed that at 150°C the product is exclusively the tellurium hexafluoride, whereas at 60°C some ditellurium decafluoride, Te_2F_{10} , is formed in addition to the hexafluoride; at approximately 0°C the fluorination product is principally tellurium tetrafluoride. Fischer and Steunenberg⁶⁸ found that finely powdered tellurium metal reacts with fluorine at liquid nitrogen temperatures to form tellurium hexafluoride. The method given by Yost⁶⁹ is probably the one most generally accepted at the present time for the preparation of tellurium hexafluoride. The method is outlined as follows:

Finely divided tellurium metal is placed in a copper tube provided with an outlet and inlet. The outlet is connected to two traps in series, one cooled to approximately -20°C and the other immersed in liquid air or a solid carbon dioxide-alcohol mixture. Elemental fluorine is first passed through a dry-ice trap, then through a nickel absorption tube containing sodium fluoride pellets at 100°C, and finally into the reaction tube. The reaction proceeds smoothly. The lower-valent fluorides are condensed to a large extent in the first trap, and the fluorides collected in the liquid air- or solid carbon dioxide-cooled trap consists principally of tellurium hexafluoride. The hexafluoride is best purified by repeated sublimation, care being taken to melt the middle fraction after each sublimation.

4.1 Handling of Tellurium Hexafluoride

Tellurium hexafluoride, being more reactive than the sulfur hexafluoride homologue, must be kept anhydrous since it reacts fairly rapidly with moisture.^{3,16,68} Anhydrous tellurium hexafluoride may be handled in glass or metal systems constructed of copper or nickel.

4.2 Physical Properties of Tellurium Hexafluoride

4.2.1 Description

Tellurium hexafluoride is a colorless gas with an unpleasant odor, similar to that of tellurium hydride or ozone.¹⁶ The formula weight of tellurium hexafluoride is 241.59 g/mole.

4.2.2 Melting Point, Boiling Point, and Vapor Pressure

The melting point and boiling points of tellurium hexafluoride found in the literature are as follows:

$$\text{M.P. } -37.8,^{62} \quad -36,^{16} \quad \text{and } -37.6 \pm 0.5^{\circ}\text{C};^{71} \quad (14)$$

$$\text{Subl.P. } -38.9,^{62} \quad -35.5,^{16} \quad \text{and } -38.3^{\circ}\text{C}.^{71} \quad (15)$$

The vapor pressure of solid tellurium hexafluoride was determined experimentally by Yost and Claussen⁶² as well as by Henkel and Klemm⁷¹ over the temperature range from approximately 193 to 233°K yielding the following equations:

$$\log P_{\text{mm}} = 9.1605 - (1,471.4/T);^{62} \quad (16)$$

$$\log P_{\text{mm}} = 8.594 - (1342/T);^{71} \quad (17)$$

where T is in °K.

The vapor pressure of liquid tellurium hexafluoride was found by Klemm and Henkel⁷¹ to obey the following equation over the temperature range from 233 to 240.7°K:

$$\log P_{\text{mm}} = 7.091 - (988/T). \quad (18)$$

4.2.3 Density of Tellurium Hexafluoride

The density of solid tellurium hexafluoride is 4.08 g/cm³ (extrapolated) at absolute zero and 3.76 g/cm³ at its melting point.⁷¹ The density of liquid tellurium hexafluoride is 2.67 g/cm³, Ref. 71, both at its melting and boiling point.

4.2.4 Critical Temperature of Tellurium Hexafluoride

The critical temperature of tellurium hexafluoride is 83.25°C¹⁶.

4.2.5 Surface Tension and Molar Susceptibility of Tellurium Hexafluoride

The surface tension at the boiling point of tellurium hexafluoride is 13.23 dynes/cm.⁷² The molar magnetic susceptibility X_M is $-66 \pm 0.5 \times 10^6$ cgs units.⁷³

4.2.6 Dielectric Constant of Tellurium Hexafluoride⁷⁴

The dielectric constant $(\epsilon - 1)10^{13}$ is equal to 3.020 for gaseous tellurium hexafluoride at 19-20°C.

4.2.7 Structure of Tellurium Hexafluoride

No report on the crystal structure of tellurium hexafluoride could be found in the open literature. The molecule has a regular octahedral structure with an interatomic distance reported as 1.82⁷⁵ and 1.84 Å.⁷⁶

4.2.8 Absorption Spectrum of Tellurium Hexafluoride

1. Infrared Absorption Spectrum of Tellurium Hexafluoride

The infrared absorption spectra of tellurium hexafluoride has been thoroughly studied by Gaunt⁷⁷ and later by Burke,⁸⁰ who confirmed the findings of Gaunt. Sachsse *et al.* also studied the infrared spectrum of tellurium hexafluoride.⁸¹ The infrared absorption spectrum of tellurium hexafluoride as determined by Gaunt is shown in Fig. 1, and the frequencies and assignment of the observed infrared absorption bands are shown in Table 2.

Fig. 1

The Infrared Spectrum of Tellurium Hexafluoride.⁷⁷ [The product of pressure and path (in cm x cm) is indicated by italic numbers written on the curves.]

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TABLE 2. Frequencies and Assignment of Observed Infrared Absorption Bands of Gaseous Tellurium Hexafluoride⁷⁷

$\nu(\text{obs})$ (cm ⁻¹)	Assignment	$\nu(\text{calc})$ (cm ⁻¹)	$\nu(\text{obs})$ (cm ⁻¹)	Assignment	$\nu(\text{calc})$ (cm ⁻¹)
427	$2\nu_5 - \nu_6$	429	1025	$\nu_1 + \nu_4$	1028
439	$\nu_3 - \nu_5$	439	1063	$\nu_3 + \nu_5$	1065
481	$\nu_2 - \nu_6$	477	1145	$2\nu_6 + \nu_3$	1146
509	$\nu_5 + \nu_6$	510	1195	$\nu_2 + \nu_5 + \nu_6$	1184
517	-	-	1255	-	-
590	$3\nu_6$	591	1272	$\nu_3 + \nu_4 + \nu_6$	1276
639	$\nu_4 + \nu_5$	640	1320	$\nu_2 + \nu_4 + \nu_5$	1314
714	$\nu_1 + \nu_4 + \nu_5$	715	1425	$\nu_2 + \nu_3$	1426
752	ν_3	-	1451	$\nu_1 + \nu_3$	1453
780	$\nu_1 + \nu_3 - \nu_2$	779	1505	-	-
849	$2\nu_4 + \nu_6$	851	1568	$\nu_1 + \nu_2 + \nu_6$	1572
871	$\nu_2 + \nu_6$	871	1748	$\nu_2 + \nu_3 + \nu_5$	1739
888	$\nu_3 + \nu_4 + \nu_6$	882	1830	$2\nu_3 + \nu_4$	1831
951	$2\nu_5 + \nu_4$	953	2098	$2\nu_2 + \nu_3$	2100
969	$3\nu_4$	981	2240	$3\nu_3$	2256

2. Raman Absorption Spectrum of Tellurium Hexafluoride

The Raman absorption spectra of tellurium hexafluoride⁸² is presented in Table 3. Raman intensities for spherically symmetric modes of tellurium hexafluoride are also reported.⁸³

TABLE 3. The Raman Frequencies of Tellurium Hexafluoride⁸²

		$\nu_1(1)^a$	$\nu_2(2)$	$\nu_5(3)$	Te-F	$I \times 10^{40b}$
State		(cm ⁻¹)	(cm ⁻¹)	(cm ⁻¹)	(Å)	(g-cm ²)
TeF ₆	Liquid	697(10) ^c	672(2)	316(4)		
	Gas	701.2(10)	674.4(1)	313(4)	1.84	425

^aMultiplicities.

^bMoment of inertia.

^cRelative intensities.

3. Frequencies of Fundamental Vibrations of Tellurium Hexafluoride

The values of the frequencies of fundamental vibrations of tellurium hexafluoride are given below in units of cm⁻¹ (Ref. 79):

Fundamentals	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6
Degree of	1	2	3	3	3	3
Degeneracy	697	672	752	325	315	197

Other frequencies have been reported⁷⁸ for these fundamentals.

4.2.9 Toxicity of Tellurium Hexafluoride

At the 27th Annual Meeting of the American Conference of Governmental Industrial Hygienists¹³ a tentative maximum safe concentration of airborne tellurium hexafluoride was given as 0.2 mg/m³, compared to 0.1 mg/m³ for airborne tellurium metal. However, Sandratskaya⁸⁴ and Kimmerle⁸⁵ found that tellurium hexafluoride is more toxic than the tellurium metal, since it causes edema of the lungs during hydrolysis. Hammond reports that airborne levels of tellurium at concentrations of 0.01 mg/m³ may present a health hazard.¹⁵

4.3 Miscellaneous Chemical Properties of Tellurium Hexafluoride

Studies by Clifford and Morris²⁵ indicate that tellurium hexafluoride is moderately soluble in anhydrous hydrofluoric acid. The reaction of tellurium hexafluoride with tellurium metal has been thoroughly studied

and will be reviewed in section 5.0. Mercury slowly decomposes the hexafluoride to metallic tellurium.

4.4 Chemical Properties of Complex Compounds of Tellurium Hexafluoride

4.4.1 Metal Fluoride Complexes with TeF_6

The ready availability of the orbitals required for hybridization enables tellurium hexafluoride to form complexes with various electron-donor types of compounds.^{3,4} Muetterties⁸⁶ found that fluorotellurates(VI), which have the limiting composition $2\text{MF} \cdot \text{TeF}_6$, may be prepared by heating an alkali metal fluoride with a large excess of tellurium hexafluoride in a pressurized vessel at 250°C ; to isolate the complexes, the reaction mixture was slowly cooled to room temperature over a period of 24 hr. The composition of the materials found as the reaction products were: $2\text{CsF} \cdot \text{TeF}_6$, $2\text{RbF} \cdot 0.52\text{TeF}_6$, and $2\text{KF} \cdot 0.32\text{TeF}_6$. Sodium, lithium, and barium fluorides were found to be inactive under the conditions studied. X-ray patterns of the cesium octafluorotellurate(VI) consisted of many weak lines which were indexed; no crystalline cesium fluoride was found. The X-ray diffraction patterns of complexes of rubidium and potassium fluoride with tellurium hexafluorides showed the presence of the alkali metal fluoride and a second crystalline phase.

The alkali metal fluorotellurates(VI) are reported to dissociate at an elevated temperature, probably in excess of 300°C , to yield the respective fluorides. Rough measurements of the dissociation pressure of cesium octafluorotellurate(VI) yielded an average value for the heat of dissociation of $0.4 \text{ kcal mole}^{-1}$ over the temperature range from 200 to 250°C . The fluorotellurates(VI) were reported to display "no stability outside of the solid state,"⁸⁶ and the lattice stability appears to be inversely related to the polarizing power of the cation. Clifford and Morris²⁵ have prepared a number of fluorotellurate(VI) salts by reacting an anhydrous hydrofluoric acid solution of tellurium hexafluoride with the base metal fluorides. The salts were isolated by evaporating the hydrofluoric acid and excess tellurium hexafluoride. The composition of the calcium and barium fluorotellurates(VI) indicated mixtures of $\text{MF}_2 \cdot \text{TeF}_6$ and $\text{MF}_2 \cdot 2\text{TeF}_6$; the silver complex formed was found to be $\text{AgF} \cdot \text{TeF}_6$.

4.4.2 Tertiary Amine Complexes with TeF_6

Muetterties⁸⁷ found that tellurium hexafluoride will react exothermally with tertiary amines to form stable complexes of the composition $2\text{R}_3\text{N} \cdot \text{TeF}_6$. Analyses of the nmr data are consistent with an octacovalent complex with geometrical isomers which undergo amine exchange through simple dissociation. The tertiary amine complexes were formed by adding the respective amine to the tellurium hexafluoride under vacuum. The trimethylamine complex is a white solid, whereas the ethyl homologue had a dark color that apparently was due to minor secondary reactions.

4.5 Thermochemical Properties of Tellurium Hexafluoride

4.5.1 Heats of Sublimation, Evaporation, and Fusion

The following thermochemical data were evaluated from vapor pressure studies on tellurium hexafluoride:

$$\Delta H_{\text{sub}} = 6.13^{88} \text{ and } 6.74^{62} \text{ kcal/mole;} \quad (19)$$

$$\Delta H_{\text{evap}} = 4.53^{71} \text{ and } 4.84^{62} \text{ kcal/mole;} \quad (20)$$

$$\Delta H_{\text{fusion}} = 1.6^{71} \text{ and } 1.9^{62} \text{ kcal/mole;} \quad (21)$$

$$\text{Trouton Constant} = 15.08 \text{ cal/mole-degree.}$$

4.5.2 Enthalpy and Energy of Formation of Tellurium Hexafluoride

The heat and energy of formation of tellurium hexafluoride by calorimetric measurements are as follows:

$$\Delta H_{\text{f}298}^{\circ} = -315^{62} \text{ and } -327.2_5 \pm 0.5_6 \text{ (Ref. 89) kcal/mole;} \quad (22)$$

$$\Delta E_{\text{f}298}^{\circ} = 326.0_7 \pm 0.5_6 \text{ (Ref. 89) kcal/mole.} \quad (23)$$

4.5.3 Entropy and Gibbs Energy of Formation

The calculated entropy and Gibbs energy are

$$\Delta S_{\text{f}298}^{\circ} = -76.94^{89} \text{ cal/deg mole} \quad (24)$$

and

$$\Delta F_{\text{f}298}^{\circ} = -304.3_1 \text{ (Ref. 89) } \pm 0.5_6 \text{ kcal/mole.} \quad (25)$$

4.5.4 Tabulation of Thermodynamic Properties

The thermodynamic properties, $-(F^{\circ}-H_0^{\circ})/T$, $(H^{\circ}-H_0^{\circ})/T$, S° , $H^{\circ}-H_0^{\circ}$, and C_p° are listed in Table 4; Table 5 contains the thermodynamic values of $-(F^{\circ}-E_0^{\circ})/T$, C_p° , and S° . These values were calculated for the ideal-gas state, assuming a rigid rotator and simple harmonic oscillator model.^{77,89}

4.5.5 Other Thermodynamic Data⁴¹

The data presented here is by Glassner⁴¹ and in part is based on estimates.

TABLE 4. Thermodynamic Properties of
Tellurium Hexafluoride⁸⁹

T (°K)	$(F^\circ - H_0^\circ)/T$ (cal deg ⁻¹ mole ⁻¹)	$(H^\circ - H_0^\circ)/T$ (cal deg ⁻¹ mole ⁻¹)	S° (cal deg ⁻¹ mole ⁻¹)	$H^\circ - H_0^\circ$ (kcal mole ⁻¹)	C_p° (cal deg ⁻¹ mole ⁻¹)
0	0	0	0	0	0
100	48.0241	9.5641	57.5882	0.9564	13.7546
200	56.0359	14.0697	79.1056	2.8139	22.6851
273.15	60.8670	16.9849	77.8519	4.6394	26.9642
298.15	62.3907	17.8700	80.2607	5.3279	28.0938
300	62.5016	17.9333	80.4349	5.3800	28.1715
400	68.0917	20.9334	89.0251	8.3734	31.4090
500	73.0213	23.2371	96.2584	11.6186	33.3345
600	77.4231	25.0272	102.4503	15.0163	34.5317
700	81.3927	26.4446	107.8373	18.5112	35.3138
800	84.9992	27.5886	112.5878	22.0709	35.8480
900	88.3039	28.5285	116.8324	25.6757	36.2271
1000	91.3522	29.3129	120.6651	29.3129	36.5049
1100	94.1781	29.9767	124.1548	32.9744	36.7142
1200	96.8116	30.5452	127.3568	36.6542	36.8756
1300	99.2753	31.0372	130.3125	40.3483	37.0025
1400	101.5918	31.4670	133.0588	44.0538	37.1040
1500	103.7766	31.8457	135.6223	47.7686	37.1864

TABLE 5. Thermodynamic Properties of
Tellurium Hexafluoride⁷⁷

T (°K)	$-(F^\circ - E_0^\circ)/T$ (cal deg ⁻¹ mole ⁻¹)	S° (cal deg ⁻¹ mole ⁻¹)	C_p° (cal deg ⁻¹ mole ⁻¹)
100	48.06	57.62	13.60
150	52.35	64.18	18.75
200	56.06	70.13	22.65
250	59.43	75.54	25.76
273	60.77	77.74	26.94
298	62.51	80.38	28.07
350	65.42	84.94	30.00
400	68.12	89.13	31.42
500	73.04	96.27	33.42

$$S_{298} = 80.67 \text{ cal/deg mole}; \quad (26)$$

$$\Delta H_{f298}^{\circ} = -315 \text{ kcal/mole}; \quad (27)$$

$$\Delta F_{f298}^{\circ} = -292 \text{ kcal/mole}; \quad (28)$$

$$\frac{(F_T - H_{298})}{T} = 35.33 \ln T - (8.1 \times 10^{-4})T + (3.5 \times 10^5)T^{-2} \\ - (12.954/T) + 160.38 \text{ cal deg}^{-1} \text{ mole}^{-1}; \quad (29)$$

$$(H_T - H_{298}) = 35.33(T - 298) + (8.1 \times 10^{-4})(T^2 - 298^2) \\ + 7 \times 10^5 \left(\frac{1}{T} - \frac{1}{298} \right) \text{ cal mole}^{-1}; \quad (30)$$

$$S_T = 35.33 \ln T + (1.62 \times 10^{-3}) T + (3.5 \times 10^5/T^2) - 125.05 \text{ e.u.}; \quad (31)$$

$$C_p = 35.33 + 1.62 \times 10^{-3}T - (7.00 \times 10^5/T^2) \text{ cal deg}^{-1} \text{ mole}^{-1}, \quad (32)$$

where T is in $^{\circ}\text{K}$.

5.0 PREPARATION OF TELLURIUM TETRAFLUORIDE

5.0.1 Reactions of Tellurium Metal with Tellurium Hexafluoride

Hartley *et al.*²⁶ found that when tellurium hexafluoride is reacted with tellurium metal powder in an alumina vessel at 200°C a colorless solid is formed which crystallizes as fine needles on the walls of the tube. The solid was identified as tellurium tetrafluoride.

Junkins *et al.*²⁷ later repeated this preparation by reacting tellurium hexafluoride with tellurium metal chips (stoichiometric amount plus 10%) in a reaction vessel at 180°C for a period of 100 hr; the hexafluoride completely reacted with the tellurium metal to form the white crystalline tellurium tetrafluoride. The tellurium tetrafluoride sublimes from the reaction zone and is deposited in a cooler region of the reduction apparatus. A simple sublimation step was used to remove the tetrafluoride from small quantities of less volatile, gray-colored lower fluorides which had been formed by localized overheating during the reduction. The fluorides were heated to 160°C and the sublimate collected on a cold finger at 0°C .

5.0.2 Reaction of Tellurium Dioxide and Selenium Tetrafluoride

Tellurium tetrafluoride may be prepared by reacting dry tellurium dioxide with selenium tetrafluoride at 80°C.⁹⁰ Campbell and Robinson⁶¹ prepared tellurium tetrafluoride from tellurium dioxide and selenium tetrafluoride in the following manner:

Selenium tetrafluoride was distilled from a break-seal storage bulb into a carefully dried, evacuated train of bulbs; the stem of the first contained the dry tellurium dioxide. The liquid was condensed on the dioxide and the mixture slowly heated by means of a water bath. As the temperature approached 80°C, there was a vigorous but steady reaction, and the tellurium dioxide dissolved. The temperature was raised until the liquid began to reflux under its own vapor pressure and was kept at that point for 15 min, after which the selenium tetrafluoride and oxyfluoride were distilled into another bulb; the last traces of the selenium tetrafluoride and oxyfluoride were removed from the residue by maintaining the system at 100°C and 10^{-2} mm for 1 hr. The product was a white crystalline solid (found: Te, 62.6%; F, 37.1%; calculated for TeF_4 : Te, 62.7%; F, 37.3%).

5.1 Handling of Tellurium Tetrafluoride^{26,27}

Tellurium tetrafluoride, unlike the hexafluoride, is very reactive; the material hydrolyzes readily and reacts with silica at 200°C. It also reacts with copper at the same temperature to form copper telluride and copper fluoride. Silver is similarly attacked, but the reactions with gold and nickel are very slow. Platinum appears inert at temperatures below 300°C.

5.2 Physical Properties of Tellurium Tetrafluoride

5.2.1 Description

Tellurium tetrafluoride is a white, crystalline, needle-shaped solid^{26,27,61} with a formula weight of 203.59 g/mole.

5.2.2 Melting Point, Boiling Point, and Vapor Pressure Measures

The melting point of tellurium tetrafluoride is $129.6 \pm 1.0^\circ\text{C}$.²⁷ Tellurium tetrafluoride is unstable at temperatures above 193.8°C, decomposing to tellurium hexafluoride and lower fluorides.²⁷ Consequently, the boiling point has not been determined.

The vapor pressure of solid and liquid tellurium tetrafluoride was determined by Junkins *et al.*²⁷ from room temperature to 193.8°C, yielding the following equations:

$$\log_{10} P_{\text{mm}} (\text{solid}) = 9.0934 - (3174.3/T); \quad (33)$$

$$\log_{10} P_{\text{mm}} (\text{liquid}) = 5.6397 - (1786.4/T), \quad (34)$$

where T is in °K.

5.2.3 Crystal Structure, Density, and Absorption Spectra

No determinations of crystal structure, density, or absorption spectra have been reported.

5.3 Chemical Properties of Tellurium Tetrafluoride

5.3.1 Complex Compounds

TeF₄ · SbF₅. Bartlett and Robinson⁹¹ formed the compound TeF₄ · SbF₅ by slowly dissolving tellurium tetrafluoride in antimony pentafluoride at 40-50°C to give a clear liquid, which on cooling deposits white crystals of TeF₄ · SbF₅.

MF · TeF₄. Edwards *et al.*⁹² found that when a mixture of tellurium dioxide and alkali fluoride, with the former in slight excess, was dissolved in warm selenium tetrafluoride and cooled, a complex fluoride crystallized as colorless crystals. The preparation is illustrated by the equation

(C₅H₅NH)₂TeF₆. Dipyridinium hexafluorotellurate(IV) is formed when tellurium dioxide and pyridine are reacted in an aqueous solution of concentrated hydrofluoric acid.⁹³

NO₂ · TeF₅. Nitronium pentafluorotellurate(IV) is formed by reacting tellurium dioxide with nitryl fluoride (NO₂F).⁹⁴

(NO₂) · TeF₆. Nitronium hexafluorotellurate(IV) is prepared by reacting tellurium tetrachloride with nitryl fluoride.⁹⁵

5.4 Thermochemical Properties of Tellurium Tetrafluoride

5.4.1 Heats and Entropies of Vaporization, Sublimation, and Fusion

Junkins *et al.*²⁷ evaluated the heats of evaporation, sublimation, and fusion from his vapor pressure studies of solid and liquid tellurium tetrafluoride.

$$\Delta H_{\text{vap}} = 8.174 \text{ kcal/mole}; \quad (35)$$

$$\Delta H_{\text{sub}} = 14.525 \text{ kcal/mole}; \quad (36)$$

$$\Delta H_{\text{fusion}} = 6.351 \text{ kcal/mole}; \quad (37)$$

$$\Delta S_{\text{vap}} = 12.62 \text{ cal/deg mole}; \quad (38)$$

$$\Delta S_{\text{sub}} = 28.39 \text{ cal/deg mole}; \quad (39)$$

$$\Delta S_{\text{fusion}} = 15.77 \text{ cal/deg mole}. \quad (40)$$

5.4.2 Other Thermodynamic Data⁴¹

The data presented here is by Glassner and in part is based on estimates.

$$\Delta H_{\text{f}298}^{\circ} = -205 \text{ kcal/mole}; \quad (41)$$

$$\Delta F_{\text{f}298}^{\circ} = -185 \text{ kcal/mole}; \quad (42)$$

$$S_{298} = 42 \text{ cal/deg mole}; \quad (43)$$

$$\begin{aligned} \frac{(F_T - H_{298})}{T} (\text{TeF}_4 - \text{solid}) &= -25.6 \ln T - 4.6 \times 10^{-3}T - \frac{8.042}{T} \\ &+ 132.2 \text{ cal deg}^{-1} \text{ mole}^{-1}; \end{aligned} \quad (44)$$

$$\begin{aligned} \frac{(F_T - H_{298})}{T} (\text{TeF}_4 - \text{gas}) &= -20 \ln T - 2.5 \times 10^{-3}T + (12.995/T) \\ &+ 56.5 \text{ cal deg}^{-1} \text{ mole}^{-1}; \end{aligned} \quad (45)$$

$$\begin{aligned} (H_T - H_{298})(\text{TeF}_4 - \text{solid}) &= 25.6(T - 298) \\ &+ 4.6 \times 10^{-3}(T^2 - 298^2) \text{ cal mole}^{-1}; \end{aligned} \quad (46)$$

$$\begin{aligned} (H_T - H_{298})(\text{TeF}_4 - \text{gas}) &= 20(T - 298) + 2.5 \times 10^{-3}(T^2 - 298^2) \\ &\text{cal mole}^{-1}; \end{aligned} \quad (47)$$

$$C_p(\text{TeF}_4 - \text{solid}) = 25.6 + 9.2 \times 10^{-3}T \text{ cal deg}^{-1} \text{ mole}^{-1}; \quad (48)$$

$$C_p(\text{TeF}_4 - \text{gas}) = 20 + 5 \times 10^{-3}T \text{ cal deg}^{-1} \text{ mole}^{-1}. \quad (49)$$

6.0 PREPARATION OF DITELLURIUM DECAFLUORIDE, Te_2F_{10} , AND TRITELLURIUM DIOXOTETRADECAFLUORIDE, $\text{Te}_3\text{F}_{14}\text{O}_2$

6.0.1 Reactions of Tellurium Metal with Fluorine in the Presence of Calcium Fluoride

English and Dale¹⁸ found that when a mixture of 100 g of approximately 250-mesh tellurium metal and 450 g of approximately 100 mesh calcium fluoride is fluorinated by elemental fluorine at a fluorine flow rate of 16 g/hr and at a temperature of $<20^\circ\text{C}$, a 20% yield of ditellurium decafluoride is obtained. Campbell and Robinson¹⁷ could not reproduce the yields reported and obtained only negligible amounts of ditellurium decafluoride.

6.0.2 Reactions of Tellurium Metal with Fluorine in the Presence of Various Metals and Metal Oxides

When tellurium is reacted with fluorine in the presence of nitrogen, oxygen, nickel powder, copper powder, alumina, or tellurium dioxide, a variety of products are formed.¹⁷ The reaction conditions and the products formed under these conditions are summarized in Table 6.

TABLE 6. Summary of Fluorination Experiments¹⁷

Solid Reactants	Fluorine Flow Rate (l/hr)	Gaseous Diluent; Flow Rate (l/hr)	Furnace Wall Temperature ($^\circ\text{C}$)	Products
Te metal	2	N_2 ; 4	40-60	Te_2F_{10} , 5-10%; TeF_6 , 80-90%
Te metal with Al_2O_3 , or Ni metal, or Cu metal; ratio 1:1	3-5	none	60-80	Te_2F_{10} , 10-16%; remainder TeF_6
Te metal with TeO_2 ; ratio 1:1	3-4	N_2 ; 10	50-60	Te_2F_{10} , 25%; $\text{Te}_3\text{F}_{14}\text{O}_2$, 2%; remainder TeF_6
Te metal with TeO_2 ; ratio 1:1	3-4	O_2 ; 10	50-60	Te_2F_{10} , 40-45%; $\text{Te}_3\text{F}_{14}\text{O}_2$, 5%; higher-b.p. material 0.5%; remainder TeF_6

The reactions summarized in Table 6 were carried out with the solids in nickel tube furnaces connected to a train of pyrex traps. The apparatus was thoroughly dried before fluorine, appropriately diluted and previously cooled to -180°C , was admitted. The products were condensed at -180°C , and after the flow of fluorine was stopped but before the traps were sealed, the reaction-tube temperature was raised to 150°C and the less volatile products were purged from the reaction tube in a nitrogen stream. The material collected was freed from most of the hexafluoride

by keeping it at -60°C in one trap connected to another at -180°C ; the pressure in the system was held at 10^{-2} mm. Before the trap at -180°C was detached, the residue was allowed to warm to -50°C . The product was then transferred in 10-cc lots to an air-cooled reflux column where the material was fractionated.

The products of the fluorination of tellurium metal and tellurium oxide as reported in Table 6 indicate the presence of a compound thought to be tritellurium dioxotetradecafluoride, $\text{Te}_3\text{F}_{14}\text{O}_2$, and possibly a higher oxyfluoride, such as $\text{Te}_6\text{F}_{26}\text{O}_5$, in addition to tellurium hexafluoride and ditellurium decafluoride. The composition of the new compound thought to be $\text{Te}_3\text{F}_{14}\text{O}_2$ was found to have a tellurium to fluoride ratio of 3:14, and since the tellurium and fluorine accounted for 95% of the material, the remainder was assumed to be oxygen. The compound $\text{Te}_3\text{F}_{14}\text{O}_2$ has a similar tellurium to fluorine ratio and contains 4.7% oxygen. The Dumas molecular weight of the new compound was found to be 715 g/mole, somewhat higher than that of $\text{Te}_3\text{F}_{14}\text{O}_2$, which is 680.8 g/mole. The differences were thought to have resulted from an inherent error in the determination.

The compositions and molecular weights of the other higher oxyfluoride product are compared with the theoretical composition and molecular weight of some proposed compounds:

	Te (%)	F (%)	O (%)	MW (g/mole)
$\text{Te}_5\text{F}_{22}\text{O}_4$	56.9	37.3	5.8	1120
$\text{Te}_6\text{F}_{26}\text{O}_5$	57.1	36.9	6.0	1340
$\text{Te}_7\text{F}_{30}\text{O}_6$	57.3	36.6	6.2	1559
Preparation	56.6	36.0	7.4*	1270, 1300, 1470 mean 1350

*Determined by difference

The new higher oxyfluoride was assumed to be $\text{Te}_6\text{F}_{26}\text{O}_5$.

6.1 Handling of Ditellurium Decafluoride, Tritellurium Dioxotetradecafluoride, and $\text{Te}_6\text{F}_{26}\text{O}_5$ ^{17,18}

Ditellurium decafluoride and tritellurium dioxotetradecafluoride are not immediately attacked by water; slow decomposition of Te_2F_{10} is noted during a period of several months in contact with water. Ditellurium decafluoride and tritellurium dioxotetradecafluoride do not react noticeably with iron, copper, or nickel, and have little effect upon elemental mercury. Ditellurium decafluoride is reported by English and Dale¹⁸ to attack pyrex, whereas Robinson and Campbell¹⁷ say it does not. $\text{Te}_6\text{F}_{26}\text{O}_5$ attacks pyrex at temperatures below 300°C .

6.2 Physical Properties of Ditellurium Decafluoride, Tritellurium Dioxotetradecafluoride, and $\text{Te}_6\text{F}_{26}\text{O}_5$

6.2.1 Formula Weights:

$$\text{Te}_2\text{F}_{10} = 445.18 \text{ g/mole}; \quad (50)$$

$$\text{Te}_3\text{F}_{14}\text{O}_2 = 680.8 \text{ g/mole}; \quad (51)$$

$$\text{Te}_6\text{F}_{26}\text{O}_5 = 1340 \text{ g/mole}. \quad (52)$$

6.2.2 Description

Ditellurium decafluoride,^{17,18} tritellurium dioxotetradecafluoride, and $\text{Te}_6\text{F}_{26}\text{O}_5$ are colorless liquids at room temperature.

6.2.3 Melting Point, Boiling Point, and Vapor Pressure

$$\text{Melting Point: } \text{Te}_2\text{F}_{10}, \quad -34 \text{ to } -33^\circ\text{C};^{18} \quad 33.7 \pm 0.2^\circ\text{C};^{17} \quad (53)$$

$$\text{Te}_3\text{F}_{14}\text{O}_2, \quad -27^\circ\text{C};^{17} \quad (54)$$

$$\text{Te}_6\text{F}_{26}\text{O}_5, \quad < 20^\circ\text{C};^{17} \quad (55)$$

$$\text{Boiling Point: } \text{Te}_2\text{F}_{10}, \quad 53^\circ/748 \text{ mm};^{18} \quad 59.0 \pm 0.2^\circ\text{C};^{17} \quad (56)$$

$$\text{Te}_3\text{F}_{14}\text{O}_2, \quad 134.5^\circ/755 \text{ mm};^{17} \quad (57)$$

$$\text{Te}_6\text{F}_{26}\text{O}_5, \quad > 300^\circ\text{C}.^{17} \quad (58)$$

The vapor pressure of liquid ditellurium decafluoride was determined experimentally by English and Dale¹⁸ over a temperature range from -33 to 54°C ; they gave the following equation:

$$\log P_{\text{mm}} = 9.20 - (2063/T), \quad (59)$$

where T is in $^\circ\text{K}$.

Vapor pressure data are not available for $\text{Te}_3\text{F}_{14}\text{O}_2$ and $\text{Te}_6\text{F}_{26}\text{O}_5$.

6.2.4 Density

$$\text{Te}_2\text{F}_{10}: 2.88,^{18} \quad 2.839^{17} \text{ g/cm}^3 \text{ at } 25^\circ\text{C}; \quad (60)$$

$$2.9372^{17} \text{ g/cm}^3 \text{ at } 0^\circ\text{C}; \quad (61)$$

$$4.0984 - 0.0042525 T \text{ } (-30 \text{ to } 30^\circ\text{C})^{17} \text{ g/cm}^3, \quad (62)$$

where T is in $^\circ\text{K}$.

$$\text{Te}_3\text{F}_{14}\text{O}_2: 2.25 \pm 0.05 \text{ g/cm}^3 \text{ at } 20^\circ\text{C};^{17} \quad (63)$$

$$\text{Te}_6\text{F}_{26}\text{O}_5: 3 \text{ to } 3.1 \text{ g/cm}^3 \text{ at } 20^\circ\text{C}.^{17} \quad (64)$$

6.2.5 Structure

Electron-diffraction studies to determine the structure of ditellurium decafluoride have not been reported, but similar studies on disulfur decafluoride⁹⁶ clearly show that the structure consists of two octahedral-SF₅ units, joined together by a sulfur-sulfur bond. Dodd and associates⁹⁷ in their treatment of the infrared and Raman absorption spectra of ditellurium decafluoride assumed that the structure of ditellurium decafluoride was similar to that of disulfur decafluoride.

No structural information is available on the oxyfluorides compounds of tellurium.

6.2.6 Surface Tension and Viscosity

The surface tension of ditellurium decafluoride is given below:¹⁷

Temperature ($^\circ\text{K}$)	311	296.2	274.5	258	257
Surface Tension (dynes/cm)	12.94	14.96	17.51	19.25	19.67
$\gamma_T = (49.2 \pm 0.2) - 0.11554T^\circ\text{K} \text{ (dynes/cm)}.$					

The viscosity of ditellurium decafluoride was studied by Hetherington and Robinson as a function of temperature; they obtained the following equation:⁹⁸

$$\eta_t = 0.01524 / (1 + 0.01365t + 0.0000175t^2) \text{ poise}, \quad (65)$$

where t is in $^\circ\text{C}$. No information on the surface tension or viscosity of $\text{Te}_3\text{F}_{14}\text{O}_2$ or $\text{Te}_6\text{F}_{26}\text{O}_5$ is reported.

6.2.7 Electrical Conductivity

The electrical conductivity of ditellurium decafluoride is (range 293-309°K) $(3.1 \pm 0.4) \times 10^{-8}$ mhos/cm. No information on electrical conductivity of the $\text{Te}_3\text{F}_{14}\text{O}_2$ or $\text{Te}_6\text{F}_{26}\text{O}_5$ is reported.

6.2.8 Absorption Spectra

Dodd *et al.*⁹⁷ assumed a $\text{F}_5\text{Te}-\text{TeF}_5$ structure with a staggered configuration (point group D_{4d}) and ruled out free rotation about the Te-Te bond in their treatment of the absorption spectra of ditellurium decafluoride. The use of the D_{4d} point group gives rise to the fundamental vibrations of Te_2F_{10} listed in Table 7.

TABLE 7. Vibrational Selection Rules for Fundamentals of Ditellurium Decafluoride⁹⁷

Symmetry Class	a_1	b_1	b_2	l_1	l_2	l_3
Number of Fundamentals	4	1	3	4	3	4
Enumeration Activity*	$\nu_1 - \nu_4$	ν_5	$\nu_6 - \nu_8$	$\nu_9 - \nu_{12}$	$\nu_{13} - \nu_{15}$	$\nu_{16} - \nu_{19}$
	R(p)	-	I(para)	I(perp)	R(dp)	R(dp)

*R is for Raman; I is for infrared.

The infrared absorption spectrum of ditellurium decafluoride⁹⁷ vapor is shown in Fig. 2; all the frequencies are collected in Table 8 with the approximate intensities again expressed as extinction coefficients (liter/mole cm) at the maxima. A feature is the high intensity of the band at 752 cm^{-1} . No bands are given above 1613 cm^{-1} : two which appeared at 3150 and 3610 cm^{-1} varied markedly in relative intensity in different measurements and were therefore rejected by Dodd *et al.*

Fig. 2. Infrared Spectrum of Ditellurium Decafluoride between 450 and 950 cm^{-1} (Ref. 97). (Figures denote pressure in mm of vapor in 10-cm cell.)

TABLE 8. Infrared Spectrum of Ditellurium Decafluoride⁹⁷

$\nu(\text{obs})$ (cm^{-1})	Intensity ^a	Assignment
468	(34)	$\nu_{10}(e_1), \nu_8(b_2)$
541	vw	$714 - 168 = 546 E_1$
667	(24)	?
714	(2160)	$\nu_9(e_1)$
734	(480)	$\nu_7(b_2)$
752	(7000)	$\nu_6(b_2)$
811	(9)	$670 + 138 = 808 E_1 + E_3$
830	(9)	?
870	(240)	$\begin{cases} 714 + 168 = 882 E_1 \\ 734 + 138 = 872 E_1 \end{cases}$
890	(2800)	$752 + 138 = 890 E_1$
967	(24)	$714 + 259 = 973 B_1 + B_2 + E_2$
1016	(5)	$752 + 259 = 1011 E_1$
1025	(6)	$\begin{cases} 714 + 319 = 1033 E_1 + E_3 \\ 752 + 2 \times 138 = 1028 B_1 + B_2 + E_2 \end{cases}$
1053	(12)	$\begin{cases} 752 + 138 + 168 = 1058 E_1 \\ 734 + 319 = 1053 E_1 \end{cases}$
1136	(8)	$670 + 468 = 1138 E_1$
1255	vw	?
1362	(12)	$752 + 138 + 475 = 1365 E_1$
1403	(4)	$\begin{cases} 714 + 682 = 1396 E_1 \\ 734 + 670 = 1404 E_1 \end{cases}$
1435	(5)	$\begin{cases} 726 + 714 = 1440 E_1 \\ 752 + 682 = 1434 B_2 \end{cases}$
1479	vw	$752 + 726 = 1478 B_2$
1530	vw	?
1613	vw	$752 + 726 + 138 = 1616 E_1$

^aThe approximate intensities are expressed as extinction coefficients (liter/mole cm).

Figure 3 shows a microphotometer record of the Raman spectrum of the liquid excited by Hg 4358 Å. In this record the strongest line at 682 cm^{-1} appears as a single line, but in the record of the same line excited by Hg 4046 Å, for which the resolution is better, the peak is seen to have a weaker companion at 670 cm^{-1} .

Fig. 3. Raman Spectrum of Liquid Ditellurium Decafluoride⁹⁷

Exposures with polarized incident light clearly distinguished these two lines, since they differ in polarization. The measured frequencies are listed in Table 9, together with indications of intensities and states of polarization. This table also includes the infrared frequencies assigned to fundamentals in Table 3. No absorption spectra are available for tritellurium dioxotetradecafluoride or $\text{Te}_6\text{F}_{26}\text{O}_5$.

6.3 Chemical Properties of Ditellurium Decafluoride and Tritellurium Dioxotetradecafluoride^{17,18}

6.3.1 Ditellurium Decafluoride

Ditellurium decafluoride vapor attacks organic stopcock greases

immediately, turning them black, and the liquid dissolves fluorinated stop-cock greases. It reacts with acetone and releases iodine from acetone solutions of potassium iodide. It was observed that distilled water or 20% aqueous sodium hydroxide had no apparent effect on liquid ditellurium decafluoride during an 18-hr exposure; however, after several months some hydrolysis was noted. Sodium metal attacks Te_2F_{10} slowly and quietly, whereas metallic potassium reacts vigorously; both reactions yield black powder. Sulfur and selenium are not attacked by the liquid at its boiling point. Neither barium fluoride nor calcium fluoride retain any of the compound after being boiled in the liquid. Although sodium fluoride appears to retain some Te_2F_{10} , the amount is not large, and the X-ray diffraction pattern of sodium fluoride which had been exposed to Te_2F_{10} for 8 hr under refluxing conditions was unchanged compared to pure sodium fluoride. Ditellurium decafluoride reacts with most substituted aromatic compounds, and all amines tested reacted very vigorously; occasionally, the reaction was so violent it was necessary to use dilute solutions. The reactions are complex and may result in the formation of tars. Catechol, α -naphthylamine, and methyldiphenylamine produce insoluble stable powders of green, dark blue, and black, respectively.

TABLE 9. Ditellurium Decafluoride: Raman Spectrum and Fundamentals Active in the Infrared⁹⁷

Raman	Infrared	Assignment
138 w dp		$\nu_{19} e_3$ TeF_5 rocking
168 s p		$\nu_4 a_1$ Te-Te stretching
259 m dp		$\left\{ \begin{array}{l} \nu_{14} e_2 \\ \nu_{15} e_2 \\ \nu_{17} e_3 \\ \nu_{18} e_3 \\ \nu_8 b_2 \\ \nu_{10} e_1 \end{array} \right\}$ deformations
319 s dp		
	468 m	
475 mp		
670 w dp		
682 vs p		
	714 vs	$\left\{ \begin{array}{l} \nu_{13} e_2 \\ \nu_{16} e_3 \\ \nu_2 a_1 \\ \nu_9 e_1 \end{array} \right\}$ Te-F stretchings
726 vs p	734 s	
	752 vs	

With saturated and halogen-substituted aliphatic hydrocarbons the ditellurium decafluoride gives colorless solution without appreciable reaction or loss of distinctive properties.

6.3.2 Tritellurium Dioxotetradecafluoride

Tritellurium dioxotetradecafluoride is unreactive toward pyrex, copper, brass, or rubber. It is, however, sorbed by most greases.

6.4 Thermochemical Properties of Ditellurium Decafluoride^{17,18}

$$\Delta H_{\text{vap}} = 9.440 \text{ kcal/mole (at boiling point).} \quad (66)$$

$$\text{Trouton Constant} = 28.8 \text{ cal/mole degree.}$$

$$\text{Critical Temperature} = 170^{\circ}\text{C.}$$

7.0 PREPARATION OF F₅-TYPE TELLURIUM COMPOUNDS

A new class of tellurium compounds which are called F₅Te-type compounds have recently been prepared by Engelbrecht and Sladky.⁹⁹ The compounds have been isolated from the distillate produced by heating barium orthotellurate, BaTeO₄, and fluorosulfuric acid, FSO₃H, in mole ratios of the respective compounds at 1:5 to 1:15. The compounds prepared by this method are presented in Table 10.

TABLE 10. F₅Te-type Compounds⁹⁹

Compound	M.P. (°C)	B.P. (°C)	Solubility in Water
F ₅ TeOH	40	60	Sol
F ₅ TeOSO ₂ F	-89	56	Insol
(F ₅ TeO) ₂ SO ₂	-50	118	Insol
(F ₅ Te)SO ₃ H	-21	133	Sol

8.0 TELLURIUM FLUORIDES AND THE TECHNOLOGY OF THE FLUORIDE VOLATILITY PROCESS

8.0.1 Fluoride Volatility Processes²⁴

Fluoride volatility processes are based on the ability to convert uranium and plutonium in nuclear fuels to volatile hexafluorides which can be readily separated from associated fuel materials (cladding and fission products) and purified by established techniques. The fluorination of the reactor fuel can be carried out with bromine trifluoride,^{100,101} chlorine trifluoride,¹⁰² bromine pentafluoride,¹⁰³ and with fluorine.^{104,105} In all cases elemental fluorine must be used if the volatile plutonium hexafluoride is to be formed.

8.0.2 Formation of Tellurium Hexafluoride in the Various Fluoride Volatility Processes

The fluorination of fission-product tellurium by the various fluorinating agents has been assumed by most workers to result in the formation of the highly volatile tellurium hexafluoride. Page,¹⁰⁰ however, reported that when 45 g of irradiated uranium tetrafluoride were fluorinated with a mixture of 100 ml of bromine trifluoride and 20 ml of bromine pentafluoride, the fluorinated fission-product tellurium did not behave as tellurium hexafluoride, but more like ditellurium decafluoride, a higher boiling compound. Fischer and Steunenberg⁶⁸ showed that tellurium hexafluoride does not form an addition compound with either bromine trifluoride or pentafluoride, and that the isomeric transition in the decay of $\text{Te}^{129\text{m}}$ or $\text{Te}^{127\text{m}}$ results in the formation of a species less volatile than tellurium hexafluoride. The latter fact, however, has little bearing on the work of Page,¹⁰⁰ since Page's entire study was carried out in an atmosphere of BrF_3 , which has been shown by Fischer and Steunenberg to refluorinate the less volatile fluoride of tellurium formed by the decay of $\text{Te}^{129\text{m}}$ and $\text{Te}^{127\text{m}}$.

Studies by Campbell and Robinson¹⁷ indicate that at high temperature ($>150^\circ\text{C}$) the only reaction product formed when tellurium metal reacts with fluorine gas is tellurium hexafluoride. These studies also indicate that at low temperature ($<80^\circ\text{C}$) a significant amount of ditellurium decafluoride may be formed when metallic tellurium is fluorinated with gaseous fluorine.

8.0.3 Removal of Tellurium Hexafluoride from the Off-gas of the Fluoride Volatility Process

The volatile fluoride or fluorides of tellurium which are formed in the fluoride volatility reactor fuel process appear to be difficult to remove from the process off-gas stream. Little quantitative information is available on the ability of such reagents as soda-lime, activated alumina, caustic solution, or activated charcoal to remove tellurium hexafluoride from these off-gases. Chilenskis,¹⁰⁶ as well as French workers,¹⁰⁷ has found that activated alumina at temperatures between 450 and 650°C is very effective in removing the tellurium hexafluoride from process off-gases. Charcoal traps, when used in series with activated alumina, are quite effective in removing small amounts of tellurium hexafluoride.¹⁰⁶ Studies by Krause and Potts¹⁰⁸ showed that sodium fluoride does not sorb tellurium hexafluoride in the temperature range from 100 to 300°C .

Studies at ORNL¹⁰⁹ indicated that an absorption system consisting of a packed column of Alundum berl saddles through which a 10% aqueous solution of potassium hydroxide is circulated at temperatures of 50 - 70°C , is relatively effective in hydrolyzing tellurium hexafluoride.

Attempts to obtain quantitative results in these hydrolysis studies were unsuccessful. The caustic-spray absorption system used for fluorine disposal in the Oak Ridge Volatility Pilot Plant has been shown capable of removing some of the tellurium, but not enough to insure that none accompanies the residual effluent.¹⁰⁵ Tellurium hexafluoride was also found to react with nickel at temperatures near 300°C. Laboratory tests of the ability of packed beds of nickel mesh in 1-in.-diameter nickel tubes to remove tellurium hexafluoride were investigated and are present in Table 11.¹⁰⁵

TABLE 11. Retention of Tellurium (%) in Beds of Nickel Mesh at 400 to 600°C¹⁰⁵

Conditions: Mixtures of 15 to 25% TeF_6 ^a passed through beds of nickel mesh (1 in. in diameter and 6 in. long) at 100 ml (STP)/min for 0.5 hr.

Temp (°C) ^b	Bed Section (in order of use)						Reactor Wall ^c	Aqueous KOH Trap	Material Balance (%)
	1	2	3	4	5	6			
400	61.8	24.8	1.9	0	0	0			88.5
500	17.7	11.6	4.7	7.2	13.4	10.0	8.7		72.9
600	8.7	4.4	4.7	3.8	0	0	41.4		63.0
400	0	24.5	38.5	1.8	0.2	0		0.7	65.7
450	20.7	44.7	1.4	0	0	0		0	66.8
480	43.6	13.0	1.0	0.7	0	0		0	58.3

^aBalance of feed gas is helium.

^bTemperatures in the last three runs were believed more accurate than others because of improvements in thermocouples.

^cDetermined by total dissolution.

The mechanism for the tellurium retention in the hot nickel bed is probably due to the formation of nickel tellurides, nickel fluoride, and metallic tellurium, not to Te_2F_{10} and TeF_4 as reported. Gunther and Steindler¹¹⁰ found that when tellurium hexafluoride and metallic nickel coupons are reacted at 500°C for 18.9 hr, nickel tellurides (NiTe , NiTe_2) and nickel fluoride are formed as reaction products. The reaction products were isolated from the corroded nickel coupons and identified by X-ray diffraction. Metallic tellurium was also found on the nickel wire used to suspend the nickel, Monel, and Inconel coupons. The source of metallic tellurium has not been definitely established, but probably resulted as a reaction product in the corrosion of the nickel, since the nickel coupons were by far the most extensively corroded of the three metals present. At this time high-temperature caustic spray towers are being considered at ORNL to remove the tellurium hexafluoride from off-gas streams.¹¹¹

To date technological investigations of the ability of various sorbents to sorb tellurium hexafluoride strongly indicate that a satisfactory sorbent has either not been found or, if found, has not been properly evaluated. The problem is further complicated by the fact that the volatile

tellurium fluoride in the off-gas may not be pure tellurium hexafluoride, but may contain such volatile fluorides as ditellurium decafluoride a substance in many respects more chemically inert than the hexafluoride.²⁴ The decafluoride may be formed in low concentration when oxide fuels are fluorinated in a fluid-bed system using low concentrations of fluorine, chlorine trifluoride, or bromine pentafluoride.

9.0 BIBLIOGRAPHY

1. Kirk, R. E., and Othmer, D. F., Encyclopedia of Chemical Technology, Vol. 13, p. 668, Interscience Publishers, Inc., New York (1951).
2. Brasted, R. C., Comprehensive Inorganic Chemistry, Vol. 8, D. Van Nostrand Co., Inc., Princeton, N. Y. (1961).
3. Kimball, G. E., J. Chem. Phys. 8, 188-198 (1940).
4. George, J. W., in Progress in Inorganic Chemistry, Vol. 2, p. 94, F. A. Cotton, ed., Interscience Publishers, Inc., N. Y. (1960).
5. Blomeke, J. O., Nuclear Properties of U²³⁵ Fission Products, ORNL-1783 (Nov 1955).
6. Zysin, Y. A., et al., Fission Product Yields and Their Mass Distribution, Consultants Bureau (1964).
7. Simek, A., and Stehlik, B., Collection Czech. Chem. Commun. 2, 303-341 (1930).
8. Guertler, W., and Pirani, M., Z. Metallk. 11, 1-7 (1919).
9. Brooks, L. S., J. Am. Chem. Soc. 74, 227-229 (1952).
10. Machol, R. E., and Westrum, E. F., Jr., J. Am. Chem. Soc. 80, 2950-2952 (1958).
11. Korneeva, I. V., et al., Zhur. Neorg. Khim 2, 1720-1724 (1957).
12. Gattow, G., and Schneider, A., Angew. Chem. 71, 189-193 (1959).
13. The 27th Annual Meeting of the American Conference of Governmental Industrial Hygienists, Houston, Texas, May 2-4, 1965.
14. Sandratskaya, S. E., Gigiena Truda i Prof. Zabolevaniya 6, No. 2., 44-50 (1962).
15. Handbook of Chemistry and Physics, 45th ed., Chemical Rubber Publishing Co. (1964-65).
16. Prideaux, E. B. R., J. Chem. Soc., 1906, 316-332.
17. Campbell, R., and Robinson, P. L., J. Chem. Soc., 1956, 3454-3458.
18. English, W. D., and Dale, J. W., J. Chem. Soc., 1953, 2498-2499.
19. Simons, J. H., J. Am. Chem. Soc. 52, 3488 (1930).
20. Cocksedge, H. E., J. Chem. Soc., 1908, 2175.
21. Damiens, A., Compt. rend. 172, 1105-1107 (1921).
22. Gutmann, V., Z. Anorg. u. Allgem. Chem. 264, 169-173 (1951).
23. Lenher, V., J. Am. Chem. Soc. 30, 737-741 (1908).

24. Steunenbergh, R. K., and Vogel, R. C., Reactor Handbook, Vol. 2, p. 263, Interscience Publishers Ltd., London (1961).
25. Clifford, A. F., and Morris, A. G., J. Inorg. Nucl. Chem. 5, 71-75 (1957).
26. Hartley, G. A. R., et al., Nature 142, 952 (1938).
27. Junkins, J. H., et al., J. Am. Chem. Soc. 74, 5749 (1952).
28. Lenher, V., J. Am. Chem. Soc. 24, 189 (1902).
29. Damiens, A., Compt. rend. 173, 583-586 (1921).
30. Baker, H. B., Trans. Roy. Soc. (London), 179, 589 (1888).
31. Rossini, F. D., et al., Selected Values of Thermodynamic Properties, U. S. Dept. of Commerce, National Bureau of Standards Circular 500 (Feb 1, 1952).
32. Slansky, C. M., and Coulter, L. V., J. Am. Chem. Soc. 61, 564 (1939).
33. Anderson, C. T., ibid., 59, 1036-1037 (1937).
34. Kubaschewski, O., and Wittig, F. E., Z. Elektrochem. 47, 433-438 (1941).
35. Purbrick, R. L., J. Chem. Phys. 30, 962-963 (1959).
36. Divers, E., and Shimose, M., J. Pr. Chem. [2]24, 218 (1881); Ber. 16, 1004 (1883).
37. Doolan, J. J., and Partington, J. R., J. Chem. Soc., 1924, 1402.
38. Glemser, O., and Porscher, W., Z. Anorg. Chem. 256, 103 (1948).
39. Berzelius, J. J., Pogg. Ann. 32, 15 (1834); Ann. Chim. phys. [2]58, 129 (1835).
40. Awad, S. A., Electrochim. Acta 7, 677-684 (1962).
41. Glassner, A., The Thermochemical Properties of the Oxides, Fluorides, and Chlorides to 2500°K, ANL-5750 (Jan 1958).
42. Soulen, J. R., et al., J. Phy. Chem. 59, 132-136 (1955).
43. Zlomanov, V. P., et al., Zhur. Neorg. Khim. 3, 1473-1477 (1958).
44. Prescher, K. E., and Schroedter, W., Z. Erzbergbau Metallhuettenw. 15, 299-303 (1962).
45. Barrow, R. F., and Hurst, H. J., Nature 201, 699 (1964).
46. Choong Shin-Piaw, Ann. Phys. 10, 173 (1938).
47. Rosen, B., Donnees Concernant les Molecules Diatomiques, Hermann et Cie, Paris (1951).
48. Duchesne, J., and Rosen, B., Nature 157, 692-693 (1946).
49. Montignie, E., Bull. Soc. Chem., 1946, 175-176.

50. Montignie, E., *Ann. Pharm. Franc.* 4, 251-253 (1946).
51. Papish, J., *J. Phys. Chem.* 22, 431 (1918).
52. Papish, J., *ibid.*, 22, 640 (1918).
53. Braumer, B., *Monatsh.* 11, 527 (1890).
54. Hutchins, C. B., Jr., *J. Am. Chem. Soc.* 27, 1158 (1905).
55. Dennis, L. M., and Anderson, R. P., *ibid.*, 36, 903 (1914).
56. Lenher, V., and Wakefield, H. F., *ibid.*, 45, 1423 (1923).
57. Morris, J. F., and Fay, H., *Am. Chem. J.* 20, 278-283 (1898).
58. Gutbier, A., and Wagenknecht, W. Z., *Anorg. Chem.* 40, 260 (1904).
59. Lenher, V., and Kao, C. H., *J. Am. Chem. Soc.* 48, 1550-1556 (1926).
60. Berg, A., *Bull. Soc. Chim.* [3]33, 1310 (1905).
61. Campbell, R., and Robinson, P. L., *J. Chem. Soc.*, 1956, 785.
62. Yost, D. M., and Claussen, W. H., *J. Am. Chem. Soc.* 55, 885-891 (1933).
63. Schuhmann, R., *J. Am. Chem. Soc.* 47, 356-363 (1925).
64. Gadzhiev, S. N., and Sharifov, K. A., *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz. Mat. i Tekhn. Nauk.* No. 1, 47-53 (1962).
65. Kozo, U., *J. Chem. Soc. (Japan)* 62, 990-994 (1941).
66. Prescher, K. E., and Schroedter, W., *Z. Erzbergbau Metallhuettenw.* 16, 352-353 (1963).
67. Mezaki, R., and Margrave, J. L., *J. Phys. Chem.* 66, 1713-1714 (1962).
68. Fischer, J., and Steunenber, R. K., Chemical and Radiochemical Studies of Tellurium in Fluoride Volatility Studies, ANL-5593 (1956).
69. Yost, D. M., in *Inorganic Synthesis*, Vol. I, p. 121, L. F. Audrieth, Ed., McGraw-Hill Book Co., Inc., New York (1939).
70. Moissan, H., *Ann. Chim. Phys.* [6]24, 239 (1891).
71. Klemm, W., and Henkel, P., *Z. anorg. allgem. Chem.* 207, 73-86 (1932).
72. Pearson, T. G., and Robinson, P. L., *J. Chem. Soc.*, 1933, 1427.
73. Henkel, P., and Klemm, W., *Z. anorg. Chem.* 222, 70 (1935).
74. Linke, R., *Z. Phys. Chem.* 48B, 193 (1941).
75. Braune, H., and Knocke, S., *ibid.*, 21B, 297-309 (1933); 23B, 163 (1933).
76. Brockway, L. O., and Pauling, L., *Proc. Natl. Acad. Sci.* 19, 68-73 (1933).
77. Gaunt, J., *Trans. Faraday Soc.* 49, 1122-1131 (1953); 51, 893-894 (1955).
78. Yost, D., *Proc. Ind. Acad. of Sci.* 8A, 333-346 (1938).

79. Landolt-Bornstein, Atom - und Molekular Physik, Part 2, Springer-Verlag, Berlin (1951).
80. Burke, T. G., J. Chem. Phys. 25, 791-792 (1956).
81. Sachsse, H., and Bartholomi, E., Z. Phys. Chem. 28B, 257-66 (1935).
82. Yost, D., et al., J. Chem. Phys. 2, 311-316 (1934).
83. Long, D. A., and Thomas, E. L., Trans. Faraday Soc. 59, 1026-1032 (1963).
84. Sandratskaya, S. E., Toksikol. Redkikh Metal. 117-135 (1963).
85. Kimmerle, G., Arch. Toxikol 18, 140-144 (1960).
86. Muetterties, E. L., J. Am. Chem. Soc. 79, 1004 (1957).
87. Muetterties, E. L., and Phillips, W. D., J. Am. Chem. Soc. 79, 2975 (1957).
88. Henkel, P., and Klemm, W., Z., Anorg. Allgem. Chem. 222, 65-66 (1935).
89. O'Hare, P. A. G., Settle, J. L., and Hubbard, W. N., to be published in Trans. Faraday Soc. (1966).
90. Dagron, C., Compt. rend. 255, 122-124 (1962).
91. Bartlett, N., and Robinson, P. L., Chemistry and Industry, 1956, 1351-1352.
92. Edwards, A. J., et al., J. Chem. Soc. 1964, 4087.
93. Aynsley, E. E., et al., J. Chem. Soc. 1953, 2802.
94. Aynsley, E. E., et al., ibid., 1954, 1119.
95. Seel, V. F., and Massot, H., Z. Anorg. 280, 186 (1955).
96. Harvey, R. B., and Bauer, S. H., J. Am. Chem. Soc. 75, 2840 (1953).
97. Dodd, R. E., et al., Trans. Faraday Soc. 53, 1545-1556 (1957).
98. Hetherington, G., and Robinson, P. L., J. Chem. Soc., 1956, 3681.
99. Engellrecht, A., and Sladky, F., Monatsh. Chem. 96(1), 159-168 (1965).
100. Page, W. R., Continuous Flow Pilot Plant for the Separation of Bromine Fluorine Compounds and Light End Fission Product Fluorides from Uranium Hexafluoride, BNL-174 (March 1952).
101. Mecham, W. J., et al., Chem. Engr. Progr. 53:72-F to 79-F (1957).
102. Schmets, J., et al., Proc. Intern. Conf. Peaceful Uses At. Energy 3rd 1964, 11, 520-527 (1965).
103. Mecham, W. J., ANL, personal communication (1965).

104. Argonne National Laboratory; Chemical Engineering Division Semi-annual Report, January-June 1965, ANL-7055.
105. Chemical Technology Division Annual Progress Report for the Period Ending May 31, 1964, ORNL-3627.
106. Chilenskas, A., ANL, personal communication, 1965.
107. Smiley, S. H., ORGDP, private communication, 1965.
108. Krause, J. H., and Potts, J. D., Kinetics of Uranium and Fission Product Fluoride Adsorption by Sodium Fluoride, TID-11398 (Jan 1959).
109. Chemical Technology Division Annual Progress Report for the Period Ending May 31, 1963, ORNL-3452.
110. Gunther, W. H., and Steindler, M. J., ANL, personal communication, (1965).
111. Cathers, G. I., ORNL, personal communication, 1965.

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10.0 APPENDIX

10.1 Tabulation of Vapor Pressure of Tellurium Hexafluoride,
Tellurium Tetrafluoride and Ditellurium Decafluoride

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TABLE 1

VAPOR PRESSURE OF SOLID TEF6

T(C)	P(MM)	LOGP(MM)	1/T(K)
-80.00	44.26	1.64603	5.177-003
-79.00	48.06	1.68182	5.151-003
-78.00	52.15	1.71724	5.124-003
-77.00	56.53	1.75230	5.098-003
-76.00	61.24	1.78700	5.072-003
-75.00	66.28	1.82135	5.047-003
-74.00	71.67	1.85536	5.021-003
-73.00	77.45	1.88903	4.996-003
-72.00	83.63	1.92236	4.971-003
-71.00	90.23	1.95537	4.947-003
-70.00	97.28	1.98804	4.922-003
-69.00	104.81	2.02040	4.898-003
-68.00	112.84	2.05245	4.874-003
-67.00	121.39	2.08418	4.851-003
-66.00	130.50	2.11560	4.827-003
-65.00	140.19	2.14673	4.804-003
-64.00	150.51	2.17755	4.781-003
-63.00	161.47	2.20809	4.759-003
-62.00	173.11	2.23833	4.736-003
-61.00	185.48	2.26829	4.714-003
-60.00	198.59	2.29796	4.692-003
-59.00	212.50	2.32736	4.670-003
-58.00	227.24	2.35649	4.648-003
-57.00	242.86	2.38535	4.626-003
-56.00	259.38	2.41394	4.605-003
-55.00	276.87	2.44227	4.584-003
-54.00	295.35	2.47034	4.563-003
-53.00	314.89	2.49816	4.542-003

TABLE 1 (contd.)

VAPOR PRESSURE OF SOLID TEF6

T(C)	P(MM)	LOGP(MM)	1/T(K)
-52.00	335.52	2.52572	4.522-003
-51.00	357.30	2.55304	4.501-003
-50.00	380.28	2.58011	4.481-003
-49.00	404.52	2.60694	4.461-003
-48.00	430.06	2.63353	4.441-003
-47.00	456.97	2.65989	4.422-003
-46.00	485.30	2.68601	4.402-003
-45.00	515.12	2.71190	4.383-003
-44.00	546.48	2.73757	4.364-003
-43.00	579.46	2.76302	4.345-003
-42.00	614.11	2.78825	4.326-003
-41.00	650.51	2.81325	4.308-003
-40.00	688.73	2.83805	4.289-003

THE ABOVE TABLES WERE GENERATED USING THE FOLLOWING EQUATIONS,

$$\text{LOG P} = (-1342.000000)/\text{T(K)} + (0.000000) * \text{LOG T(K)} + (8.594000)$$

TO -40.00 DEGREES (C)

TABLE 2

VAPOR PRESSURE OF LIQUID TEF6

T(C)	P(MM)	LOGP(MM)	1/T(K)
-40.00	713.48	2.85338	4.289-003
-39.50	728.54	2.86245	4.280-003
-39.00	743.85	2.87148	4.271-003
-38.50	759.41	2.88047	4.262-003
-38.00	775.22	2.88943	4.253-003
-37.50	791.30	2.89834	4.244-003
-37.00	807.64	2.90722	4.235-003
-36.50	824.25	2.91606	4.226-003
-36.00	841.12	2.92486	4.217-003
-35.50	858.27	2.93363	4.208-003
-35.00	875.70	2.94235	4.199-003
-34.50	893.40	2.95105	4.190-003
-34.00	911.38	2.95970	4.181-003
-33.50	929.65	2.96832	4.173-003
-33.00	948.21	2.97690	4.164-003
-32.50	967.06	2.98545	4.155-003

THE ABOVE TABLES WERE GENERATED USING THE FOLLOWING EQUATIONS,

$$\text{LOG P} = (-988.000000)/T(K) + (0.000000) \cdot \text{LOG T}(K) + (7.091000)$$

TO -32.50 DEGREES (C)

TABLE 3

VAPOR PRESSURE OF SOLID TEF4

T(C)	P(MM)	LCGP(MM)	1/T(K)
25.00	0.03	-1.55325	3.354-003
26.00	0.03	-1.51766	3.343-003
27.00	0.03	-1.48231	3.332-003
28.00	0.04	-1.44719	3.321-003
29.00	0.04	-1.41231	3.310-003
30.00	0.04	-1.37765	3.299-003
31.00	0.05	-1.34323	3.288-003
32.00	0.05	-1.30903	3.277-003
33.00	0.05	-1.27505	3.266-003
34.00	0.06	-1.24129	3.256-003
35.00	0.06	-1.20775	3.245-003
36.00	0.07	-1.17443	3.235-003
37.00	0.07	-1.14133	3.224-003
38.00	0.08	-1.10843	3.214-003
39.00	0.08	-1.07575	3.204-003
40.00	0.09	-1.04328	3.193-003
41.00	0.10	-1.01101	3.183-003
42.00	0.10	-0.97895	3.173-003
43.00	0.11	-0.94709	3.163-003
44.00	0.12	-0.91543	3.153-003
45.00	0.13	-0.88397	3.143-003
46.00	0.14	-0.85271	3.133-003
47.00	0.15	-0.82164	3.124-003
48.00	0.16	-0.79077	3.114-003
49.00	0.17	-0.76008	3.104-003
50.00	0.19	-0.72959	3.095-003
51.00	0.20	-0.69929	3.085-003
52.00	0.21	-0.66917	3.076-003

TABLE 3 (contd.)

VAPOR PRESSURE OF SOLID TEF4

T(°C)	P(MM)	LGFP(MM)	1/T(K)
53.00	0.23	-0.63924	3.066-003
54.00	0.25	-0.60949	3.057-003
55.00	0.26	-0.57992	3.047-003
56.00	0.28	-0.55053	3.038-003
57.00	0.30	-0.52132	3.029-003
58.00	0.32	-0.49229	3.020-003
59.00	0.34	-0.46343	3.011-003
60.00	0.37	-0.43474	3.002-003
61.00	0.39	-0.40623	2.993-003
62.00	0.42	-0.37788	2.984-003
63.00	0.45	-0.34971	2.975-003
64.00	0.48	-0.32170	2.966-003
65.00	0.51	-0.29385	2.957-003
66.00	0.54	-0.26618	2.949-003
67.00	0.58	-0.23866	2.940-003
68.00	0.61	-0.21130	2.931-003
69.00	0.65	-0.18411	2.923-003
70.00	0.70	-0.15707	2.914-003
71.00	0.74	-0.13019	2.906-003
72.00	0.79	-0.10347	2.897-003
73.00	0.84	-0.07690	2.889-003
74.00	0.89	-0.05049	2.881-003
75.00	0.95	-0.02422	2.872-003
76.00	1.00	0.00189	2.864-003
77.00	1.07	0.02786	2.856-003
78.00	1.13	0.05367	2.848-003
79.00	1.20	0.07934	2.840-003
80.00	1.27	0.10487	2.832-003

TABLE 3 (contd.)

VAPOR PRESSURE OF SOLID TEF4

T(C)	P(MM)	LOGP(MM)	1/T(K)
81.00	1.35	0.13025	2.824-003
82.00	1.43	0.15549	2.816-003
83.00	1.52	0.18058	2.808-003
84.00	1.61	0.20554	2.800-003
85.00	1.70	0.23035	2.792-003
86.00	1.80	0.25503	2.784-003
87.00	1.90	0.27957	2.777-003
88.00	2.01	0.30398	2.769-003
89.00	2.13	0.32825	2.761-003
90.00	2.25	0.35238	2.754-003
91.00	2.38	0.37639	2.746-003
92.00	2.51	0.40026	2.739-003
93.00	2.65	0.42400	2.731-003
94.00	2.80	0.44761	2.724-003
95.00	2.96	0.47110	2.716-003
96.00	3.12	0.49446	2.709-003
97.00	3.29	0.51769	2.702-003
98.00	3.47	0.54079	2.694-003
99.00	3.66	0.56377	2.687-003
100.00	3.86	0.58663	2.680-003
101.00	4.07	0.60937	2.673-003
102.00	4.29	0.63198	2.666-003
103.00	4.51	0.65448	2.659-003
104.00	4.75	0.67685	2.651-003
105.00	5.00	0.69911	2.644-003
106.00	5.26	0.72125	2.637-003
107.00	5.54	0.74328	2.631-003
108.00	5.82	0.76518	2.624-003

TABLE 3 (contd.)

VAPOR PRESSURE OF SOLID TEF4

T(C)	P(MM)	LGPP(MM)	1/T(K)
109.00	6.12	0.78698	2.617-003
110.00	6.44	0.80866	2.610-003
111.00	6.76	0.83022	2.603-003
112.00	7.11	0.85168	2.596-003
113.00	7.46	0.87302	2.590-003
114.00	7.84	0.89425	2.583-003
115.00	8.23	0.91538	2.576-003
116.00	8.64	0.93639	2.570-003
117.00	9.06	0.95730	2.563-003
118.00	9.51	0.97810	2.557-003
119.00	9.97	0.99879	2.550-003
120.00	10.46	1.01938	2.544-003
121.00	10.96	1.03987	2.537-003
122.00	11.49	1.06025	2.531-003
123.00	12.04	1.08053	2.524-003
124.00	12.61	1.10070	2.518-003
125.00	13.21	1.12078	2.512-003
126.00	13.83	1.14075	2.505-003
127.00	14.48	1.16062	2.499-003
128.00	15.15	1.18040	2.493-003
129.00	15.85	1.20008	2.487-003
130.00	16.58	1.21966	2.480-003

THE ABOVE TABLES WERE GENERATED USING THE FOLLOWING EQUATIONS.

$$\text{LOG } P = (-3174.300000)/T(K) + (0.000000) \cdot \text{LOG } T(K) + (9.093400)$$

TC: 130.00 DEGREES (C)

TABLE 4

VAPOR PRESSURE OF LIQUID TEF₄

T(C)	P(MM)	LOGP(MM)	1/T(K)
130.00	16.17	1.20859	2.480-003
131.00	16.58	1.21956	2.474-003
132.00	17.00	1.23047	2.468-003
133.00	17.43	1.24133	2.462-003
134.00	17.87	1.25213	2.456-003
135.00	18.32	1.26288	2.450-003
136.00	18.77	1.27358	2.444-003
137.00	19.24	1.28422	2.438-003
138.00	19.72	1.29481	2.432-003
139.00	20.20	1.30536	2.426-003
140.00	20.69	1.31585	2.420-003
141.00	21.20	1.32629	2.415-003
142.00	21.71	1.33668	2.409-003
143.00	22.23	1.34702	2.403-003
144.00	22.77	1.35731	2.397-003
145.00	23.31	1.36755	2.391-003
146.00	23.86	1.37774	2.386-003
147.00	24.43	1.38789	2.380-003
148.00	25.00	1.39798	2.374-003
149.00	25.59	1.40803	2.369-003
150.00	26.18	1.41803	2.363-003
151.00	26.79	1.42798	2.358-003
152.00	27.41	1.43789	2.352-003
153.00	28.04	1.44775	2.347-003
154.00	28.68	1.45756	2.341-003
155.00	29.33	1.46733	2.336-003
156.00	30.00	1.47705	2.330-003
157.00	30.67	1.48673	2.325-003

TABLE 4 (contd.)

VAPOR PRESSURE OF LIQUID TEF₄

T(C)	P(MM)	LOGP(MM)	1/T(K)
158.00	31.36	1.49636	2.319-003
159.00	32.06	1.50595	2.314-003
160.00	32.77	1.51549	2.309-003
161.00	33.50	1.52499	2.303-003
162.00	34.23	1.53445	2.298-003
163.00	34.98	1.54386	2.293-003
164.00	35.75	1.55323	2.288-003
165.00	36.52	1.56256	2.282-003
166.00	37.31	1.57184	2.277-003
167.00	38.11	1.58108	2.272-003
168.00	38.93	1.59028	2.267-003
169.00	39.76	1.59944	2.262-003
170.00	40.60	1.60856	2.257-003
171.00	41.46	1.61764	2.251-003
172.00	42.33	1.62667	2.246-003
173.00	43.22	1.63567	2.241-003
174.00	44.12	1.64462	2.236-003
175.00	45.03	1.65353	2.231-003
176.00	45.96	1.66241	2.226-003
177.00	46.91	1.67125	2.221-003
178.00	47.87	1.68004	2.217-003
179.00	48.84	1.68880	2.212-003
180.00	49.83	1.69752	2.207-003
181.00	50.84	1.70620	2.202-003
182.00	51.86	1.71484	2.197-003
183.00	52.90	1.72344	2.192-003
184.00	53.95	1.73201	2.187-003
185.00	55.02	1.74054	2.183-003

TABLE 4 (contd.)

VAPOR PRESSURE OF LIQUID TEF4

T(C)	P(MM)	LOGP(MM)	1/T(K)
186.00	56.11	1.74903	2.178-003
187.00	57.21	1.75749	2.173-003
188.00	58.33	1.76591	2.168-003
189.00	59.47	1.77429	2.164-003
190.00	60.62	1.78263	2.159-003
191.00	61.79	1.79094	2.154-003
192.00	62.98	1.79922	2.150-003
193.00	64.19	1.80746	2.145-003
194.00	65.41	1.81566	2.141-003
195.00	66.65	1.82383	2.136-003
196.00	67.91	1.83196	2.132-003
197.00	69.19	1.84006	2.127-003
198.00	70.49	1.84813	2.122-003
199.00	71.81	1.85616	2.118-003
200.00	73.14	1.86415	2.113-003

THE ABOVE TABLES WERE GENERATED USING THE FOLLOWING EQUATIONS,

$$\text{LOG P} = (-1786.400000)/T(K) + (0.000000) \cdot \text{LOG T(K)} + (5.639700)$$

TO 200.00 DEGREES (C)

TABLE 5

VAPOR PRESSURE OF LIQUID TE2F10

T(C)	P(MM)	LGGP(MM)	1/T(K)
-33.00	4.07	0.60954	4.164-003
-32.00	4.42	0.64516	4.147-003
-31.00	4.79	0.68049	4.130-003
-30.00	5.19	0.71553	4.113-003
-29.00	5.63	0.75028	4.096-003
-28.00	6.09	0.78474	4.079-003
-27.00	6.59	0.81893	4.063-003
-26.00	7.13	0.85284	4.046-003
-25.00	7.70	0.88648	4.030-003
-24.00	8.31	0.91985	4.014-003
-23.00	8.97	0.95295	3.998-003
-22.00	9.68	0.98579	3.982-003
-21.00	10.43	1.01836	3.966-003
-20.00	11.24	1.05068	3.950-003
-19.00	12.10	1.08275	3.935-003
-18.00	13.02	1.11456	3.919-003
-17.00	14.00	1.14613	3.904-003
-16.00	15.05	1.17745	3.889-003
-15.00	16.16	1.20852	3.874-003
-14.00	17.35	1.23936	3.859-003
-13.00	18.62	1.26996	3.844-003
-12.00	19.97	1.30033	3.829-003
-11.00	21.40	1.33046	3.815-003
-10.00	22.93	1.36036	3.800-003
-9.00	24.55	1.39004	3.786-003
-8.00	26.27	1.41950	3.771-003
-7.00	28.10	1.44873	3.757-003
-6.00	30.04	1.47775	3.743-003

TABLE 5 (contd.)

VAPOR PRESSURE OF LIQUID TE2F10

T(C)	P(MM)	LOGP(MM)	1/T(K)
-5.00	32.10	1.50654	3.729-003
-4.00	34.29	1.53513	3.715-003
-3.00	36.60	1.56350	3.702-003
-2.00	39.05	1.59167	3.688-003
-1.00	41.65	1.61962	3.674-003
0.00	44.40	1.64737	3.661-003
1.00	47.31	1.67492	3.648-003
2.00	50.38	1.70227	3.634-003
3.00	53.63	1.72942	3.621-003
4.00	57.07	1.75638	3.608-003
5.00	60.69	1.78314	3.595-003
6.00	64.52	1.80971	3.582-003
7.00	68.56	1.83609	3.570-003
8.00	72.82	1.86228	3.557-003
9.00	77.32	1.88829	3.544-003
10.00	82.06	1.91411	3.532-003
11.00	87.05	1.93975	3.519-003
12.00	92.30	1.96521	3.507-003
13.00	97.84	1.99049	3.495-003
14.00	103.66	2.01560	3.483-003
15.00	109.78	2.04053	3.470-003
16.00	116.22	2.06529	3.458-003
17.00	122.99	2.08988	3.446-003
18.00	130.11	2.11431	3.435-003
19.00	137.58	2.13856	3.423-003
20.00	145.43	2.16265	3.411-003
21.00	153.66	2.18657	3.400-003
22.00	162.31	2.21033	3.388-003

TABLE 5 (contd.)

VAPOR PRESSURE OF LIQUID TE2F10

T(C)	P(MM)	LOGP(MM)	1/T(K)
23.00	171.37	2.23394	3.377-003
24.00	180.87	2.25738	3.365-003
25.00	190.84	2.28066	3.354-003
26.00	201.28	2.30379	3.343-003
27.00	212.21	2.32677	3.332-003
28.00	223.66	2.34959	3.321-003
29.00	235.65	2.37227	3.310-003
30.00	248.19	2.39479	3.299-003
31.00	261.31	2.41716	3.288-003
32.00	275.04	2.43939	3.277-003
33.00	289.38	2.46147	3.266-003
34.00	304.38	2.48341	3.256-003
35.00	320.04	2.50521	3.245-003
36.00	336.41	2.52686	3.235-003
37.00	353.49	2.54838	3.224-003
38.00	371.33	2.56976	3.214-003
39.00	389.94	2.59100	3.204-003
40.00	409.36	2.61210	3.193-003
41.00	429.61	2.63307	3.183-003
42.00	450.72	2.65391	3.173-003
43.00	472.73	2.67462	3.163-003
44.00	495.67	2.69519	3.153-003
45.00	519.56	2.71564	3.143-003
46.00	544.45	2.73595	3.133-003
47.00	570.36	2.75615	3.124-003
48.00	597.32	2.77621	3.114-003
49.00	625.39	2.79615	3.104-003
50.00	654.59	2.81597	3.095-003

TABLE 5 (contd.)

VAPOR PRESSURE OF LIQUID TE2F10

T(C)	P(MM)	LOGP(MM)	1/T(K)
51.00	684.96	2.83566	3.085-003
52.00	716.53	2.85524	3.076-003
53.00	749.36	2.87469	3.066-003
54.00	783.47	2.89402	3.057-003

THE ABOVE TABLES WERE GENERATED USING THE FOLLOWING EQUATIONS,

$$\text{LOG } P = (-2063.000000)/T(K) + (0.000000)*\text{LOG } T(K) + (9.200000)$$

TO 54.00 DEGREES (C)

10.2 Collection of Abstracts

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Note: Unless otherwise noted, numbers preceding abstracts refer to Chemical Abstracts; Nuclear Science Abstracts are designated by "NSA."

1.0 PREPARATION OF TELLURIUM METAL

42:8761

Tellurium, new alloying element. Eugène Lemaire. *Génie civil* 125, 66-8(1948).—A review of the ores of Te, extrn., purification, and properties of the metal and of its alloys. Ann Nicholson Hird

46:3927

Less familiar metals of commercial importance. Robert A. Lubker (Armour Research Foundation, Chicago). *Mech. Eng.* 74, 3-8, 18(1952).—A review is given, covering availability, production processes, alloys, costs, properties and uses of Li, Na, Ca, Be, B, Ga, In, Th, Ge, Ti, Zr, Hf, Nb, V, Ta, Mo, W, Se, Te, and Rh. R. W. Ryan

48:12003

The rare metals. Clifford A. Hampel (18223 Dixie Highway, Homewood, Ill.). *Rare Metals Handbook* (Reinhold Publishing Corp., New York, N.Y.) 1954.

Tellurium.

John R. Stone and Peter E. Caron. *Ibid.* 405-15.

Physical properties of metals. Clifford A. Hampel. *Ibid.* 623-43.—Reviews with many references. A. W. W.

50:6756

Yukhtanov, D. M.: Proizvodstvo selena i tellura (Production of Selenium and Tellurium). Moscow: Gosudarst. Nauch.-Tekh. Izdatel. Lit. po Chernoi i Tsvetnoi Met. 1955. 95 pp.

53:18561

Sublimation of tellurium. S. A. Semerkovich and N. N. Astashev (Inst. Semiconductors, Acad. Sci. U.S.S.R., Leningrad). *Soviet Phys.—Tech. Phys.* 3, 677-82(1958) (English translation); *Zhur. Tekh. Fiz.* 28, 725-31.—Te with only trace impurities can be prepd. by sublimation of com.-grade Te. Gerald S. Golden

56:11286

Production of tellurium of increased purity. V. I. Davydov, B. V. Teplyakov, and G. K. Romanov. *Tsvetnye Metally* 34, No. 11, 52-4(1961).—Tech. TeO₂ contg. 41% Te was sulfatized by roasting in 2 stages, the 2nd stage at 500-50° to eliminate most Se, and then leached with ~110% of the NaOH required to form Na₂TeO₃. The soln. was neutralized, eliminating much Si, Fe, Cr, Mg, Cu, and Al, and the ppt. was washed with hot H₂O to decrease the Se content, and melted with flour 20-5 and borax 10% by wt. of the dry ppt. and KOH 25-30% by wt. of SiO₂. Recovery of Te metal was ~80%; 10% was recovered in the slag, and 10% was lost in the fumes. The product contained 99.8-99.9% Te. Holding the fused mass at 340-50° for several hrs. decreased the Se content. E. M. Elkin

57:5757

Ultrapurification of In, Sb, Bi, As, and Te. Raymond Beau (Les Produits Semi-Conducteurs, Antony, France). *Ultrapurif. Semicond. Mater., Proc. Conf., Boston, Mass.* 1961, 173-85(Pub. 1962). Detailed procedures were presented for the purification of the above elements by chem. means. The elements and the compds. made from them were then purified by zone refining when possible. The following purity levels were obtained: In (99.999); Sb (99.999); Bi (99.995); As (99.999%); and Te (spectrographically pure). Norman E. Pickering

57:14828

Methods for preparation of high-purity metals. Fritz Ensslin. *Z. Erzbergbau Metallhuettenw.* 15, No. 8, 419-22 (1962). A description and discussion of methods for metal purification, such as fractional distn., sublimation, crystn., induced pptn., solvent extraction, ion exchange, redn. of oxides with H, electrolysis, and zone melting. By using these methods, Ge, Ni, As, Sb, Zn, Bi, Pb, Tl, Cd, Cu, Te, GeO₂, CdS, TeO₂, and In salts were prepd. $\leq 99.9985\%$ pure. 20 references. H. Stoertz

59:12383

The production of high-purity tellurium. R. v. Kujawa (Humboldt Univ., Berlin). *Phys. Status Solidi* 3(6), 1089-97(1963). Te can be made with a concn. of elec. active impurity atoms of 10¹⁴/cc. by vacuum distn. or sublimation plus zone melting. This impurity level was detd. by Hall coeff. and elec. cond. measurements. Arc spectra show the impurity atom concn. to be 10¹⁶/cc. The discrepancy is suggested to be due to elec. neutral impurities. P. H. Lewis

1.1 STRUCTURAL STUDIES OF TELLURIUM METAL

48:13330

Lattice constants of tellurium, mercury telluride, and mercury selenide. U. Zorll (Martin Luther Univ., Halle a.d. Saale, Ger.). *Z. Physik* 138, 167-9(1954).—By electron diffraction with the use of the lattice const. of LiF, ($a = 4.020 \pm 0.002$) Å., those of hexagonal Te and HgTe and HgSe were detd. Both compds. formed by action of Hg vapor on thin Te and Se layers. Results: Te: $a = 4.45$ Å., $c = 5.88$ Å., HgTe: $a = 6.429 \pm 0.006$ Å., HgSe: $a = 6.074 \pm 0.006$ Å. James L. Lauer

53:14845

X-ray powder patterns for mineral identification. I. Native elements and sulfides. Heinrich Neumann and Knut Heier. *Avhandl. Norske Videnskaps-Akad. Oslo. I. Mat.-Naturv. Kl.* 1955, No. 2, 12 pp.—X-ray powder patterns are given for acanthite, agularite, alabandite, algodonite, altaite, antimony, argentite, argentopyrite, arsenic, arsenopyrite A and B, aurostibite, badenite, berzelianite, bismuth, bismuthinite, bornite, braggite, bravoite, breithauptite, calaverite, carrollite, cattierite, chalcocite, chalcopyrite, chloanthite, cinnabar, clausenthalite, cobaltite, coloradoite, cooperite, copper, covellite, crookesite, cubanite, diamond, digenite, dimorphite, domykite, dyscrasite, empressite, eucairite, frobergite, galena, gersdorffite, glaucodot, gold, graphite, greenockite, guanajuatite, gudmundite, hauerite, hedleyite, herzenbergite, hessite, iridosmium, iron, joesite, kermesite, klockmannite, krennerite, laurite, lautite, lead, linnaeite, loellingite A and B, marcasite, maucherite, melonite, metacinnabar, millerite, molybdenite, montbrayite, nagyagite, naumannite, niccolite, nickel-iron, onofrite, orpiment, osmiridium, palladium, paraganajuatite, parammelsbergite, parkerite, penroseite, pentlandite, petzite, platinum, polydymite, pyrite, pyrrhotite, rammelsbergite, realgar, renierite, rickardite, safflorite A and B, selenium, shandite, siegenite, silver, skutterudite, smaltite, sperrylite, sphalerite, stannite, sternbergite, stibnite, stromeyerite, sulfur, sylvanite, tantalum, tellurium, tellurobismuthite, tetradymite, tiemannite, tin, tungstenite, ullmannite, umangite, vaesite, vallerite, violarite, wehrilite, weisite, wurtzite. The patterns were obtained with a 0.1-mm.-diam. glass fiber covered with an extremely thin film of adhesive; this was rolled in the powd. mineral. Nine-cm. cameras and filtered Fe radiation were used. (Cu radia-

1.1 STRUCTURAL STUDIES OF TELLURIUM METAL (Contd.)

tion gives equiv. results.) Intensities were measured by Speedomax recording photometer, weak lines and β -lines omitted, and spacings measured in A. X-ray powder data are vertical lines, the height of which are the intensity of that line. The difference from the 0 point to the line is the distance from the midpoint to the line on the film. Lines are in the 1.5–10-A. range.

59:12262

Wyckoff, Ralph W. G.: *Crystal Structures*. Vol. 1. 2nd ed. New York: John Wiley and Sons. 1963. 580 pp. \$18.60.

1.2 TELLURIUM CHEMISTRY

48:13521.

Chemical analysis by means of the hygrobalance. III. Hiroshi Amano (Tohoku Univ., Sendai). *J. Chem. Soc. Japan*, Pure Chem. Sect. 75, 499–502(1954); cf. *C.A.* 48, 11126i.—The following substances were tested for hygroscopicity and found to be not hygroscopic at the indicated temp.: ZnO 700°, Zn₂P₂O₇ 800°, Mn₂P₂O₇ 800°, Hg₂Cl₂ 105°, PbCrO₄ 700°, PbMoO₄ 700°, PbSO₄ 700°, Se 110°, Te 150°, TiO 1000°. Silica pptd. by H₂SO₄ is hygroscopic. IV. *Ibid.* 502–6.—The following substances are not hygroscopic and can be recommended as the forms to be weighed: K₂PtCl₆ 350°, Mg₂P₂O₇ 700°, MoO₃ 500°, V₂O₅ 800°, WO₃ 800°, AgCl, AgBr, AgI, AgCN, AgSCN 130°. Zinc triple acetate is less hygroscopic than the Mg triple acetate used as the pptg. agent for Na. K₂Na[Co(NO₂)₆] is hygroscopic. K. Yamasaki

NSA 16:8752

8752 COMPREHENSIVE INORGANIC CHEMISTRY.

Robert C. Brasted. Volume Eight. Sulfur, Selenium, Tellurium, Polonium, and Oxygen. Princeton, N. J., D. Van Nostrand Company, Inc., 1961. 314p.

Emphasis is placed largely on chemical properties and relationships and their interpretation in terms of theoretical concepts of atomic and molecular structure, the deductions from the periodic system, and the basic ideas relating to theories of solution. Information is also presented on the history, occurrence, preparation, compounds, separation processes, and uses of the elements. (N.W.R.)

55:26640

Kudryautsev, A. A.: *Khimiya i tekhnologiya selena i tellura* (Chemistry and Technology of Selenium and Tellurium). Moscow: "Vysshaya Shkola." 1961. 285 pp.

60:3488

Polarimetric determination of semimicro amounts of orthotellurate. John G. Lanese and Bruno Jaselskis (Univ. of Michigan, Ann Arbor). *Anal. Chem.* 35(12), 1880–1(1963). Te(VI) in the range 0.15–1.5 mg./ml. can be detd. with an error <2% by optical rotatory measurements at 312 m μ in a 0.33M soln. of d-tartrate at pH 12. Large amts. of Te(IV) and Se(IV)(VI) and moderate amts. of As(V) do not interfere. Pb, Cd, and Sn can be masked by EDTA and Cu and Ag by cyanide. Nitrate must be absent. T. B. Hoover

61:14157

Recent results in the inorganic chemistry of sulfur, selenium, and tellurium. Lajos Barcza. *Magy. Tud. Akad. Kem. Tud. Oszt. Közlemény.* 22(1), 47–88(1964). 144 references. SRTT

1.3 RADIOCHEMISTRY OF TELLURIUM

47:12025

Preparation of carrier-free tellurium tracer by use of selenium carrier. L. E. Glendenin (Oak Ridge Natl. Lab., Oak Ridge, Tenn.). *Natl. Nuclear Energy Ser. Div. IV, 9, Radiochem. Studies: The Fission Products*, Book 3, 1617–19 (1951).—Te was cosepd. on Se pptd. by reduction to the element with SO₂ in 3M HCl. Te and Se were sepd. by the pptn. of Se with SO₂ in 12M HCl. The yield was about 50% of Te with a purity of more than 99%. V. H. Dibelcr

Preparation of carrier-free tellurium tracer. L. Jacobson and R. Overstreet (Univ. California Radiation Lab., Berkeley). *Natl. Nuclear Energy Ser. Div. IV, 9, Radiochem. Studies: The Fission Products*, Book 3, 1620–2(1951).—Large quantities of carrier-free Te tracer were obtained by the cosepn. of Te from other fission products with Cu and Ru sulfides. Means were provided for obtaining the tracer as Te(VI) or Te(IV). V. H. Dibelcr

NSA 10:3890

3890 ORNL-1783

Oak Ridge National Lab., Tenn.

NUCLEAR PROPERTIES OF U²³⁵ FISSION PRODUCTS.

J. O. Blomeke, comp. Nov. 2, 1955. 60p. Contract W-7405-eng-26. \$0.40(OTS).

Tables are presented that list the U²³⁵ fission-product decay chains and the current best single values of their fission yields and cross sections. The fission products are also tabulated according to decreasing order of half life, thermal-neutron capture cross section, gamma energy, and beta energy. (auth)

50:16449

Chemical and radiochemical studies of tellurium in fluoride volatility processes. J. Fischer and R. K. Steunenberg (Argonne Natl. Lab., Lemont, Ill.). *U.S. Atomic Energy Comm. ANL-5593*, 19 pp.(1956).—Studies were made to clarify the behavior of fission product Te in fluoride volatility processes for the recovery of U from spent reactor fuels. The chem. nature of mixts. of TeF₆ and BrF₃ was investigated in the gas phase at 75 and 100°, and in the liquid phase at 25°. The gas-phase behavior of TeF₆ in BrF₃ was studied at 75°, and liquid mixts. of TeF₆ and Br were examd. at 25°. In none of these systems was there evidence for a chem. reaction which would produce Te compds. of low volatility. Quant. radiochem. observations were made on the partial reduction of TeF₆ and the sepn. of daughter isomers owing to the internal conversion of γ -rays of Te^{127m} and Te^{129m}. It was found that Te activity could be sepd. from BrF₃ by distn. The activity remaining after the volatilization of a mixt. of TeF₆ and UF₆ was a small fraction of the short-lived isomers Te¹²⁷ and Te¹²⁹. S. B.

54:16263

Application of radioactivating analysis for determination of microimpurities in tellurium. O. E. Zvyagintsev and V. I. Shamaev. *Radiokhimiya* 1, 717–23(1959).—By using the slow-irradiation method, detn. of Cu, Ni, As, Sb, Au, Cd, Co, Ca, Cr, Se, Ag, Hg, and In in high-purity Te was developed. Sensitivity in g. was from 3.8×10^{-7} (Ca) to 1.5×10^{-11} (Au). 32 references. E. Ryshkewitch

1.3 RADIOCHEMISTRY OF TELLURIUM (Contd.)

54:23987

Separation of iodine-132 from fission products. Margaret W. Greene, Geo. Samos, and Walter D. Tucker (to U.S. Atomic Energy Commission). U.S. 2,942,943, June 28, 1960. Tellurium can be sepd. from U and its other fission products by selective absorption on chromatographic-grade Al_2O_3 . Since fission-product Te^{132} is the radioactive parent of I^{132} (half-life 2.4 hrs.), the Al_2O_3 on which the Te is adsorbed can be used as a portable source of high-purity I^{132} . Thus, neutron-irradiated U-foil was dissolved in concd. HNO_3 , the soln. dild. to $M HNO_3$, and passed through a column of Al_2O_3 . Only Te and Mo were absorbed. The Mo was selectively eluted with concd. NH_4OH . Te can be eluted in 2-4M NaOH, and the desired amt. reabsorbed on Al_2O_3 by adjusting the pH of the soln. to 8-10.5. Periodic elution of I^{132} is accomplished with 0.001-0.01M NH_4OH .

W. T. Carnall

NSA 16:1359

1359 HISTORICAL REVIEW OF THE UTILIZATION OF ISOTOPE TRACERS. Georg von Hevesy. p.536-70 of "Radioactive Isotopes in Physiology, Diagnostics, and Therapy. Volume I." Berlin, Springer-Verlag, 1961. (In German)

A historical review is given of the development of the utilization of isotope tracers. All the works published up to 1946 are cited, but then only the publications of new methods for the utilization of radioactive isotopes are given. The elements discussed as tracers are hydrogen, phosphorus, carbon, sodium, potassium, rubidium, cesium, calcium, strontium, barium, rare earths, americium, zirconium, vanadium, manganese, chromium, niobium, tantalum, molybdenum, rhenium, iron, platinum metals, cobalt, nickel, silver, gold, beryllium, magnesium, zinc, cadmium, mercury, gallium, indium, nitrogen, arsenic, antimony, oxygen, sulfur, selenium, tellurium, fluorine, chlorine, bromine, iodine, astatine, and the rare gases. (J.S.R.)

55:23085

Radiochemistry of tellurium. G. W. Leddicotte. U.S. At. Energy Comm. NAS-NS 30-38, 42 pp.(1961).—A review with 102 references. P. M. B.

NSA 16:22583

22583 (BM-RI-6004) RADIOISOTOPES AS TRACERS IN VOLATILIZATION STUDIES OF SELENIUM AND TELLURIUM. J. V. Batty, A. M. Poston, Jr., and H. L. Gibbs (Bureau of Mines. Salt Lake City Metallurgy Research Center). July 1961. 12p.

Selenium-75 and Te^{123} were successfully employed as tracers in metallurgical research for developing an improved method for volatilizing the elements from low-tenor raw materials. Methods were devised and evaluated for admixing the radioactive tracer with typical raw materials and then following the deportment of the selenium and tellurium by radiometric methods with occasional chemical analysis checks. Both radioisotopes followed the same volatilization patterns and were effective tracers for following the deportment of the natural isotopes in the ores, for finding Se and Te that apparently was lost, and for obtaining fast and reliable quantitative analyses. An improved analysis method for Te remaining in fused residues was also developed. (P.C.H.)

62:10023

Zysin, Yu A., Lbov, A. A., and Sel'chenkov, L. I.: Fission Product Yields and Their Mass Distribution. Translated from Russian. New York: Consultants Bureau. 1964. 121 pp. International Directory of Isotopes. 3rd ed. Vienna: International Atomic Energy Agency. 1964. 487 pp.

1.4 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM

14:664

The melting points of the pure elements. W. GUERTLER AND M. PIRANI. Z. Metallkunde 11, 1-7(1919).

Ag	961°	Fe	1530°		Se	217°	
Al	658°	Fl	—223°	Nd	840°	Si	1420°
As	850° (?)	Ga	30°	Ni	1452°	Sr < Ca < Ba	
Au	1063°	Ge	958°	O	—218°	Sn	232°
B	2400°	H	—259°	Os	2700 (?)	Ta	2800°
Ba	850°	Hg	—39.7°	B	930°	Te	450°
Be	1300° (?)	I	113.5°	Pb	327.4°	Th > Pt	1800°
Bi	270°	In	155°	Pd	1545°	Ti	2000° (?)
C	>3600°	Ir	2350°	Pr	940° (?)	Tl	301°
Ca	809°	K	62.4°	Pt	1760°	U	<1850°
Cb	1700°	La	810°	Ra	700°	V	1800°
Cd	321°	Li	186°	Rb	38°	W	303°
Ce	700°	Mg	651°	Rh	1960°	Y	1490°
Cl	—101.5°	Mn	1210°	Ru	2450° (?)	Zn	419.4°
Co	1490°	Mo	(?)	S	119.2°	Zr	1700° (?)
Cr	1520°	N	—210°	Sa	1300° (?)		
Cs	26°	Na	975°	Sb	630°		
Cu	1084°						

W. T. H.

W. T. H.

1.4 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM (Contd.)

18:2985

The vapor pressure of tellurium. J. J. DOOLAN AND J. R. PARTINGTON. *Trans. Faraday Soc.* (advance proof) 1924.—A measured quantity of inert gas was passed in a steady stream over the heated metal. The loss in wt. of metal was obtained at 3 fixed temps. At least 3 rates of flow of gas were used at each temp. The app. is described. A weak point in the method appears to be the introduction of a cold boat contg. the solid element, causing a drop in temp. which persists until the element has melted. Results at temps. below the m. p. of Te were unreliable. A table gives observed results at different temps. and rates of flow. From the values of the vapor pressure, taken in pairs, the values for the latent heat of vaporization, per mol., were calcd. by the equation: $\log (p_2/p_1) (\lambda/4.57) (T_1 - T_2)/T_1 T_2$. These values do not agree closely and are given as approximations. This result may be due to the cooling effect.

W. H. BOYNTON

24:4228

Melting point of pure tellurium. A. ŠIMEK AND B. STEHLÍK. *Collection Czechoslov. Chem. Communications* 2, 303-14(1930).—Com. Te was purified until spectroscopically pure. Heating curves showed no crit. point from room temp. to m. p. Te m. 452.0° in vacuo. This point is lowered in H and CO₂ by 0.15-0.2°, resp., because of soln. of the gases.

ANN NICHOLSON HIRD

31:6095

The heat capacities of selenium crystals, selenium glass and tellurium at low temperatures. C. Travis Anderson. *J. Am. Chem. Soc.* 59, 1036-7(1937).—Exptl. data were obtained on Se (glass), Se (c), and Te (c) from about -220° to 25°. For Se (c) and Te (c), the "third law" values of the entropies are, resp., 10.49 ± 0.40 and 12.85 ± 0.50 cal. deg.⁻¹ mol.⁻¹; for Se (glass), 11.15 ± 0.40 cal. deg.⁻¹ mol.⁻¹.

F. D. R.

33:8099

Heat capacity of crystalline tellurium from 15° to 300° abs. and the entropy at 298.1° abs. Cyril M. Slansky and Lowell V. Coulter. *J. Am. Chem. Soc.* 61, 564 (1939).—Heat-capacity data are recorded. The entropy is 11.88 ± 0.10 e. u.

B. C. P. A.

36:4404

The heat of formation of magnesium telluride. The specific heat of tellurium and Supremax glass. O. Kubaschewski and F. E. Wittig. *Z. Elektrochem.* 47, 433-8 (1941).—The heat of formation of MgTe was measured at 500° by direct combination of the elements in the high-temp. calorimeter (C. A. 34, 935°). In order to retard the course of the reaction, which at 500° occurs as a kind of explosion, the Mg (as diln. medium) was added in excess, namely, 5 parts Mg to 1 part Te. The wt. of Te should not exceed 0.5-0.8 g. For the heat of formation of MgTe there results a value of 25 ± 2.5 kg.-cal./g. mol. For the calcn. of this value, among others, knowledge of the specific heat C_p of solid Te as well as of Supremax glass was necessary. For solid Te the following values of C_p were obtained: 0.0533 (250°); 0.0540 (300°); 0.0551 (350°); and 0.0565 (400°); for Supremax glass in the temp. interval 150-630° the following equation was found: $c_p = 0.1882 + 9.49 \times 10^{-6} (t - 22)$. The heats of formation of the 16 compds. obtained from Na, Li, Mg and Ca with the elements I, Te, Sb and Sn were compared with one another.

K. Wieland, K. H. Slagle

41:4687

Energies of highest-valency ionization of heavy metal-iodides. B. V. Nekrasov. *J. Gen. Chem.* (U.S.S.R.) 16, 1567-8(1946)(in Russian).—For the Cu-Zn-Ga-Ge-As

row, the exptl. values of the energy of highest ionization E were found to coincide very sharply with those calcd. by the formula $E = 29.9 + 89.1 Z + 67.24 Z^2 - 9.608 Z^3 + 0.7725 Z^4$ (kcal./g. atom) where Z = pos. charge no. of the core; similarly, for the Ag-Cd-In-Sn-Sb row, the formula $E = 25.0 + 103.7 Z + 53.21 Z^2 - 8.717 Z^3 + 0.7917 Z^4$ is valid. The as yet unknown E values for Se and Br (6-fold ionization) were extrapolated by the 1st formula, those for Te and I (7-fold ionization) by the 2nd, with the result: Se 82.9, Te 73.9, Br 108.8, I 98.4 e.v. N. T.

46:2866

Vapor pressures of tellurium and selenium. L. S. Brooks (Mound Lab., Miamisburg, O.). *J. Am. Chem. Soc.* 74, 227-9(1952).—The vapor pressures of Te and Se up to one-third and about one atm., resp., were measured with quartz Bourdon gages. The results are described by the equation $\log p = A - B/T$, where p is the pressure in mm., T is the abs. temp., A is 7.5999 ± 0.0136 and 8.0886 ± 0.0048 and B is 5960.2 ± 14.5 and 4989.5 ± 4.5 for Te and Se, resp. From these equations the b.ps. were estd. to be 989.8 ± 3.8 and 684.9 ± 1.0 ° and the heats of vaporization calcd. as 27.26 ± 0.07 and 22.82 ± 0.02 kcal./mole for Te and Se, resp.

Jack G. Calvert

47:7307

The low-temperature specific heat of tellurium. Warren DeSorbo (General Elec. Co., Schenectady, N.Y.). *J. Chem. Phys.* 21, 764-5(1953).—A comparison is made between the 1-dimensional and "interaction" continuum models of Te based on exptl. values of the sp. heat. For Te 60% "hard" nodes and 40% "soft" nodes are calcd. For Se 80% "hard" nodes and 20% "soft" nodes are calcd.

Henry Leidheiser, Jr.

51:11964

Experimental vacuum-distillation of nonferrous metals and alloys. Max J. Spendlove (U.S. Bur. of Mines, College Park, Md.). *Vakuum-Tech.* 6, 15-18(1957).—The vapor pressures from Kelley free energy values of As from 450° to 800° and Cd, Zn, Te, Mg, Sb, Bi, Pb, and Sn from 450° to 1200° are tabulated.

William J. Kirkpatrick

1.4 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM (Contd.)

52:10674

Determination of the vapor pressure of solid tellurium. I. V. Korneeva, A. S. Pashinkin, A. V. Novoselova, and Yu. A. Priselkov (M. V. Lomonosov State Univ., Moscow). *Zhur. Neorg. Khim.* 2, 1720-4 (1957).—The vapor pressure of Te was detd. by evapn. from a solid surface and from the surface of a powd. sample by using a modification of an app. described earlier (Priselkov, *C.A.* 49, 8651a; Schäfer and Hörnie, *C.A.* 45, 4163h). The exptl. data can be described by the equation $\log P_{\text{mm, Hg}} = -(7599.758/T) + 9.753$. The heat of sublimation was calcd. as 34.76 kcal./mole. J. Rovtar Leach

52:16822

Vapor pressure of liquid tellurium. Robert E. Machol and Edgar F. Westrum, Jr. (Univ. of Michigan, Ann Arbor). *J. Am. Chem. Soc.* 80, 2950-2 (1958).—The vapor pressure of liquid Te was measured with a SiO_2 Bourdon gage and could be represented by $\log P_{\text{mm.}} = -10,663.14/T + 64.73140 - 18.61687 \log T + 0.00341783 T$ from the triple point to 855°. The magnitudes of these parameters indicated that the van der Waals consts. of Te vapor must be unusually large. The extrapolated b.p. was 994° and the heat of vaporization was 33.8 - 0.009t (°C.) kcal./mole. J. C. Arthur, Jr.

53:4885

Empirical method for estimating the electron affinities of atoms. A. P. Ginsberg and J. M. Miller (Columbia Univ.). *J. Inorg. & Nuclear Chem.* 7, 351-67 (1958).—Electron affinities of Be, B, C, N, O, Mg, Al, Si, P, S, Zn, Ga, As, Se, Cd, In, and Te were estd. as, resp., $-0.12(2p^0P_{1/2})$ and $0.90(3s^2S_{1/2})$, 0.56 ± 0.02 , 1.59 ± 0.01 , -0.10 ± 0.04 , 1.60 ± 0.14 , $-0.56(3p^0P_{1/2})$ and $-0.24(4s^2S_{1/2})$, 0.43 ± 0.05 , 1.63 , 0.75 , 2.24 , $-0.90(4p^0P_{1/2})$ and $-0.13(5s^2S_{1/2})$, 0.18 ± 0.04 , 1.2 , 0.65 , 2.2 , $-0.6(5p^0P_{1/2})$ and $0.0(6s^2S_{1/2})$, 0.2 , and 2.30 e.v. in good agreement with expt. For the corresponding unineg. ions, the $(n)p$ to $(n+1)s$ excitation energies were, resp., -1.02 , 0.19 , 1.34 , 0.68 , 1.98 , -0.32 , 0.74 , 1.60 , 1.07 , 2.55 , -0.76 , 0.3 , 1.4 , 1.0 , -0.6 , and -0.5 e.v.; for F^- , Cl^- , and Hg^- these values are, resp., 4.09 , 4.27 , and -0.5 e.v. Removal-energy electron state effects are also calcd. for Sc, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu atoms; the method used differs from other empirical electron affinity calcs. in that one known affinity is extrapolated for the affinities of the other elements in the period. Jack J. Bulloff

53:13713

Measurement of vapor pressures by the Baur-Brunner method. Vapor pressures of zinc, selenium, and tellurium. G. Gattow and Armin Schneider (Univ. Göttingen, Ger.). *Angew. Chem.* 71, 189-93 (1959).—The Baur-Brunner method for measuring vapor pressures (*C.A.* 29, 973^g), which is based on static measurement of the b.p. of the substance in an inert gas having variable pressure, was refined for the detn. of the vapor pressure of Zn, Se, and Te. With Zn the general equation for the vapor pressure between 550° and 650° is $\log p_{(\text{Zn})} = -(6.079 \times 10^3/T) + 8.011$, and the heat of evaporation is $L_e = 27.8 \pm 0.8$ kcal./mol.; the corresponding data for Se and Te are: $\log p_{(\text{Se})} = -(5.510 \times 10^3/T) + 8.668$ (temp. range 400-550°); $L_e = 25.5 \pm 0.5$ kcal./mol., and $\log p_{(\text{Te})} = -(6.196 \times 10^3/T) + 7.977$ (temp. range 550-750°); $L_e = 28.3 \pm 0.5$ kcal./mol. B. Reitzner

54:4134

Thermodynamic properties of nonstoichiometric nickel tellurides and of tellurium. Robert E. Machol (Univ. of Michigan, Ann Arbor). *Univ. Microfilms* (Ann Arbor, Mich.), L.C. Card No. Mic 59-3938, 137 pp.; *Dissertation Abstr.* 20, 1193-4 (1959). P. M. B.

54:8231

Calculation of the cation hydration entropy. S. I. Drakin and V. A. Mikhailov (D. I. Mendeleev Chem. Technol. Inst., Moscow). *Zhur. Fiz. Khim.* 33, 1544-50 (1959); *C.A.* 50, 13570b.—A theoretical method of calcg. the cation hydration entropy was developed and used in the calcn. of the hydration entropy of 34 cations. The results agreed satisfactorily with exptl. detns. A refinement in the earlier method of calcn. reduced the difference between the exptl. and the calcd. detns. of the ions that did not have the electron configuration of the inert gas atoms. The results of hydration energy and entropy calcn. were used in calcg. the cation heats of hydration. W. M. Sternberg

55:15140

The work of electron emission. R. M. Vasenin. *Nauch. Trudy Moskov. Tekhnol. Inst. Legkoi Prom.* 1958, No. 11, 208-28.—Factors influencing the work function, ϕ , are reviewed. A plot of $\log \phi$ vs. DZ/A , where $D = d$, $A = \text{at. wt.}$, and $Z = \text{the no. of free electrons}$, is given for periods II to VI. The plot is linear for each period, but the 6th period line is discontinuous in the lanthanide region. Ga, Mn, Nb, and Mo deviate from their resp. lines. A straight line is also obtained when ϕ is plotted vs. the inverse at. radius for periods IV, V, and VI. Cr, Ir, Os, and Mn (all cryst. forms) fall off the line. The 6th period is discontinuous; the 2 linear sections have different slopes. If the covalent radius is used for Ge, As, and Se, they fall on the 4th period line with values of 4.59, 4.64, and 4.8 e.v., resp. Sn, Sb, and Te deviate somewhat while Hg and Tl do not conform. ϕ may be represented by $m(DZ/A)^n$ or $a + b/r$, where m , n , a , and b are empirical consts. and differ for the various periods. A plot of ϕ vs. at. no. allows it to be estd. for Tc, Po, Fr, Ra, and Ac. Av. values of 4.3 e.v. for Cr and 4.4 e.v. for Mn were estd. S. Levinson

56:8197

Paramagnetic nuclear resonance of dimethyl and diethyl telluride; electronegativity of tellurium. Gotthard Klose (Univ. Leipzig, E. Ger.). *Z. Naturforsch.* 16a, 528 (1961).—The proton resonance spectrum of Me_2Te consists of an intense center line with 2 less intense lines on either side and 2 weak satellites. The inner satellites result from indirect spin-spin coupling between the Me protons which are bound to the Te^{123} and Te^{125} isotopes. The outer satellites result from the equiv. coupling between C^{13} and the protons. Et_2Te gives a spectrum similar to that of the Et group of EtOH. The theoretical spectrum corresponds closely to the observed spectrum. The electronegativity of Te was calcd. from the C^{13} coupling const. and the chem. shift. Values of 2.1-2.4 were obtained from several empirical expressions. Irving Auerbach

58:7382

Empirical bond energies. Frank Wilson, Jr. (Edwards Air Force Base, Calif.). *U.S. Dept. Com., Office Tech. Serv., AD 257,383*, 16 pp. (1961). A consistent set of bond-energy values are calcd. on the assumption that bond-energy nonconstancies are a min. when detd. from compds. in which all the constituent elements exhibit their normal valency. Several empirical rules

1.4 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM (Contd.)

for estg. the heats of vaporization and fusion are included. This report contains sufficient data for estg. heats of formation of compds. In many cases, estns. can be made within a few kcal. 15 references. CA

NSA 16:31604

31604 IDEAL GAS THERMODYNAMIC FUNCTIONS OF SOME SELECTED ELEMENTS. D. E. Poland, J. W. Green, and J. L. Margrave (Univ. of Wisconsin, Madison). *J. Chem. Eng. Data*, 7: 389-90 (July 1962).

Tables are presented for the free-energy functions $(-F^\circ - H^\circ_0)/T$ and enthalpy functions $(H^\circ - H^\circ_0)/T$ of the elements Tc, Ru, Te, I, Hf, Tl, Pb, Bi, Po, Rn, Ra, Ac, and Th at 200 to 7000°K. (D.L.C.)

58:7437

Calculations on the low-temperature specific heat of selenium and tellurium. L. S. Kothari and V. K. Tewary (Univ. Delhi, India). *J. Chem. Phys.* 38, 417-19 (1963). A model of lattice vibrations for linear lattices is proposed in which longitudinal and transverse components of vibrations are considered sep., unlike the model proposed by Tarasov (CA 44, 4742f). This model was applied to interpret the sp. heat data for Se and Te obtained by DeSorbo (CA 48, 6805a). Agreement with the exptl. results is good. CA

60:7828

Regularity in appearance of native metals and elements. F. A. Letnikov. *Izv. Akad. Nauk Kaz. SSR, Ser. Geol. Nauk* 1963(6), 101-3. Comparison of the isobaric-isothermal potentials (ΔZ) of sulfides and oxides of elements found in rocks and in deposits in natural form (native Au, Pt, Cu, Pb, etc.) was made to det. the causes of the appearance of native metals in rocks and in deposits. The Gibbs-Helmholtz equation ($\Delta Z = \Delta H - T\Delta S$) was used for calcn. of ΔZ . The elements were arranged in the order of decreasing ΔZ for oxides and sulfides forming at 298, 500, 700, 900, 1000, and 1500°. For example, the series for oxides at 298° is K, Fe, Cd, Co, Ni, Sb, Bi, Pb, As, Tl, Te, Cu, Os, Ru, Se, Ir, Pd, Rh, Hg, Pt, Ag, and Au. A perusal of the calcd. series of the isobaric-isothermal potentials of elements showed that the last members of the series occur as free metals in nature. This permitted L. to define a native metal as those of min. ΔZ (i.e. chem. affinity to anion) in each given series. BLJR

61:395

Specific volume of molten metals and alloys at elevated temperatures. I. L. D. Lucas (Inst. Rech. Siderurgie, St.-Germain-en-Laye, France). *Mem. Sci. Rev. Met.* 61, 1-24 (1964). II. *Ibid.* 97-116. The method of measuring the max. pressure of Ar bubbles was used for calcn. of the d. of molten metals at high temps. The furnace manometer system and operation of the app. are described. Two measurements of the pressure to produce the bubbles are made at 2 different levels below the surface of the molten metal. The surface tension effects are eliminated by this differential method. The following ds. at the m.p. were found: Ag 9.33, Cu 8.03, Zn 6.57, Sn 6.978, Si 2.52, Ge 5.49, Sb 6.465, Bi 10.06, Te 5.797, Fe 7.01, Co 7.65, Ni 7.72, Pd 10.49, and Pt 18.90. Measurements at different temps. were made of various compds. of the Fe-C, Fe-P, Fe-Si, and Fe-C-P systems. The influence of the P and Si content on the variation of the sp. vol. was detd. 129 references. F. Schosberger

1.5 TOXICITY OF TELLURIUM AND TELLURIUM COMPOUNDS

31:1105

The minimum fatal doses of selenium, tellurium, arsenic and vanadium. Kurt W. Franke and Alvin L. Moxon. *J. Pharmacol.* 58, 454-9 (1936).—Min. doses (in mg. per kg.) fatal to at least 75% of young rats were: Se (as Na_2SeO_3) 3.25 to 3.50, Se (as Na_2SeO_4) 5.25 to 5.75, Te (as Na_2TeO_3) 2.25 to 2.50, Te (as Na_2TeO_4) 20.0 to 30.0, As (as Na_2HAsO_3) 4.25 to 4.75, As (as Na_2HAsO_4) 14.0 to 18.0, V (as NaVO_3) 4.0 to 5.0, Mo (as $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$) above 160.0. T. H. Rider

55:4/16

Comparative investigation into the inhalation toxicity of the hexafluorides of sulfur, selenium, and tellurium. Georg Kimmeler (Farbenfabriken Bayer Akt.-Ges., Wuppertal-E., Ger.). *Arch. Toxikol.* 18, 140-4 (1960).—Inhalation tests on rabbits, guinea pigs, rats, and mice showed the very high toxicity of SeF_6 and TeF_6 in contrast to the harmlessness of SF_6 . A 4-hrs. exposure to 10 p.p.m. SeF_6 and 5 p.p.m. TeF_6 caused death of the animals via edema of the lungs. In contrast, SF_6 , SeF_4 , and TeF_4 are hydrolyzed in the respiratory tract, and the hydrolytic products act directly upon the alveolar epithelium. G. Kimmeler

55:25059

Toxicology of selenium and tellurium and their compounds. Edward A. Cerwenka and W. Charles Cooper (Canadian Copper Refiners Ltd., Montreal). *Arch. Environmental Health* 3, 189-200 (1961).—A review with 67 references. Raymond Zehnpfennig

57:7559

Research on tellurium as an industrial poison. S. E. Sandratskaya (1st. Med. Inst., Moscow). *Gigiena Truda i Prof. Zabolevaniya* 6, No. 2, 44-50 (1962). The toxicities of condensed aerosols of TeO_2 (high dispersity, 90% particles smaller than 1 μ , concn. 10 mg./cu. m. and 50 mg./cu. m.) and dispersed aerosols of amorphous powders of Te, and TeO_2 (coarsely dispersed, predominating fraction 6-10 μ and greater) were studied in rats. The toxicity, the role in biochem. processes, and the cumulative effect of these aerosols were examd. with respect to blood compn. (hemoglobin and erythrocytes content, content of protein fractions) and nervous system function. The highest toxicity was exhibited by the condensed aerosol of TeO_2 . No difference in characteristics and degree of toxicity of dispersed aerosols of Te and TeO_2 was found. The max. permissible concn. of Te in the atm. (0.01 mg./cu. m.) assures safety. J. Pixova

60:2247

Biological effects of rare, dispersed, and other metals and their compounds used in industry—tellurium. S. E. Sandratskaya. *Toxikol. Redkikh Metal.* 1963, 117-35. The toxicity of different aerosols contg. Te or TeO_2 , the symptoms, and the mechanism of Te poisoning were examd. Subacute poisoning was effected by daily digestive administering of Te or TeO_2 to rats in doses of 40-80 mg./kg. for 10 days or by administering 600 mg./kg. 4 times in the course of 14 days. The peroral toxicity of Te and TeO_2 is low. Pigmentation of stomach mucous membrane, lipid infiltration of the liver, and changes in kidneys were found. Chronic intoxication was studied by daily 2-hr. inhalation of differently dispersible aerosols contg. Te and TeO_2 in concns. 0.01-0.1 mg./l. The expts. lasted 13-15 weeks. A loss of wt., somnolence, irritation of respiratory tract, and loss of fur was observed. All organs and expired air had a garlic odor. The

1.5 TOXICITY OF TELLURIUM AND TELLURIUM COMPOUNDS (Contd.)

concn. 0.1 mg./l. was lethal for about 50% of the rats. The decrease of the no. of erythrocytes and of hemoglobin level, accompanied by the rise of urinary bilirubin, indicated a hemolytic mechanism. The erythrocyte catalase activity was lowered. The blood serum protein fractions, examd. by paper electrophoresis, were considerably changed. A decrease of albumins and of the albumin/globulin ratio, and a rise of β - and α_2 -globulins was marked. Blood serum SH groups, detd. titrimetrically, were lowered 1.5-2.6-fold. It is probable that Te causes inhibition of the SH compd. synthesis. In 61-70% of the rats the benzidine reaction in urine was pos.; chronaximetric data were considerably changed. The ^{127}Te distribution after oral administration was: blood and kidneys > spleen, liver, and lungs > heart and adrenal glands > muscles and brain. In blood, 90% of Te was in the erythrocytes. In the feces and urine, resp., 78.8% and 2.7% of the ^{127}Te was excreted. Pathol.-histol. changes were found in liver, kidneys, lungs, and stomach. The max. permissible concn., which is 0.01 mg./m.³, agrees with these results.

Ivo Hynie

61:6252

The toxicology of tellurium. L. Vignoli and J. P. Defretin (Fac. Med. Pharm., Marseille, France). *Ann. Biol. Clin.* (Paris) 22(3-4), 399-417(1964). A review with 45 references.

SFTT

2.0 PREPARATION OF TELLURIUM OXIDES

18:2654

Tellurium monoxide. J. J. DOOLAN AND J. R. PARTINGTON. *J. Chem. Soc.* 125, 1402-3(1924).—Expts. are described which confirm the statement of Divers and Shimose (Ber. 16, 1004(1883)) that Te sulfoxide, TeSO_3 , is stable in vacuum up to 180° and above this decomps. into SO_2 and TeO . TeSO_3 was prepd. by the method of D. and S. and a tube of it evacuated by a Sprengel pump through a tube filled with borax. No change of appearance was produced during 2.5 hrs. at $35-40^\circ$. Slight browning and shrinking were noticed at 65° and the former increased steadily up to 180° , when the color began to darken to black. After some time at 255° the entirely black mass was washed with dil. Na_2CO_3 , hot water and EtOH and dried. The gray powder thus obtained resembled the metal but its density was considerably lower. Analysis gave $\text{Te} = 87.84$; calcd. (TeO) = 88.85%. It decolorized KMnO_4 soln. practically instantaneously even in the cold. The statement of D. and S. that no swelling occurred when heated with SO_2 was verified. A. R. M.

43:3304

Tellurium compounds. E. Montignie. *Z. anorg. Chem.* 253, 90-1(1945).—Prepn. and properties of $\beta\text{-TeO}_3$ (C.A. 42, 1836g) are described. $2\text{TeO}_2 \cdot \text{HIO}_4$, prepd. from TeO_2 dissolved in concd. periodic acid, and evapd. in a vacuum desiccator, decomposes on heating to I and TeO_2 ; hot KOH gives KIO_4 and TeO_2 . Compds. of TeO_2 with KMnO_4 , chromate, MoO_3 , WO_3 , UO_3 , and ortho- and metaphosphoric or arsenic acid could not be prepd. $\text{K}_2\text{TeO}_6 \cdot 2\text{H}_2\text{O}$, prepd. from $\text{K}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O}$ and 30% H_2O_2 allowed to stand 5-6 days at 10° in a vacuum, is water-sol., slightly sol. in alc., and insol. in ether; it is stable in a sealed tube at 100° , but intense light causes O to be evolved, even at room temp. That $\text{K}_2\text{TeO}_6 \cdot 2\text{H}_2\text{O}$ is a salt of a peroxy acid, not $\text{K}_2\text{TeO}_4 \cdot \text{H}_2\text{O}_2 \cdot \text{H}_2\text{O}$, is shown by the facts that $\text{K}_2\text{Cr}_2\text{O}_7$ and dil. H_2SO_4 do not give the blue color characteristic for H_2O_2 , and the compd. is not decompd. at room temp. by powd. Pt. Peter M. Bernays

43:2885

The existence of tellurium(II) oxides. Oskar Glemser and Werner Poscher. *Z. anorg. Chem.* 256, 103-6(1948).—Attempts to prep. TeO according to $\text{TeO}_2 + \text{Te} \rightarrow 2\text{TeO}$ gave a mixt. of the reactants as detd. by x-ray diffraction patterns. The thermal decompn. of TeSO_3 and the reaction of Te with NO_2 gave products shown by chem. analysis to contain Te and O in 1:1 ratio. X-ray diffraction indicated a mixt. of Te and TeO_2 . M. J. S.

49:5184

Inorganic syntheses. III. Ludwig F. Audrieth (Editor-in-chief), John C. Bailar, Jr., Harold S. Booth, W. Conard Fernelius, Walter C. Schumb, Ralph C. Young (Associate editors), and Janet D. Scott (Consultant on nomenclature and indexing). 1950, 230 pp. New York, McGraw-Hill Book Co., \$3.75; cf. C.A. 40, 6009⁴, 6353³, 7025⁴.

Tellurium(IV) oxide. H. Marshall (Canadian Copper Refiners Ltd., Montreal East, Quebec). 143-5.—Cover 20 g. of com. Te in a 1-l. beaker with 200 ml. H_2O and treat slowly with 95 ml. of concd. HNO_3 (d. 1.42). Agitate the mixt. occasionally for 5 to 10 min., and filter immediately. Add 65 ml. of concd. HNO_3 to the filtrate and boil the soln. until oxides of N have been expelled. Filter the soln. through asbestos, and evapd. slowly on a water bath until the soln. vol. is reduced to 100 ml. Filter the cryst. deposit from the cooled soln., wash with H_2O , and air-dry. Heat the crystals at $400-30^\circ$ for 2 hrs. in a 400-ml. beaker covered by an inverted 1-l. beaker. Yield 21 g. (84%).

2.1 STRUCTURAL AND SPECTRAL STUDIES OF TELLURIUM OXIDES

32:8934

Band spectra of selenium and tellurium and of their oxides in the extreme ultraviolet. Choong Shin-Piaw. *Ann. phys.* [11], 10, 173-290(1938).—An exhaustive survey of Se and Te spectra has led to the discovery of new band systems of Se_2 , Te_2 , SeO_2 , TeO_2 , SeO and TeO , in the ultraviolet region between 3900 and 1600 Å. Two systems of absorption bands, attributed, resp., to Se_2 and a polyatomic mol. of Se, lie in the regions 1938-1852 Å. and 1842-1777 Å. The Se_2 bands are shaded toward the violet from well-defined heads; the others are diffuse. Three systems of absorption bands, shaded toward shorter waves, and attributed to Te_2 , lie in the regions 2495-1975 Å. The absorption bands of SeO_2 form 3 systems in the region 3803-2068 Å.; the TeO_2 bands lie between 4029 and 3227 Å. Emission bands of SeO and SeO_2 have been measured between 3942 and 2767 Å.; the TeO bands, both in emission and absorption, lie in the region 3881-2776 Å. Vibrational analyses have been made for all these band systems except a few. The first systems of Se_2 and Te_2 bands are found to originate in the fundamental states of their resp. mols. The analysis of the SeO_2 and TeO_2 bands furnishes data for the mol. consts. that show a regular variation in passing from SO_2 to TeO_2 . The SeO bands exhibit a double structure of strong and weak bands which are arranged into 2 systems having a common normal state but different excited states. A dissoc. energy of 5.45 v. is found for the normal state. The TeO emission bands exhibit predissozn. at band (6,0) in the $\nu'' = 0$ progression, the missing bands appearing in absorption. Dissozn. energies of 0.4 and 2.7 v. have been derived for the normal and excited states, resp., of TeO . Variations in the mol. consts. of SO , SeO and TeO are noted. C. C. Kiess

40:5337

Electronic spectra of some bent triatomic molecules. Jules Duchesne and B. Rosen (Univ. Liège). *Nature* 157, 692-3(1946); cf. C.A. 35, 7827⁹; *Mem. soc. roy. sci. Liège* 1, No. 2, 429(1943).—The b system of TeO_2 was investigated at 3000-4500 Å.: all bands of the system have been correlated with only one valence symmetrical frequency in each state, with $\nu_1'' = 815 \text{ cm}^{-1}$ and $\nu_1' = 650 \text{ cm}^{-1}$. Fainter bands toward 3000 Å. are arranged in several series with $\nu \cong 200 \text{ cm}^{-1}$. 16 references.

G. M. Petty

2.1 STRUCTURAL AND SPECTRAL STUDIES OF TELLURIUM OXIDES (Contd.)

53:15755

Emission spectrum of TeO. R. L. Purbrick (Willamette Univ., Salem, Ore.). *J. Chem. Phys.* 30, 962-3(1959).—Emission bands of TeO were discovered on the long wavelength side of previously reported bands. Wave lengths, intensities, and sq. arrays of the bands were given.

Henry Leidheiser, Jr.

NSA 17:38044

38044 (AEC-tr-5734(p.255-66)) A SURVEY OF NEUTRON DIFFRACTION INVESTIGATIONS CONDUCTED IN THE NUCLEAR RESEARCH INSTITUTE IN 1960 AND 1961. K. Blinowski, J. Leciejewicz, and J. Sosnowski. (Translation)

A survey of work on elastic nuclear scattering of slow neutrons by solids is presented. The structures of PbO, PbO₂, TeO₂, and WC were investigated as well as the so-called parasitic reflections of neutrons in crystal monochromators. (D.C.W.)

60:14021

Rotational structure in the electronic spectrum of tellurium monoxide. R. F. Barrow and H. J. Hurst (Univ. Oxford, Engl.). *Nature* 201(4920), 699(1964). In some preliminary observations of the absorption spectrum of TeO taken in a 2nd order of a 6.65-m. concave grating spectrograph, a band at 31,301 cm.⁻¹ shows the simple 2-branch structure expected for a 0⁺-0⁺ transition. R and P branches of the 3 most abundant mols., ¹³⁰TeO, ¹²⁸TeO, and ¹²⁶TeO, are well resolved. The analysis indicates an internuclear distance of 1.828 Å.

J. J. McGovern

60:15316

Vibrational spectra and the structure of some oxides in crystalline and glassy states. V. P. Cheremisinov. *Tr. Fiz. Inst., Akad. Nauk SSSR* 25, 153-208(1964). Studies with Raman and infrared spectroscopy were made to clarify, on the basis of vibrational spectra, the structure of various cryst. and glassy oxides. The development of a new method for obtaining Raman spectra of powd. substances is reported. The Raman spectra of cryst. As₂O₃, Sb₂O₃, As₂O₅, Sb₂O₅, TeO₂, and GeO₂ (2 modifications), and of glassy As₂O₃, GeO₂, and TeO₂ were investigated. The vibrational spectra of cryst. and glassy As₂O₃, GeO₂, and TeO₂ are similar in fundamental characteristics. As₂O₃ has mol. structure and consists of As₄O₆ mols. An analogous result was also obtained for the Sb₂O₃ specimens.

GPJR

61:152

Change of the refractive index of semiconductor films when intensely illuminated. S. N. Chechurin (State Univ., Leningrad). *Fiz. Tverd. Tela* 4(3), 813-14(1962). The expts. by Ishiguro (CA 50, 11099g) were repeated by using films of Ge, CdS, CdSe, TeO₂, PbS, Au, and Pt on microscope slides. When illuminated from the glass side with a cine-projector bulb (300 w.), the systems showed shifts of interference bands, corresponding to an increase of the refractive index. The insertion of a water filter reduced the shift by the factor of 2-3. The effects obtained were sometimes even greater than those obtained by Ishiguro. However, the effect virtually disappeared when the film was transferred onto a metal gauze. The shift was due to the change of the refractive index of the glass substrate and to its thermal expansion, whereas the film only absorbed light and converted it to heat. This was confirmed by further expts. From *Phys. Abstr.* 65(778), Abstr. No. 18793(1962).

TCSB

2.2 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM OXIDES

19:1085

The free energy and heat content of tellurium dioxide and of amorphous and metallic tellurium. The reduction potential of tellurium. REINHARDT SCHUHMAN. *J. Am. Chem. Soc.* 47, 356-63(1925).—The e. m. f. of the cell $\text{Te(s)} + \text{TeO}_2(\text{s}), \text{HClO}_4, \text{H}_2(\text{g})$ was measured at 25° and 45° and at various concns. of HClO_4 . The e. m. f. was independent of concn. and time. Free energy and heat content of TeO_2 were $-64,320$ and $-77,700$ cal. at 25°. The e. m. f. and temp. coeffs. were the same for metallic Te and for Te prepd. by pptg. hot with SO_2 . These forms give the same X-ray pattern. The soly. of TeO_2 was measured in 0.1 to 0.7 N HClO_4 . The ion formed is univalent such as $\text{TeO}(\text{OH})^+$ or $\text{Te}(\text{OH})_3^+$. The molal reduction potential of Te is -0.5590 v. F. R. B.

24:499/

The melting point of tellurium dioxide. A. ŠIMEK AND B. STEHLÍK. *Collection Czechoslov. Chem. Comm.* 2, 447-56(1930); cf. *C. A.* 24, 4228.— TeO_2 m. $732.6 \pm 0.1^\circ$. This value was detd. by a special extrapolation from heating curves. TeO_2 crystallizes from the melt; it is uniaxial and pos.; d. = 6.02. V. F. HARRINGTON

41:1553

The determination of dissociation energies by the Birge-Sponer extrapolation. A. G. Gaydon (Imperial Coll., London). *Proc. Phys. Soc. (London)* 58, 525-38(1946).—A crit. examn. is made of the Birge-Sponer method (*C. A.* 21, 851) of detg. dissocn. energies of diat. mols. Dissocn. energies of certain classes of mols. as detd. by linear extrapolation are compared with values detd. independently. For the ground states of ordinary mols. the linear extrapolation tends to give too high results, often by around 20%. For mols. in which ionic binding is important the extrapolation often comes too low, sometimes much too low. For the mols. in which one atom has a $^1\text{S}_0$ ground state the linear extrapolation is much too high. The method appears to work satisfactorily for ionized mols. Excited states of mols. cannot, in general, be relied on to give good extrapolations. These empirical observations are discussed in terms of the potential-energy curves and the binding forces in the mols. at large internuclear distances. Comparison of linear-extrapolated dissocn. energies with those accurately detd. is made for the following mols.: H_2 , KH, AgH, OH, HCl, HBr, HI, Li_2 , Na_2 , K_2 , CO, NO, CN, O_2 , SO, S_2 , Se_2 , TeO, N_2 , P $_2$, As $_2$, Bi $_2$, ClF, Cl $_2$, ICl, Br $_2$, IBr $_2$, I $_2$. These include the non-ionic mols. for which adequate data are available. For mols. contg. an atom with $^1\text{S}_0$ ground state data are given for ZnH, CdH, HgH, BeH, CaH, SrH, BaH. For mols. with partially ionic binding the dissocns. are given for the following and also the difference between ionization potential and the electron affinity (The true dissocn. is much higher than extrapolated value.): LiI, NaCl, NaBr, NaI, KCl, KBr, KI, TiCl, TiBr, GaI. For ionized mols. data are given for H_2^+ , HCl^+ , O_2^+ , N_2^+ , CO^+ . Where data are adequate for a good graphical extrapolation for a ground state, the result should be satisfactory. Where, for a non-ionic mol., the lower levels appear to converge linearly, the true dissocn. energy tends to be around 80% of that given by linear extrapolation, being perhaps a little nearer this extrapolated value for light mols. and rather lower for heavy mols. When dissocn. leads to an atom in a $^1\text{S}_0$ state the levels do not usually converge linearly; the true dissocn. energy is then often not much over half the linearly extrapolated value. Extrapolations for excited states should be treated with caution, especially when ionic forces are likely to be important; satisfactory values can be obtained for the lower excited states of mols. composed of nonmetals, especially if a graphical method is used. For mols. with largely ionic bonding the linear Birge-Sponer extrapolation does not appear satisfactory; in a no. of examples it gives a value which is too low. For ionized mols. there appears little evidence to suggest any failure of the linear extrapolation. S. Tolansky

41:5355

Determination of the vapor pressure of solid salts. IV. The vapor pressures of WO_3 , MoO_3 , CdO , and TeO_2 , and their thermodynamic values. Kozo Ueno. *J. Chem. Soc. Japan* 62, 990-4(1941).—From the measurement of the vapor pressure the heat of sublimation ΔH_T , the change of free energy in sublimation ΔF_T and the entropy change ΔS_T are calcd. The results:

Substance	Av. temp. of measurement $T^\circ\text{K.}$	ΔH_T kcal./mol.	ΔF_T kcal./mol.	$\Delta F_{\text{sub.}}$ extrapolated	ΔS_T cal./deg. mol.
WO_3	1368.1	112.6	32.7	95.2	58.4
MoO_3	928.1	63.7	20.5	49.8	46.5
CdO	1028.1	61.4	26.2	51.2	34.2
TeO_2	904.8	57.5	21.4	45.6	39.9

T. Katsuragi

49:5943

Vaporization of inorganic substances: B_2O_3 , TeO_2 , and Mg_3N_2 . John R. Soulen, Prasom Sthapitanonda, and John L. Margrave (Univ. of Wisconsin, Madison). *J. Phys. Chem.* 59, 132-6(1955).—Over the range 1331-1808°K. the vaporization of B_2O_3 can be satisfactorily described by assuming monomeric $\text{B}_2\text{O}_3(\text{g})$ as the main vapor species. The vapor pressure is given by the equation, $\log p_{\text{atm.}} = 6.742 - (16,960/T)$. For vaporization, ΔH_0° is 89.4 kcal./mole. The heat of fusion of TeO_2 is 3.2 kcal./mole, the heat of vaporization is 51.7 kcal./mole, and the heat of sublimation is 54.9 kcal./mole. The vapor pressure of TeO_2 over the temp. range 846-1006°K. is given by $\log p_{\text{atm.}} = 8.067 - (12,000/T)$; over the temp. range 1006-1211°K. it is given by $\log p_{\text{atm.}} = 7.367 - (11,300/T)$. The dissocn. energy of Mg_3N_2 is estd. as 7.2 kcal./mole. The evapn. behavior of Mg_3N_2 is characteristic of a mol. or atom with a low accommodation coeff. Mg_3N_2 vaporizes by a complex mechanism which apparently involves $\text{Mg}_2(\text{g})$ in one of the early steps; at equil., the vaporization products are $\text{Mg}(\text{g})$ and $\text{N}_2(\text{g})$. Henry Leidheiser, Jr.

53:17615

Determination of the vapor pressure over solid tellurium dioxide. V. P. Zlomanov, A. V. Novoselova, A. S. Pashinkin, Yu. P. Simanov, and K. N. Semenenko (M. V. Lomonosov State Univ., Moscow). *Zhur. Neorg. Khim.* 3, 1473-7(1958).—The vapor pressure of solid TeO_2 was measured for the temp. range 457-704°. The phase compn. of TeO_2 was

2.2 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM OXIDES (Contd.)

detd. by thermal and x-ray analysis for samples prepd. by pptn. and crystd. from a melt. The results show that over the entire temp. range TeO_2 is in a tetragonal lattice ($a = 4.796$, $c = 7.588$ Å.). The vapor pressure is described by the formula $\log P_{\text{mm}} = -(13169/T) + 12.257$. The value of ΔH_{854}° was calcd. as 60.1 ± 0.6 kcal. J. R. L.

53:16626

Free-energy functions for gaseous monoxides. L. Brewer and M. S. Chandrasekharaiah (Univ. of California, Berkeley). *U.S. At. Energy Comm. UCRL-8713*, 17 pp. (1959).—Free-energy functions for 58 gaseous monoxides are tabulated for every 500° interval from room temp. up to 3000°K . Electronic contributions were estd. by means of a simple ionic model approximation. Rotational and vibrational contributions were calcd. from available data on fundamental vibrational frequencies and equil. internuclear sepns. or from estns. of these obtained from Badger's rule or by interpolation. All mol. consts. for the alkali metal oxides were estd. Martin Allen

57:4114

The enthalpy of formation of TeO_2 . S. N. Gadzhiev and K. A. Sharifov. *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz. Mat. i Tekhn. Nauk* 1962, No. 1, 47–53. Measurements in a special calorimeter gave following data: $\Delta E_{298}^\circ \text{TeO}_2$ (tetragonal) = -90.0 ± 0.3 kcal./mole and $\Delta H_{298}^\circ \text{TeO}_2$ (tetragonal) = -90.6 ± 0.3 kcal./mole. G. P. Rosenbaum

57:7941

Vapor pressure of solid tellurium dioxide. K. E. Prescher and W. Schroedter (Tech. Univ., Berlin). *Z. Erzbergbau Metallhuettenw.* 15, 299–303(1962). The vapor-pressure curve was measured with a Knudsen cell. At $600\text{--}733^\circ$ the following relation was established: $\log p_{\text{mm}} = -13,292.9/T + 12.4185$. The thermal reaction of TeO_2 according to the equation $2\text{TeO}_2 + \text{O}_2 = 2\text{TeO}_3$ was studied. H. Stoertz

57:9241

Thermodynamic functions of the anharmonic oscillator and vibrating rotator. II. Rotation partition function of diatomic molecules in the multiplet- Σ -electron states. D. Papousek (Univ. Purkyne, Brno). *Collection Czech. Chem. Commun.* 27, 1–8(1962)(in German); cf. *CA* 56, 4113e. Computation of the rotation partition function of diat. mols. in the multiplet- Σ -electron states is discussed. The rotation partition function of heteronuclear mols. can be written in the form $(^{2S+1}Q_r)_v = (2S+1)(^1Q_r)_v + Q(S)$, where S is the resulting electron spin, $(^1Q_r)_v$ is the rotation partition function for the $^1\Sigma$ -state, and $Q(S)$ is a small correction, which may be neglected in calcg. the thermodynamic functions. The thermodynamic functions of SO , SeO , and TeO in the ideal-gas state were computed for the $X^3\Sigma$ -state to the anharmonic-oscillator and vibrating-rotator approxn. E. Erdos

57:15897

Thermodynamic properties of inorganic substances. IV. The high-temperature heat contents of TeO_2 and Na_2TeO_4 . Reiji Mezaki and John L. Margrave (Univ. of Wisconsin, Madison). *J. Phys. Chem.* 66, 1713–14(1962); cf. *CA* 53, 5853b; 54, 6287f; 55, 15098i. The heat contents of TeO_2 and Na_2TeO_4 contained in gold capsules were measured in a drop-type calorimeter at $446\text{--}1146$ and $421\text{--}804^\circ\text{K}$, resp. The heat of fusion of TeO_2 is 6.95 ± 0.10 kcal./mole. CA

59:10819

Molar heat and heat of fusion of tellurium dioxide. Karl Ernst Prescher and Wolfgang Schroedter (Tech. Univ., Berlin). *Z. Erzbergbau Metallhuettenw.* 16, 352–3(1963). Measurements are made from 352 to 1064°K . For molar heat, the value obtained is $15.077 + 0.0033666 T[\text{cal./degree mole}]$ ($298\text{--}1006^\circ\text{K}$). For heat of fusion the value obtained is 7.3 kcal./mole. H. Stoertz

60:15212

Thermochemistry of tellurous acid and sodium tellurite. E. Sh. Ganelina, B. P. Troitskii, and V. S. Yakovleva. *Zh. Prikl. Khim.* 37(3), 677–9(1964). Freshly pptd. tellurous acid dried at room temp. above CaCl_2 crystd. with 1 mol. of H_2O and had the compn. $\text{H}_2\text{TeO}_3 \cdot \text{H}_2\text{O}$. The thermal effects of the following processes were either detd. exptl. or calcd. from exptl. data obtained: $\text{Na}_2\text{TeO}_3(c) + 5\text{H}_2\text{O}(liq) \rightarrow \text{Na}_2\text{TeO}_3 \cdot 5\text{H}_2\text{O}(c) - 11230$, $\text{TeO}_2(c) + 2\text{H}_2\text{O}(liq) \rightarrow \text{H}_2\text{TeO}_3 \cdot \text{H}_2\text{O}(s) - 2550$, $\text{TeO}_2(c) + \text{H}_2\text{O}(liq) \rightarrow \text{H}_2\text{TeO}_3(s) + 1060$, $\text{H}_2\text{TeO}_3(s) + \text{H}_2\text{O}(liq) \rightarrow \text{H}_2\text{TeO}_3 \cdot \text{H}_2\text{O}(s) - 3610$, $\text{H}_2\text{TeO}_3 \rightleftharpoons 2\text{H}^+ + \text{TeO}_3^{--} + 20010$, $[\text{Te}(\text{OH})_6]^{--} - 2\text{OH}^- \rightarrow \text{Te}(\text{OH})_4 + 14820$, and $(\text{TeO}_2)_4 \rightarrow (\text{TeO}_2)_2 + 4670$ kcal./mole. where (c) is crystal, (g) is gas, and (s) is solid. The high thermal effect of hydration of Na_2TeO_3 was due to formation of $\text{Te}(\text{OH})^-$ since 2 mols. H_2O split off at $\leq 65\text{--}70^\circ$, while the remaining 3 mols. H_2O split off at $> 100^\circ$. GZJR

60:15316

Vibrational spectra and the structure of some oxides in crystalline and glassy states. V. P. Cheremisinov. *Tr. Fiz. Inst., Akad. Nauk SSSR* 25, 153–208(1964). Studies with Raman and infrared spectroscopy were made to clarify, on the basis of vibrational spectra, the structure of various cryst. and glassy oxides. The development of a new method for obtaining Raman spectra of powd. substances is reported. The Raman spectra of cryst. As_2O_3 , Sb_2O_3 , As_2O_5 , Sb_2O_5 , TeO_2 , and GeO_2 (2 modifications), and of glassy As_2O_3 , GeO_2 , and TeO_2 were investigated. The vibrational spectra of cryst. and glassy As_2O_3 , GeO_2 , and TeO_2 are similar in fundamental characteristics. As_2O_3 has mol. structure and consists of As_2O_6 mols. An analogous result was also obtained for the Sb_2O_3 specimens. GPJR

3.0 PREPARATION AND PROPERTIES OF TELLURIUM TETRAFLUORIDE

33:1616

Tellurium tetrafluoride. G. A. R. Hartley, T. H. Henry and R. Whytlaw-Gray. *Nature* 142, 952(1938).—Fluorine passed over Te in a tube of cryst. alumina gives a colorless, needle-like, cryst. compd. analyzing Te = 62.5%, F = 38.7% corresponding to the compd. TeF_4 . This compd. is reactive toward glass and silica and unstable in the presence of moisture. It has not been isolated previously. J. W. Shipley

47:1520

Preparation and properties of tellurium tetrafluoride. J. H. Junkins, H. A. Bernhardt, and E. J. Barber (Union Carbide & Carbon Corp., Oak Ridge, Tenn.). *J. Am. Chem. Soc.* 74, 5749–51(1952).— TeF_4 is prep'd. from Te and F in a 2-step process. TeF_6 is formed by the direct combination of the elements at 200° in the presence of excess F; this is reduced to TeF_4 with additional Te at 180° . TeF_4 is unstable in the presence of traces of H_2O , $\text{TeF}_4 + 2\text{H}_2\text{O} \rightarrow \text{TeO}_2 + 4\text{HF}$. It attacks glass and Cu at 200° : $\text{TeF}_4 + \text{SiO}_2 \rightarrow \text{TeO}_2 + \text{SiF}_4$; $\text{TeF}_4 + 4\text{Cu} \rightarrow \text{Cu}_2\text{Te} + 2\text{CuF}_2$. Ag is attacked similarly, but reactions with Au and Ni are very slow, and Pt is inert at temps. below 300° . The m.p. of TeF_4 , 129.6° , was det'd. from warming and cooling curves obtained in a special m.-p. app. Vapor pressures from room temp. to 193.8° , found by means of a static, Ni, diaphragm-type, elec. pressure transmitter (Junkins, *et al.*, *C.A.* 46, 10746e) are summarized by the equations: $\log P_{\text{mm.}}$ (solid) = $9.0934 - 3174.3/T$; $\log_{10} P_{\text{mm.}}$ (liquid) = $5.6397 - 1786.4/T$. From these equations thermodynamic properties of TeF_4 are calcd.; ΔH (vaporization) = 8174, ΔH (sublimation) = 14,525, and ΔH (fusion) = 6351 cal./mole; ΔS (vaporization) = 12.62 and ΔS (fusion) = 15.77 entropy units. Jack G. Calvert

50:8360

Reaction of tellurium dioxide and selenium tetrafluoride: preparation of tellurium tetrafluoride. R. Campbell and P. L. Robinson (King's Coll., Newcastle-upon-Tyne, Engl.). *J. Chem. Soc.* 1956, 785.— TeO_2 appears to be unreactive at least up to 93° , the b.p. of SeF_4 , but at approx. 80° TeO_2 reacts smoothly and quant. according to $\text{TeO}_2 + 2\text{SeF}_4 \rightarrow \text{TeF}_4 + 2\text{SeOF}_2$. TeF_4 can be readily recovered in pure cryst. condition by evapg. the excess of SeF_4 and SeOF_2 . Sidney Arden

57:10759

Preparation and some properties of the tetrafluorides of selenium and tellurium and of the oxyfluoride SeOF_2 . Christian Dagron. *Compt. Rend.* 255, 122–4(1962). By a method described earlier (*CA* 51, 10285f), TeF_4 and SeOF_2 were obtained by reacting SeF_4 with TeO_2 . Distn. at reduced pressure removes excess SeF_4 and SeOF_2 . The TeF_4 residue is sublimed repeatedly at 120° , at reduced pressure. SeF_4 is sep'd. from the mixt. of SeF_4 and SeOF_2 by repeated fractional distn.; (125° fraction, 760 mm.). The fluoride content, as KF, was det'd. volumetrically by lake formation with Th nitrate in the presence of the azo compd. of chromotropic and sulfanilic acids. Most ions interfere; and only small amts. of alk. chlorides or Ag can be tolerated. The vapor pressures of SeF_4 and SeOF_2 are plotted, the former showing the linear relation $\log p = 8.88 - 2284/T$, the latter $\log p = 8.70 - 2316/T$. The b.p. of SeF_4 and SeF_2 at 760 mm. were 107.7° and 125° , resp. Esther W. Claffy

57:13411

Fluorides preparation. William C. Smith (E. I. du Pont de Nemours & Co.). U.S. 3,026,179, Mar. 20, 1962, Appl. June 7, 1957; 3 pp. The fluorides and oxy-

fluorides are made from the reactions, under anhyd. conditions, between SF_4 and oxides of P, As, S, Se, or Te, or between SF_4 and metal phosphates, arsenates, sulfates, selenates, or tellurates. Franklin F. Y. Wang

58:9872

Halogenosales de los elementos Te (IV), Sn (IV), Tl (III), Sn (II). Salamanca, Spain: Universidad. 1961. 146 pp.

3.1 THE CHEMISTRY OF TELLURIUM TETRAFLUORIDE

48:1193

New pyridine complexes of tellurium tetrafluoride. E. E. Aynsley and G. Hetherington (King's Coll., Newcastle-upon-Tyne, Engl.). *J. Chem. Soc.* 1953, 2802–3; cf. *C.A.* 23, 3678.— TeF_4 and pyridine in dry Et_2O yielded $(\text{C}_5\text{H}_5\text{N})_2\text{TeF}_4$ (I), a white ppt. I, with aq. HF and evapn. on steam-bath, gave $(\text{C}_5\text{H}_5\text{NH})\text{TeF}_6$ (II), pale-green crystals. Treatment of II with HCl gave yellow needles of $(\text{C}_5\text{H}_5\text{NH})_2\text{TeCl}_6$ (III). Similarly HBr gave red needles of $(\text{C}_5\text{H}_5\text{NH})_2\text{TeBr}_6$ (IV). On dissolving II in hot HI and cooling, small black needles of $(\text{C}_5\text{H}_5\text{NH})_2\text{TeI}_6$ (V), were deposited. When pyridine was added to a soln. of TeO_2 in aq. HF, and the soln. evap'd. on the steam-bath, buff-colored needles of $(\text{C}_5\text{H}_5\text{NH})_2\text{TeF}_6$ (VI) crystd. When VI was treated with HCl, III was produced. Similarly HBr and HI gave IV and V, resp. Also III gave IV, and V; and IV gave V, on treatment with the appropriate acid. Of these complex halides, the fluorides are the least stable, the order of stability being $\text{II} \text{ and VI} < \text{III} < \text{IV} < \text{V}$. I, II, V, and VI are reported for the first time. R. E. Dunbar

52:19640

Fluoro. . onium compounds. F. Seel and O. Detmer (Tech. Hochschule, Stuttgart, Ger.). *Angew. Chem.* 70, 163–4(1958).— SF_4 , SeF_4 , TeF_4 , OSF_4 , ClF_3 , BrF_3 , and IF_7 form fluoro. . onium compds. with BF_3 , AsF_3 , SbF_3 , and SO_3 , e.g. $\text{SF}_4^+\text{BF}_4^-$, $\text{OSF}_4^+\text{AsF}_6^-$, $\text{ClF}_3^+\text{SbF}_6^-$, $\text{IF}_7^+\text{AsF}_6^-$, thus exhibiting a preference for electron octets or duodets rather than groups of 6, 10, or 14 valence electrons in the salt structures. By means of this fluoro. . onium salt formation, gaseous fluoro compds. such as SF_4 , OSF_4 , SeF_4 , ClF_3 , and IF_7 can be stored as stable, solid, materials, the original compds. being regenerated with alkali fluoride. Dorothy H. Feely

56:3102

Coordination compounds formed by tetrafluorides of the sulfur subgroup. Neil Bartlett and P. L. Robinson (King's Coll., Newcastle-Upon-Tyne, Engl.). *J. Chem. Soc.* 1961, 3417–25.—

TeF_4 plus SbF_5 gave the adduct $\text{TeF}_4\cdot\text{SbF}_5$ (m.p. 206°). $\text{TeF}_4\cdot\text{SbF}_5$ reacted quietly with H_2O and TeO_2 was pptd. BF_3 did not react with TeF_4 . Howard M. Dess

57:5556

Nitrosylfluoride-hydrogen fluorides. Fritz Seel, Walter Birnkraut, and Dietmar Werner (Univ. Saarlandes, Saarbruecken, Ger.). *Ber.* 95, 1264–74(1962). The reaction of NOF, NOCl, NOBr, $(\text{NOF})_2\text{SiF}_4$, $\text{NOCl}\cdot\text{AlCl}_3$, and N_2O_4 with liquid HF gave the stable, distillable $\text{NOF}(\text{HF})_2$ (I), $b_{735} 94^\circ$, and $\text{NOF}(\text{HF})_2$ (II), $b_{735} 68^\circ$. I reacts with many elements and compds. to yield interesting F derivs. NOCl and HF in a ratio of 1:6 distd. into polyethylene bottles at -70° , the mixt. warmed with occasional shaking to -40° , where reaction began, heated to 50° ,

3.1 THE CHEMISTRY OF TELLURIUM TETRAFLUORIDE (Contd.)

and distilled gave II and I. NO and Cl (2:1) passed slowly at -20 to -15° into liquid HF and distd. gave I and II. The vapor ds. were 3.51 g. I/l. and 5.65 g. II/l. Various elements were treated with I and heated to above 94° to give: $\text{BeF}_2 \cdot 2\text{NOF}$, $\text{BF}_3 \cdot \text{NOF}$, AlF_3 , GaF_3 , $\text{SiF}_4 + \text{SiF}_4 \cdot 2\text{NOF}$, $\text{GeF}_4 + \text{GeF}_4 \cdot 2\text{NOF}$, $\text{SnF}_4 + \text{SnF}_4 \cdot 2\text{NOF}$, $\text{PF}_5 \cdot \text{NOF}$, $\text{AsF}_5 \cdot \text{NOF}$, $\text{SbF}_5 \cdot \text{NOF}$, BiF_3 , $\text{SeF}_6 \cdot \text{NOF}$, $\text{TeF}_6 \cdot \text{NOF}$, $\text{TiF}_4 + \text{TiF}_4 \cdot 2\text{NOF}$, $\text{ZrF}_4 + \text{ZrF}_4 \cdot 2\text{NOF}$, $\text{VF}_5 \cdot \text{NOF}$, $\text{MoF}_6 \cdot \text{NOF}$, $\text{WF}_6 \cdot 1-2\text{NOF}$, $\text{UF}_6 \cdot \text{NOF}$, MnF_3 , $\text{FeF}_3 \cdot \text{NOF}$, CuF_2 , ZnF_2 , CdF_2 , $\text{HgF}_2 + \text{Hg}_2\text{F}_2$. Mg, graphite, Pb, F, Cl, Br, I, Co, Ni, Pt, Ag, and Au did not react with I.

F. W. Hoffmann

62:212

The fluorotellurates (IV). A. J. Edwards, M. A. Mouty, R. D. Peacock, and A. J. Suddens (Univ. Birmingham, Engl.). *J. Chem. Soc.* 1964(Oct.), 4087-8(Eng). The fluorotellurates of K, Rb, and Cs were prepd. by treating TeO_2 with the above metal fluorides in the presence of warm SeF_4 . The metal fluorotellurate crystallizes out upon cooling. Attempts to prep. the hexafluorotellurates(IV) was a failure.

J. F. Shultz

4.0 PREPARATION AND PROPERTIES OF TELLURIUM OXYFLUORIDES

48:6896

The preparation and some reactions of nityl fluoride. E. E. Aynsley, G. Hetherington, and P. L. Robinson (Kings Coll., London). *J. Chem. Soc.* 1954, 1119-24.—NO₂F is obtained in almost quant. yield from NaNO₂ by the action of F. The reactions of NO₂F with many elements and with nonmetallic fluorides and oxides are detailed. Certain of these reactions lead to new compds.: (NO₂)₂GeF₆, (NO₂)₂SeF₆, (NO₂)TeF₆, (NO₂)IF₆ have been prepd. All are white solids at room temp. James J. Henry

50:3133

Nitrososulfuryl fluoride. F. Seel and H. Massat (Univ. Würzburg, Ger.). *Z. anorg. u. allgem. Chem.* 280, 186-96 (1955).—Attempts to improve the synthesis of NOSO₂F (Balz and Mailänder, *C.A.* 28, 3328⁹) were not successful. NOSO₂F m. 8° (3100 atm.) and is 70% dissocd. at 19° (430 atm.) in the gas phase. Values are given for the pressures of the vapor in equil. with the solid from -70 to -20° and in equil. with a suspension of the solid in liquid SO₂ from -45 to -10°. The reaction of NOSO₂F with each of the following substances is discussed. The major products are in parentheses and are italicized if new substances. In general the reaction occurs at -10° or lower in liquid SO₂. Solid metals (no attack observed, passive fluoride layer?), Hg (Hg₂F₂, NO), Cl₂ and Br₂ (NOX, SO₂XF), I₂ and S (no reaction), Se ((NO)₂SeF₆), P₄ (NOPF₆ on surface), As (NOAsF₆), Sb (NOSbF₆), H₂O (SO₂, N₂O₃, HF; then, NO, H₂SO₄), alk. H₂O (SO₃⁻, NO₂⁻, F⁻), BF₃ (NOBF₄, SO₂), SiF₄ ((NO)₂SiF₆, SO₂), BCl₃ (BF₃, NOCl, or NOBF₄, NOCl), AlCl₃ (AlF₃), SiCl₄ ((NO)₂SiF₆), TiCl₄ ((NO)₂TiF₆, sublimes at about 180° in vacuum), SnCl₄ ((NO)₂SnF₆), RCl₃ (NOPF₆ and PF₃, NO), AsCl₃ (NOAsF₆, NO), SbCl₃ (NOSbF₆, NO), SeCl₄ ((NO)₂SeF₆), TeCl₄ ((NO)₂TeF₆, m. 100° (decompn.)), IF₃ (I₂, NO, unidentified volatile F compd.), IF₅ (unstable NOIF₆), POCl₃ (slowly, NOCl, and POF₃), SOCl₂ (NOCl), PSCl₃ and SO₂Cl₂ (no reaction), SO₃ (NOSO₃F), NO₂ (NOSO₃F), Me₂C: CMe₂ (resin), C₆H₆ (yellow-orange color), Me₄NCl (Me₄NF, NOCl), Ph₃CCl (Ph₃CF), MeOH (MeONO, HF), HOAc (AcONO, HF), Ac₂O (AcONO, AcF), AcCl (AcF), PhCOCl (PhCOF), satd. hydrocarbons, EtI, Me₃CCl, PhCH₂Cl, and Cl₂C:CCl₂ (no reaction).

51:4857

The fluorination of tellurium. Ditellurium decafluoride and tellurium oxyfluorides. R. Campbell and P. L. Robinson (King's Coll., Newcastle upon Tyne, Engl.). *J. Chem. Soc.* 1956, 3454-8.—The product of the reaction of Te with F is TeF₆ exclusively at 150° and mostly Te₂F₁₀ at 0°. The yield of Te₂F₁₀ at 50-80° is increased by addn. of solids, especially TeO₂, to the Te. Dilm. of the F with O or N increases the yield of Te₂F₁₀, but with either gas Te₃-F₁₄O₂ and a more complex oxyfluoride are formed. Data for Te₂F₁₀, m. -33.7°, b₇₆₀ 59°, d₂₅ 2.839, agree well with data of English and Dale (*C.A.* 48, 69g). It was stored in Pyrex for several months without change. Te₃F₁₄O₂ is a colorless liquid, m. -27°, b₇₆₀ 134.5°, d₂₀ 2.25. It distd. without decompn. or attack in Pyrex. The higher oxyfluoride, possibly Te₄F₂₆O₅, is a colorless liquid, b. >300°, d₂₀ 3.0-3.1. It was stored without change in Pyrex at room temp., but it attacked Pyrex well below its b.p. J. C. Brosheer

61:15639

Fluorotelluric acids. L. Kolditz and I. Fitz (Humboldt- Univ., Berlin). *Z. Chem.* 4(9), 350-1 (1964). Telluric acid (I) 5 g. and 50.5 g. 40% HF were irradiated with infrared in a Pt crucible to give mono-, di-, tri-, and tetrafluorotelluric acids. The compds. were sepd. by paper chromatography, using 75 ml. iso-PrOH-25 ml. H₂O-5 g. CCl₃CO₂H as a solvent. The chromatograms were developed with ZnCl₂ soln. after 24 hrs. The

acids could also be sepd. by thin layer chromatography on cellulose in 2.5 hrs. Heating 9.184 g. I and 138.2 g. 40% HF until the reaction mixt. weighed 105.6 g. and stirring with 31.64 g. C₆H₅N in 20 g. Et₂O gave [C₆H₅N][TeO(OH)F₄]. If the reaction mixt. was evapd. to 60 g. and stored in Cu over P₂O₅ for 7-8 months, 3C₆H₅N.(HO)₄TeF₈.8HF crystd. K. Bezemer

61:1484

Pentafluoro orthotelluric acid, HOTeF₅. A. Engelbrecht and F. Sladky (Univ. Innsbruck, Austria). *Angew. Chem.* 76(9), 379-80 (1964). BaTeO₄ when heated with HSO₃F (mole ratio 1:10) for 3 hrs. at 160° yields a mixt. of volatile Te compds. Major component is HTeOF₅, b.p. 60 ± 1°. Walter Wagner

62:15735

Chemistry of tellurium fluoride compounds. I. New F₅Te-type compounds from the reaction of barium tellurate with fluorosulfonic acid. A. Engelbrecht and F. Sladky (Univ. Innsbruck, Austria). *Monatsh. Chem.* 96(1), 159-68 (1965) (Ger). The following F₅Te-type compds. were recovered from the distillates produced by heating BaTeO₄ with HSO₃F (mole ratios varied between 1:5 and 1:15) to the HSO₃F-distn. temp.: F₅TeOH (I), m. 40°, b. 60° (*CA* 61, 1484h); F₅TeOSO₂F (II), m. -89°, b. 56°; (F₅TeO)₂SO₂ (III), m. -50°, b. 118°; and F₅TeOSO₃H (IV), m. -21°, b. 133°. The reactions required 1-4 hrs., and the relative amts. of I-IV in the crude distillate depended on the degree of hydration of BaTeO₄. Thus, BaTeO₄.(H₂O)_{1.5-2} favored the yield of I and IV, whereas anhyd. BaTeO₄ favored that of II. The compds. were sepd. by fractional distn. and fractional crystn. The exptl. detd. mol. wts. of the purified I, II, and III are 243, 335, and 525, resp.; IV could not be purified because of its instability. I and IV showed characteristic acid reactions; II and III were practically insol. in H₂O and fairly resistant toward hydrolysis. The compds. have a garlic-like odor, and inhalation of their vapors, even in low concns., causes delayed transitory asthma. The exact degree of toxicity must still be detd. It is suggested that the difference in behavior between Te and Se, the reaction BaSeO₄ with HSO₃F yields SeO₂F₂ (*CA* 52, 5191a), is due to the tendency of Te toward a higher coordination no. Hertha R. Freche

5.0 PREPARATION AND PROPERTIES OF DITELLURIUM DECAFLUORIDE

48:69

Ditellurium decafluoride. W. D. English and J. W. Dale (Defence Research Chem. Labs., Ottawa, Can.). *J. Chem. Soc.* 1953, 2498-9.— Te_2F_{10} , obtained in 20% yields by direct fluorination of Te in the presence of CaF_2 , is a colorless, heavy, remarkably volatile liquid, m. -34° to -33° , $b_{748} 53^\circ$. Heat of evapn. at the normal b.p. is 9440 cal./mole (calcd.); Trouton const., 28.8 cal. mole $^{-1}$ deg. $^{-1}$; n_D^{20} , 1.298; d_4^{25} , 2.88. It is fairly stable and can be stored for several months. It attacks glass. J. A. A.

51:790

Viscosities of iodine pentafluoride and ditellurium decafluoride. G. Hetherington and P. L. Robinson (King's College, Newcastle upon Tyne, Engl.). *J. Chem. Soc.* 1956, 3681.—Viscosity (η) of IF_5 from 14.55 to 69.30° gave a max. of 26.66 and min. of 11.17. These measurements indicate that $\eta_t = \eta_0 / (1 + At + Bt^2)$, where $A = 0.04231$, $B = 0.000014$, and $\eta_0 = 0.04325$ poise. Viscosity of Te_2F_{10} varies from 2.542 at -30.0° to 0.930 at 44.9° and the consts. for the above equation were $A = 0.01365$, $B = 0.0000175$, and $\eta_0 = 0.01524$ poise. C. J. Boner

51:4857

The fluorination of tellurium. Ditellurium decafluoride and tellurium oxyfluorides. R. Campbell and P. L. Robinson (King's Coll., Newcastle upon Tyne, Engl.). *J. Chem. Soc.* 1956, 3454-8.—The product of the reaction of Te with F is TeF_6 exclusively at 150° and mostly Te_2F_{10} at 0° . The yield of Te_2F_{10} at $50-80^\circ$ is increased by addn. of solids, especially TeO_2 , to the Te. Diln. of the F with O or N increases the yield of Te_2F_{10} , but with either gas $\text{Te}_3\text{F}_{14}\text{O}_2$ and a more complex oxyfluoride are formed. Data for Te_2F_{10} , m. -33.7° , $b_{760} 59^\circ$, d_4^{25} 2.839, agree well with data of English and Dale (C.A. 48, 69g). It was stored in Pyrex for several months without change. $\text{Te}_3\text{F}_{14}\text{O}_2$ is a colorless liquid, m. -27° , $b_{755} 134.5^\circ$, d_{20} 2.25. It distd. without decompn. or attack in Pyrex. The higher oxyfluoride, possibly $\text{Te}_6\text{F}_{26}\text{O}_8$, is a colorless liquid, b. $>300^\circ$, d_{20} 3.0-3.1. It was stored without change in Pyrex at room temp., but it attacked Pyrex well below its b.p. J. C. Brosheer

53:14687

Molecular vibrations of Group VI decafluorides. I. Infrared and Raman spectra of disulfur decafluoride and ditellurium decafluoride. R. E. Dodd, L. A. Woodward, and H. L. Roberts (King's Coll., Newcastle-upon-Tyne, Engl.). *Trans. Faraday Soc.* 53, 1545-56(1957).—The infrared absorption spectra in the vapor were measured over the range 2-25 μ . The Raman spectra of the liquids were photographed and the states of polarization of the lines detd. qualitatively. The results were discussed in terms of the staggered $\text{F}_2\text{X}-\text{XF}_2$ model (point group D_{4d}). Assignments of the observed frequencies to fundamentals and combinations were proposed. Both compds. were prepd. by direct fluorination of the elements. There were 19 fundamental frequencies, 11 active in the Raman effect (4 of them polarized), 7 active in the infrared, and 1 totally inactive. No fundamental was active in both kinds of spectrum. II. Force field calculations for sulfur decafluoride. L. A. Woodward and H. L. Roberts. *Ibid.* 1557-62.—The fundamental frequencies are: $\nu_1(a_1) = 913$; $\nu_2(a_1) = 690$; $\nu_3(a_1) = ?$; $\nu_4(a_1) = 247$; $\nu_5(b_2) = 938$; $\nu_7(b_2) = 684$; $\nu_8(b_2) = 571$ cm. $^{-1}$. Force consts. were calcd. by using the staggered $\text{F}_2\text{S}-\text{SF}_2$ model (D_{4d}) and a simple valence force field with repulsions between nearest-neighbor nonbonded F atoms. The totally sym. deformation frequency ν_1 , presumed to have escaped observation because of low intensity, was calcd. to be about 642 cm. $^{-1}$

V. R. Deitz

6.0 PREPARATION OF TELLURIUM HEXAFLUORIDE

36:2490

Inorganic syntheses. I. Harold S. Booth (Editor-in-chief), L. F. Audrieth, John C. Bailar, Jr., W. Conard Fernelius, Warren C. Johnson and Raymond Kirk. 197 pp. (1939) New York, McGraw-Hill Book Co., \$3.00.—

44. Sulfur, selenium and tellurium hexafluorides. Don M. Yost. *Ibid.* 121-2.—S, Se, or Te of moderate fineness is placed in a Cu tube and F passed over. The exit is provided with a trap cooled with concd. HCl-ice to remove the lower fluorides formed. The hexafluorides are collected by cooling with either solid CO₂-alc. or liquid air. SF₆ can be purified by bubbling through water and drying with P₂O₅. SeF₆ and TeF₆ are purified by sublimation at low temp.

48:69

Ditellurium decafluoride. W. D. English and J. W. Dale (Defence Research Chem. Labs., Ottawa, Can.). *J. Chem. Soc.* 1953, 2498-9.—Te₂F₁₀, obtained in 20% yields by direct fluorination of Te in the presence of CaF₂, is a colorless, heavy, remarkably volatile liquid, m. -34° to -33°, b₇₄₈ 53°. Heat of evapn. at the normal b.p. is 9440 cal./mole (calcd.); Trouton const., 28.8 cal. mole⁻¹ deg.⁻¹; n_D²⁰, 1.298; d₄²⁰, 2.88. It is fairly stable and can be stored for several months. It attacks glass. J. A. A.

51:4857

The fluorination of tellurium. Ditellurium decafluoride and tellurium oxyfluorides. R. Campbell and P. L. Robinson (King's Coll., Newcastle upon Tyne, Engl.). *J. Chem. Soc.* 1956, 3454-8.—The product of the reaction of Te with F is TeF₆ exclusively at 150° and mostly Te₂F₁₀ at 0°. The yield of Te₂F₁₀ at 50-80° is increased by addn. of solids, especially TeO₂, to the Te. Diln. of the F with O or N increases the yield of Te₂F₁₀, but with either gas Te₂F₁₄O₂ and a more complex oxyfluoride are formed. Data for Te₂F₁₀, m. -33.7°, b₇₆₀ 59°, d₄²⁰ 2.839, agree well with data of English and Dale (*C.A.* 48, 69g). It was stored in Pyrex for several months without change. Te₃F₁₄O₂ is a colorless liquid, m. -27°, b₇₅₅ 134.5°, d₂₀, 2.25. It distd. without decompn. or attack in Pyrex. The higher oxyfluoride, possibly Te₆F₂₆O₆, is a colorless liquid, b. >300°, d₂₀, 3.0-3.1. It was stored without change in Pyrex at room temp., but it attacked Pyrex well below its b.p. J. C. Brosheer

54:11656

The dissociation energy of fluorine and the magnetic deflection of its molecular beams. Thomas A. Milne and Paul W. Gilles (Univ. of Kansas, Lawrence). *J. Am. Chem. Soc.* 81, 6115-20 (1959).—A beam of F from a furnace was directed onto a film of Te coated on a microscope slide. A preliminary Stern-Gerlach expt. in which the at. and mol. components of the beam were sepd. showed that at. F reacts with Te to produce a volatile product, whereas mol. F does not react. Densitometric measurement of the developed slides allowed a calcn. of the partial pressure of at. F in the furnace using the Knudsen equation. The disson. energy was detd. by a 3rd-law calcn. at 2 temps. and by a 2nd-law calcn. using data from a temp.-variation study. The most consistent value of D₀, 41.3 ± 0.5 kcal./mole, is obtained by assuming all F atoms react and that the sole reaction product is TeF₆. W. J. Hayles

6.1 THE CHEMISTRY OF TELLURIUM HEXAFLUORIDE

34:1524

Directed valence. George E. Kimball. *J. Chem. Phys.* 8, 188-98 (1940).—The problem is treated from a group-theory point of view. G. M. Petty

47:4187

The possible use of 4f orbitals in bonding: The enhanced stability of the higher oxidation states of iodine, tellurium, and antimony; the nonexistence of perbromic acid. T. Z. Hugus, Jr. (Univ. of California, Berkeley). *J. Am. Chem. Soc.* 74, 1076-7 (1952).—f orbitals can always be substituted for p orbitals in a hybridization complex, but only in particular symmetry groups can s and d orbitals be replaced by f orbitals. Octahedral bonding can occur with d²sp³ and d²sf², but not with f²sp³. f electrons can contribute to bonding in compds. of the elements immediately preceding the rare earths; certain chem. properties of these elements are thereby explained. Felix Saunders

51:12724

Lewis character of tellurium hexafluoride. E. L. Muetterties and W. D. Phillips (E. I. du Pont de Nemours & Co., Wilmington, Del.). *J. Am. Chem. Soc.* 79, 2975 (1957); cf. *C.A.* 51, 8564i.—TeF₆ reacts exothermically with tertiary amines to form stable adducts of the compn. TeF₆·2R₃N. Pyridine formed a complex that was highly dissoed. at 25°, but amides, ethers, and nitriles did not absorb TeF₆ at 25°. TeF₆ is a relatively weak Lewis acid. The nuclear magnetic resonance data are consistent with the behavior of an octavalent complex which has geometrical isomers and undergoes amine exchange through simple disson. of the complex. At about -180°, the 3 F resonances can be ascribed to the 3 possible isomers. On steric grounds, the 2 peaks of relative intensity 1 probably arise from the 1,8- and 1,3-isomers and the peak of relative intensity 0.4 from the 1,2-isomer. Above about -180° slight disson. of the complexes leads to amine exchange which occurs at different rates for the 3 isomers. At higher temps. the 3 isomers are indistinguishable in the nuclear magnetic resonance spectrum because of fast amine exchange. At temps. above 25°, the complex is highly dissoed. in soln. and the position of resonance is a measure of the equil. const. for the disson. Without supporting data, these conclusions cannot be considered rigorously established. Felix Saunders

51:8564

Fluotellurates. E. L. Muetterties (E. I. du Pont de Nemours & Co., Wilmington, Del.). *J. Am. Chem. Soc.* 79, 1004 (1957).—The behavior was studied of TeF₆ and SeF₆ toward various inorg. fluorides. Neither showed strong interaction or F exchange with covalent fluorides, but TeF₆ reacted with certain ionic fluorides to form new fluotellurate salts. Se did not form fluoselenates. The fluotellurates (limiting compn. 2MF·TeF₆) were prepd. by heating MF with 100% excess TeF₆ in a pressure vessel to 250° and cooling the mixt. to room temp. during 24 hrs. The fluotellurates dissoed. at high temps. to yield the starting materials: Fluotellurates added to water yielded TeF₆ and the alkali metal fluoride. The fluotellurates were unstable outside the solid state. Felix Saunders

51:17550

Hydrogen fluoride solvent system. I. A qualitative survey of acids. A. F. Clifford, H. C. Beachell, and W. M. Jack (Univ. of Delaware, Newark). *J. Inorg. & Nuclear Chem.* 5, 57-70 (1957).—The relative acidity of fluorides such as BF₃, SiF₄, GeF₄, SnF₄, TiF₄, SeF₄, PF₅, AsF₅, SbF₅, IF₅,

6.1 THE CHEMISTRY OF TELLURIUM HEXAFLUORIDE (Contd.)

VF₃, NbF₅, TaF₅, TeF₆, MoF₆, WF₆, and ReF₆ in HF soln. was detd. both by their soly. in HF and by the ability of their HF solns. to dissolve metallic fluorides, whose expected order of basicity was CoF₂ = MnF₂ = CrF₂ < HgF₂ < AgF₂ < CuF₂ < NiF₂ = CoF₂ < CaF₂ < AgF < NaF. An addnl. criterion of acid strength was the ability of these solns. to dissolve metals such as, in order of increasing electropositivity, Hg, Ag, Cu, Pb, Sn, Nb, Cr, Zn, Mn, Mg, and Ca. SbF₅ dissolves exothermally in HF; from the soln. white hexafluoroantimonic acid (I) may be frozen out. Lanthanide fluorides dissolve in I in HF.

Heptafluorotelluric acid (VI), prepd. similarly to V, is inert to CuF₂, AgF₂, HgF₂, CoF₂, MnF₂, Mg, Mn, and Cr. Silver heptafluorotellurate is moderately sol.

The strengths of the fluoro acids are, for the elements investigated: Sb^V > As^V = Bi^{III} > P^V = Sn^{IV} = Re^{VI} = W^{VI} = Mo^{VI} = V^V > IV = Te^{VI} = Ge^{IV} = Ta^V = Nb^V > Se^{IV} = Si^{IV} = Ti^{IV} > Sb^{III} = Al^{III} = Cr^{III} = Be^{II} > F = Cl^{III} = O = S^{VI} = N = C. II. Salts of the fluoro acids. Solvolysis. A. F. Clifford and A. G. Morris (Univ. of Delaware, Newark). *Ibid.* 71-5.—Solid salts of volatile fluoroacids were reaction. The action of ClF₃ on P in HF gave PF₅ which on reaction with AgF, BaF₂, and NaF, and evapn. of HF and the volatile fluoroacid yielded, resp., silver, barium, and sodium hexafluorophosphates. Similarly, sodium and barium hexafluoroarsenates, sodium hexafluoroantimonate (soly. 0.2M in HF at 2°), KBF₄ (soly. 0.48M in HF at 2°), silver heptafluorotellurate, barium fluoride monoheptafluorotellurate, barium heptafluorotellurate, calcium fluoride monoheptafluorotellurate, calcium heptafluorotellurate, barium hexafluoroselenite, sodium pentafluoroselenite, barium hexafluoroiodate, barium fluoride monohexafluoroiodate, sodium hexafluoroiodate, barium pentafluorogermanate, barium hexafluorogermanate, and sodium pentafluorogermanate were prepd. These salts were sol. in HF. Solns. of LiF, NaF, and KF in HF similarly evapd. gave the respective monohydrogen difluorides. With BaF₂ in HF, evapn. gave barium monohydrogen trifluoride. Observed solvolysis of the salts gives an acid strength series BF₃ = SbF₅ = AsF₅ = PF₅ > GeF₄ > TeF₆ > IF₅ > SeF₄.

6.2 SPECTRAL AND STRUCTURAL STUDIES OF TELLURIUM HEXAFLUORIDE

26:5239

Spatial chemistry. I. Low-boiling fluorides. OTTO RUFF, FRITZ EBERT AND WALTER MENZEL. *Z. anorg. allgem. Chem.* 207, 48-60(1932).—Measurements were made on F₂, ClF, OF₂, BF₃, NF₃, ClF₃, AsF₃, BrF₃, CF₄, SiF₄, AsF₅, BrF₅, SbF₅, SF₆, TeF₆, MoF₆, WF₆, IF₇. It was attempted to det. the size of the mols. and the arrangement and size of the constituents. The packing d., which at the b. p. is 52.3% and at 0°K. is 74%, det. the size of the mols., subject to changes in mol. structure, dissoen. or assocn. As a working hypothesis it is assumed that the constituents of mols. not only touch but also interpenetrate both in the case of the same or different constituents. For purposes of calcn. these deformed mols. are replaced by smaller ones that just touch.

ALFRED HOFFMAN

27:3160

The determination of the structures of the hexafluorides of sulfur, selenium and tellurium by the electron diffraction method. L. O. BROCKWAY AND LINUS PAULING. *Proc. Natl. Acad. Sci.* 19, 68-73(1933).—The at. configurations and interatomic distances in SF₆, SeF₆ and TeF₆ have been detd. by methods similar to the electron diffraction methods used by Mark and Wierl (*C. A.* 24, 2371) for the study of gas mols. The observed intensities were compared with theoretical intensity curves calcd. for each of several models. A well-defined beam of electrons traveling with a uniform velocity was caused to intersect a jet of gas, the scattered electrons being recorded on a film set at right angles to the direction of the original beam. Photographs of Au were used as standards. Photographs of CCl₄ gave consistent values for the C-Cl sepn. for any

6.2 SPECTRAL AND STRUCTURAL STUDIES OF TELLURIUM HEXAFLUORIDE (Contd.)

one photograph but the values depended somewhat on the density of the photographic film. The hexafluoride photographs were always compared with those of the CCl_4 and a correction (never more than 3%) was made for the difference in d. of the films. Rather indistinct films of Br_2 and Cl_2 gave interatomic distances within 2% of the values from band spectral data. The F atoms are located at the corners of an octahedron about the central atom. The S-F sepn. is 1.58 ± 0.03 ; Se-F, 1.70 ± 0.03 ; Te-F, 1.84 ± 0.03 A. U. Interatomic distances agree well with those expected of an ionic structure.

L. L. QUILL

27:4160

Electron diffraction by gaseous SF_6 , SeF_6 and TeF_6 . H. Braune and S. Knoke. *Z. physik. Chem.* B21, 297-309(1933).—The structures of gaseous SF_6 , SeF_6 and TeF_6 were studied by means of electron diffraction. The distances from the central atom to the F atom were, resp., 1.56, 1.67 and 1.82 A. U.

C. M. MURPHY

28:2229

The electronic structure of hexafluorides. Thomas G. Pearson and Percy L. Robinson. *J. Chem. Soc.* 1933, 1427-9.—The d. and the surface tension of SF_6 were measured over a range of temp., and the parachor calcd. therefrom indicates that the octet valency rule is maintained in this compd., 2F atoms being attached to the S atom by covalent linkages and the remaining 4 by semipolar singlet links. The parachors of SeF_6 and TeF_6 reveal a structure identical with that of SF_6 . A. L. H.

28:5335

Raman spectra and molecular constants of SF_6 , SeF_6 and TeF_6 . Don M. Yost, Carsten C. Steffens and Siegfried T. Gross. *J. Chem. Physics* 2, 311-16(1934).—A theoretical treatment gives the frequency formulas for the fundamental modes of vibration of a regular octahedral mol. The 3 lines observed in the Raman spectra of SF_6 , SeF_6 and TeF_6 are assigned to the 3 vibrations permitted by selection rules, the strongest line in each case corresponding to the completely sym. vibration. Ests. are made of the forbidden frequencies. These data permit ests. of the virtual entropy = 70.5 cal./degree and the free energy of formation = 238,000 cal. for gaseous SF_6 at 298° (cf. C. A. 27, 2088).

C. D. West

29:4264

The infrared spectra, normal vibrations and intermolecular forces of selenium and tellurium hexafluorides. H. Sachsse and E. Bartholomé. *Z. physik. Chem.* B28, 257-66(1935); cf. C. A. 29, 141.—The infrared spectra of SeF_6 and TeF_6 were measured between 3 and 25 μ . Combination of these results with unpublished data on the sp. heats gave the normal vibrations of the mol. With these and some general force laws, the 7 force consts. were obtained. The results are similar to those for SF_6 with a Coulombian central force system and certain angular forces caused by the interaction of neighboring atoms.

G. M. MURPHY

30:373

Relation between the internuclear distances and force constants of molecules and its application to polyatomic molecules. Richard M. Badger. *J. Chem. Physics* 3, 710-14(1935); cf. C. A. 28, 2996⁶; Clark, C. A. 28, 7143⁹; Allen and Longair, C. A. 29, 4671⁹.—The relation between internuclear distances and force consts. is found to persist in polyat. mols. The internuclear distances of CCl_4 , SiCl_4 , SnCl_4 , SF_6 , SeF_6 and TeF_6 were predicted from vibrational data alone, and were found to agree well with exptl. values.

G. M. P.

30:5882

Absorption spectra of halides and oxyhalides of S, Se and Te. S. L. Hussain and R. Samuel. *Current Sci.* 4, 734-6(1936).—Measurements of absorption bands corresponding to successive splitting off of halogen atoms from S, Se and Te halides give satisfactory values of heats of formation.

G. W. King

33:4873

The Raman spectra of volatile fluorides—applications of Raman spectra to chemical problems. Don M. Yost. *Proc. Indian Acad. Sci.* 8A, 333-40(1938).—The stretching and bending force consts. of the following compds. are calcd. from Raman spectrum data: BF_3 , BCl_3 , BBr_3 , PF_3 , PCl_3 , PBr_3 , AsF_3 , AsCl_3 , CF_4 , CCl_4 , SiF_4 and SiCl_4 . The entropies S°_{298} cal./degree are calcd. for all the compds. but the B halides. The vibrational frequencies of SF_6 , SeF_6 and TeF_6 are tabulated. The Raman spectrum obtained from SOF_2 is $\Delta\nu$ 326 (1), 395 (6), 529 (8), 729 (9), 795 (9), 1312 (10).

James H. Hibben

43:5651

Molecular force fields. VIII. Vibration frequencies of some octahedral XY_6 molecules. D. F. Heath and J. W. Linnett. *Trans. Faraday Soc.* 45, 264-71(1949); cf. C. A. 43, 4571f.—The orbital valency force field (O.V.F.F.) and simple valency force field (S.V.F.F.), both including reasonable repulsion between nonbonded atoms, were applied to SF_6 , SeF_6 and TeF_6 . O.V.F.F. reproduces the observed frequencies much more satisfactorily than does S.V.F.F. However, O.V.F.F. does not account satisfactorily for the frequency of the vibration of symmetry F_{2u} , which is lower than might have been expected. The bonding orbitals of the central atom accommodate themselves during the vibration to the distortion by a change of hybridization, rendering the distortion easier. There seems to be a major difference between the vibrational behavior of UF_6 and that of SF_6 , SeF_6 and TeF_6 .

Victor R. Deitz

48:6829

Infrared spectra and molecular structure of some group VI hexafluorides. J. Gaunt (Atomic Energy Research Establishment, Harwell, Engl.). *Trans. Faraday Soc.* 49, 1122-31(1953).—The spectra were investigated between 400 and 5000 cm^{-1} . Only UF_6 was free of traces of SiF_4 . The 6 fundamental vibration frequencies (cm^{-1}) for each mol. are: SF_6 , 775, 644, 932, 613, 524, 344; SeF_6 , 708, 662, 780, 437, 405, 260; TeF_6 , 701, 674, 752, 327, 313, 197; MoF_6 , 736, 641, 742, 269, 319, 240; WF_6 , 769, 670, 712, 256, 322, 216; and UF_6 , 668, 532, 626, 189, 202, 144.

6.2 SPECTRAL AND STRUCTURAL STUDIES OF TELLURIUM HEXAFLUORIDE (Contd.)

Interpretation was based on belief that these mols. belong to the O_h point group and have a totally symmetric octahedral structure. There is conclusive evidence in favor of the completely sym. structure. The thermodynamic properties were calcd. and compared for UF_6 with calorimetric measurements. Victor R. Deitz

50:2293

Infrared spectrum of tellurium hexafluoride from 25 to 40 μ . J. Gaunt (At. Energy Research Establishment, Harwell, Engl.). *Trans. Faraday Soc.* 51, 893-4(1955).—The low-frequency fundamental, ν_4 , has been observed for only SF_6 , SeF_6 , MoF_6 , and WF_6 (C.A. 46, 7432a). A strong band of TeF_6 having P , Q , and R branches was observed, with the aid of a CsBr prism, centered at 325 cm^{-1} ; it was assigned to ν_4 . The observed value was in good agreement with the value of 327 cm^{-1} previously derived from the relevant combination bands. A crystal of additively colored CsBr which began to transmit at 6 μ , and had over 80% transmission from 15 to 40 μ , was placed immediately in front of the entrance slit of the spectrometer and it was found that the stray light was almost completely eliminated. Victor R. Deitz

51:858

Infrared spectra of selenium hexafluoride and tellurium hexafluoride. T. G. Burke (Union Carbide Nuclear Co., Oak Ridge, Tenn.). *J. Chem. Phys.* 25, 791-2(1956).—Comparisons were made between B.'s results and the published work of Gaunt (C.A. 48, 6829b; 50, 2293d). The 2 works were in good agreement. Discrepancies involved only weak bands of combination vibrations and in no instance did they affect the interpretation with respect to the mol. configuration. Henry Leidheiser, Jr.

53:19557

Force constants for the hexafluorides XF_6 . Salvatore Califano (Univ. Naples). *Atti accad. nazl. Lincei, Rend., Classe sci. fis., mat. e nat.* 25, 284-91(1958).—Force consts. for the hexafluorides of S, Se, Te, Mo, W, U, Re, Ir, Np, and Pu were calcd. from spectroscopic data in 2 ways: (1) with a quadratic potential function and 4 interaction consts.; and (2) with a Urey-Bradley potential function. Consts. obtained by the 1st method reproduced the exptl. frequencies exactly, but those from the 2nd method gave good approxns. to the frequencies only for the 1st 5 compds. J. D. Porter

58:7517

Mean amplitudes of vibration and Bastiansen-Morino shrinkage effects in some octahedral XY_6 molecules. E. Meisingseth and S. J. Cyvin (Norges Tek. Hoegskole, Trondheim, Norway). *Acta Chem. Scand.* 16, 2452-3(1962)(in English). Spectroscopic calcs. of mean amplitudes of vibration and shrinkage effects of the hexafluorides of S, Se, Te, Mo, W, and U are reported. M. Jeevanadam

59:3330

Potential field and force constants of some octahedral XY_6 -type molecules. G. Nagarajan (Annamalai Univ., Annamalai-

gar, India). *Bull. Soc. Chim. Belges* 71, 276-85(1963)(in English). Vibrational analyses for octahedral XY_6 -type mols. of the symmetry point group O_h are reported. The construction and orientation of symmetry coordinates (F and G matrixes) by the methods of Wilson are deduced. By using the redundant symmetry coordinates, a unique set of force consts. is obtained for SF_6 , SeF_6 , TeF_6 , MoF_6 , WF_6 , UF_6 , NpF_6 , PuF_6 , ReF_6 , OsF_6 , IrF_6 , and PtF_6 . S. Nowinska

59:7092

Raman intensities. IX. Vibrational intensities for spherically symmetric modes of CH_4 , CD_4 , CF_4 , SiF_4 , SF_6 , SeF_6 , and TeF_6 . D. A. Long and E. L. Thomas (Univ. Coll. Swansea, Wales). *Trans. Faraday Soc.* 59, 1026-32(1963); cf. CA 59, 138d. The Raman intensities for the $\nu_1(a_1)$ modes of gaseous CH_4 , CD_4 , CF_4 , SiF_4 , SF_6 , SeF_6 , and TeF_6 relative to the $\nu_1(a_1)$ mode of CH_4 were detd. The Raman cell had a vol. of about 7 l. and could withstand pressures of 3 atm. It incorporated 4 concave mirrors each of radius of curvature of 110 cm. The mean deviation in the results was $<\pm 2\%$ and $\pm 5\%$ for the derived bond polarizabilities. Victor R. Deitz

59:12299

Vibrational spectra. Mean amplitudes of vibration and thermodynamic functions of the dioxides of chlorine, sulfur, and selenium. G. Nagarajan (Annamalai Univ., Annamalaiagar, India). *Bull. Soc. Chim. Belges* 72(7-8), 524-36(1963)(in English). An elaborate discussion of the various methods used for studying the mol. structure and vibrational spectra of ClO_2 , SO_2 , and SeO_2 is given. The computed numerical values of the mean-sq. amplitude quantities, generalized mean-sq. amplitudes (mean-sq. parallel amplitudes, mean-sq. perpendicular amplitudes, and mean cross products), and mean amplitudes of vibration for the temps. $T = 0$ and $T = 298^\circ K$. are given for these mols. By using the fundamental frequencies, as well as the normal frequencies, the molar thermodynamic functions were calcd. on the basis of a rigid-rotator, harmonic-oscillator approxn. for the temp. range 100-1700°K. Kathleen S. Erb

60:1229

The mean-square amplitudes of interatomic distances in hexafluoride molecules. M. Kimura and K. Kimura (Univ., Nagoya, Japan). *J. Mol. Spectry.* 11(5), 368-77(1963). Possible values of force consts. are estd. by using fundamental frequencies and a general quadratic potential function for hexafluorides of S, Se, Te, Mo, W, Re, Os, Ir, Pt, U, Np, and Pu. The root-mean-sq. amplitudes of interat. distances are calcd. from these force consts. and fundamental frequencies. According to the magnitudes of root-mean-sq. amplitudes hexafluoride mols. are classified into the following groups: (1) SF_6 , SeF_6 , and TeF_6 , contg. np electrons, (2) mols. from MoF_6 to PtF_6 contg. $4d$ or $5d$ electrons, and (3) UF_6 , NpF_6 , and PuF_6 , contg. $5f$ electrons. RCKP

61:5094

Infrared spectra of some hexahalogeno complexes. Jiro Hiraishi, Ichiro Nakagawa, and Takehiko Shimanouchi (Univ. Tokyo). *Spectrochim. Acta* 20(5), 819-28(1964)(in English). Infrared spectra of hexachloro complexes were measured from 14 to 35 μ . A strong band, 350 ~ 300 cm^{-1} , was assigned to the triply degenerate stretching vibration, ν_3 . A normal coordinate treatment was made for these complex ions on the basis of the mol. force field adequate for some hexafluorides. The nature of metal-halogen coordination bonds was discussed on considering the bond-stretching force consts. obtained. The result is in agreement with that of the pure quadrupole resonance study of halogens. RCSQ

6.3 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM HEXAFLUORIDE

26:5239

Some physical properties of SF_6 , SeF_6 , TeF_6 , and CF_4 . WILHELM KLEMM AND PAUL HENKEL. *Z. anorg. allgem. Chem.* 207, 73-86(1932).—The m. ps. in the order SF_6 , SeF_6 , TeF_6 , CF_4 are $-50 \pm 0.5^\circ$, $-34.8 \pm 0.5^\circ$, $-37.6 \pm 0.5^\circ$, $-186.8 \pm 0.5^\circ$. The solid ds. at -273° : 2.74, 3.54, 4.08, 2.1; at the m. p.: 2.51, 3.27, 3.76, 1.98; d. of liquid at m. p.: 1.85, 2.26, 2.67, 1.91. The substances expand greatly on melting. Tables of the heats of sublimation, of fusion and of vaporization and of vapor pressures are given.

ALFRED HOFFMAN

27:2088

The thermochemical constants of the hexafluorides of sulfur, selenium and tellurium. DON M. YOST AND WM. H. CLAUSEN. *J. Am. Chem. Soc.* 55, 885-91(1933).—Exptl. data were obtained on the vapor pressures and the melting and sublimation points of $\text{SeF}_6(\text{s})$ and $\text{TeF}_6(\text{s})$, and on the heats of formation of SF_6 , SeF_6 and TeF_6 . SeF_6 reacts with NH_3 slowly at 200° , and much more rapidly at 330° , to give Se , N_2 and HF . For $\text{S}(\text{s}) + 3\text{F}_2(\text{g}) = \text{SF}_6(\text{g})$, the authors calc. $\Delta F_{298}^\circ = -235 \text{ kg.-cal.}$ A lower liquid fluoride of Te was discovered.

F. D. ROSSINI

27:4724

Refractivity of gaseous fluorides. Wilhelm Klemm and Paul Henkel. *Z. anorg. allgem. Chem.* 213, 115-25(1933).—The following mol. refractive indices (reduced to 0°) were detd., by mean of an interferometer, for the wave length $\lambda = 587.6 \times 10^{-4}$: BF_3 , 6.00, CF_4 , 7.23, SiF_4 , 8.40, GeF_4 , 10.2, SF_6 , 11.39, SeF_6 , 13.37, TeF_6 , 15.00. Mol. refractive indices, mol. dispersions and at. refractions of the fluorides were compared with the values of the other halides of the same elements, and corresponding variations were found.

J. H. REEDY

28:2583

The dielectric coefficients of gases. II. The lower hydrides of C and Si, O, N, oxides of N and C and fluorides of Si and S. H. E. WATSON, G. GUNDU RAO AND K. L. RAMASWAMY. *Proc. Roy. Soc. A* 143, 558-88(1934); cf. C. A. 25, 5320.—The dielec. consts. of 17 gases were measured at 2 or 3 temps. and their elec. moments deduced from the results. Only C_3H_8 , CO , NO and N_2O have measureable elec. moments, the value for N_2O being discussed in relation to suggested structures for the mol. Compressibilities were also detd. by making measurements at different pressures. The construction and calibration of a precision variable condenser capable of measuring a change in capacity of $0.4 \mu\text{F}$ with an accuracy of 0.0001 μF is described.

MORRIS MUSKAT

29:2433

The vapor pressure of the hexafluorides of selenium and tellurium. Paul Henkel and Wilhelm Klemm. *Z. anorg. allgem. Chem.* 222, 65-6(1935).—For SeF_6 , $\log p = 8.614 - (1303/T)$; for TeF_6 , $\log p = 8.594 - (1342/T)$. The heats of sublimation σ and the ratios σ/T are, resp.: SF_6 5.57, 26.5; SeF_6 5.95, 26.3; TeF_6 6.13, 26.1.

ALBERT L. HENNE

29:2799

Magnetochemical investigations. XII. The magnetic behavior of some liquid fluorides. Paul Henkel and Wilhelm Klemm. *Z. anorg. allgem. Chem.* 222, 70-2(1935); cf. preceding abstr.—The specific magnetic susceptibility and the mol. susceptibility as found, and as computed by the Angus method are listed: GeF_4 , -0.33 ± 0.01 , -49 ± 2 , -40 ; SF_6 , -0.300 ± 0.003 , -44 ± 0.5 , -45 ; SeF_6 , -0.266 ± 0.008 , -51 ± 2 , -51 ; TeF_6 , -0.273 ± 0.001 , -66 ± 0.5 , -61 ; MoF_6 , -0.124 ± 0.005 , -26 ± 1 , -55 ; WF_6 , -0.137 ± 0.003 , -40 ± 1 , -66 ; UF_6 , $+0.12$, $+43$, about -70 .

30:3708

The molar heat of a few gases at low temperatures according to the thermal-conductivity method. A. BUCKEN AND A. BERTRAM. *Z. physik. Chem.* B31, 361-81(1936); cf. C. A. 28, 962².—The relative thermal conductivities of Kr , N_2 , CO_2 , CH_4 , C_2H_4 , C_2H_6 and SF_6 were measured with respect to Ar . An oxidized Ni wire was used at temps. about $3/4$ of the abs. b. p. of the gases. Since the normal vibrations and mol. heats of these substances were known, it could be shown that under these conditions the accommodation coeff. of the wire was approx. unity. Similar expts. were then performed with SeF_6 , TeF_6 , CF_2Cl_2 , C_2H_2 , C_2N_2 and CF_4 and the mol. heats calcd. from the thermal cond. The normal vibrations were also obtained and compared with those detd. from optical data. For the higher temp., where the accommodation coeff. begins to deviate from the max. value of unity, theoretical considerations suggested a simple formula which gives satisfactory results in combination with the thermal-cond. data.

G. M. MURPHY

36:2458

The refractive indexes of PF_5 and OsO_4 and the dielectric constants of OsO_4 , SF_6 , SeF_6 and TeF_6 . R. LINKE. *Z. physik. Chem.* B48, 193-6(1941).—The refractive indexes of PF_5 and OsO_4 were detd. at various low pressures and calcd. for normal conditions with regard to the linear pressure dependence as: $\text{PF}_5: (n-1)_{\text{D}} \cdot 10^4 = 6.416 \pm 0.018$; $\text{OsO}_4: (n-1)_{\text{D}} \cdot 10^4 = 1.113 \pm 0.024$. The dielec. consts. ϵ were also detd. at various pressures and calcd. for normal pressure. T and $(\epsilon-1) \times 10^{13}$, resp., are: SF_6 292.4, 2.108; SeF_6 293.2, 2.481; TeF_6 292.1, 3.020; OsO_4 429.2, 2.767; OsO_4 561.2, 2.751. The resulting atomic polarizations are discussed.

R. WEBER

6.3 THERMOCHEMICAL AND THERMODYNAMIC PROPERTIES OF TELLURIUM HEXAFLUORIDE (Contd.)

NSA 12:2733

2733 ANL-5750

Argonne National Lab., Lemont, Ill.

THE THERMOCHEMICAL PROPERTIES OF THE OXIDES, FLUORIDES, AND CHLORIDES TO 2500°K. Alvin Glassner. 1957. 70p. Contract W-31-109-eng-38. \$0.45 (GPO).

This report supersedes ANL-5107.

Tables of thermochemical and thermodynamic properties of oxides, fluorides, and chlorides to 2,500°K are presented. (W.L.H.)

54:13880

Some liquids for use in large bubble chambers. B. Hahn, G. Riepe, and A. W. Knudsen (Univ. Fribourg, Switz.). *Rev. Sci. Instr.* **30**, 654-5(1959).—Liquids C_2F_6 , C_4F_{10} , SF_6 , C_2ClF_6 , and $CBrF_3$, and mixts. of SF_6 with C_2ClF_6 are suitable for use in large bubble chambers designed for particle-decay studies. Desirable properties are relatively short radiation length, convenient operating pressure, and nontoxicity. Operating characteristics are tabulated. Properties of TeF_6 are discussed. A. A. Scott

60:8881

The fluorides and oxyfluorides of sulfur, selenium, and tellurium. Richard Tunder (Aerospace Corp., Los Angeles, Calif.). *U.S. Dept. Com., Office Tech. Serv., AD 273,048*, 38 pp. (1961). The relative reactivity of the fluorides of S, Se, and Te increases with increasing at. wt. and with decreasing valence state of the central atom. Substitution of a group larger or less electroneg. than F into one of these fluorides increases its reactivity. Of the oxyfluorides discussed, apparently only SOF_4 forms complexes to any great degree. The fluorosulfonates and fluorosulfonates are themselves products of complexing with SO_2 and SO_3 . Sexivalent fluorides and quadrivalent fluorides of these elements are discussed. The S oxyfluorides, SOF_2 , SOF_4 , and SO_2F_2 , and the more complex oxyfluorides, FO_2SOSO_2F and FO_2SOOSO_2F , are also discussed. From *U.S. Govt. Res. Rept.* **37(11)**, 9(1962). TCVD

7.0 NUCLEAR TECHNOLOGY AND TELLURIUM HEXAFLUORIDE

50:16449

Chemical and radiochemical studies of tellurium in fluoride volatility processes. J. Fischer and R. K. Steunenberg (Argonne Natl. Lab., Lemont, Ill.). *U.S. Atomic Energy Comm. ANL-5593*, 19 pp.(1956).—Studies were made to clarify the behavior of fission product Te in fluoride volatility processes for the recovery of U from spent reactor fuels. The chem. nature of mixts. of TeF_6 and BrF_3 was investigated in the gas phase at 75 and 100°, and in the liquid phase at 25°. The gas-phase behavior of TeF_6 in BrF_3 was studied at 75°, and liquid mixts. of TeF_6 and Br were examd. at 25°. In none of these systems was there evidence for a chem. reaction which would produce Te compds. of low volatility. Quant. radiochem. observations were made on the partial reduction of TeF_6 and the sepn. of daughter isomers owing to the internal conversion of γ -rays of Te^{127m} and Te^{129m} . It was found that Te activity could be sepd. from BrF_3 by distn. The activity remaining after the volatilization of a mixt. of TeF_6 and UF_6 was a small fraction of the short-lived isomers Te^{127} and Te^{129} . S. B.

53:2709

Continuous-flow pilot plant for the separation of bromine-fluorine compounds and light-end fission product fluorides from uranium hexafluoride. W. R. Page, C. J. Raseman, E. I. Goodman, and C. H. Scarlett (Brookhaven Natl. Lab., Upton, N.Y.). *U.S. Atomic Energy Comm. BNL-174*, 38 pp.(1952)(Declassified Apr. 27, 1955).—The sepn. by distn. of UF_6 from BrF_3 , BrF_5 , and light-end fission product fluorides (such as those of Te and I) was studied in a 2-column still. Each column was a 2-in. Al pipe 9 ft. long, packed with single-turn Al helices. The still was operated at 2–3 atm. gage and had a capacity of 3 gal./hr. With mixts. of heptane and methylcyclohexane, the height equiv. theoretical plate (HETP) was 3.1–3.6 in. When a mixt. of BrF_3 , UF_6 , and the volatile fluorides from fluorination of irradiated UF_4 was distd., most of the Te was stripped from the feed as TeF_6 in the 1st column, and 3.5% of the Te appeared in the bottoms fraction. In the 2nd column this bottoms fraction was sepd. into overhead UF_6 contg. <0.1% Br and $1/80$ of the Te activity in the feed to the 2nd column, and a bottoms fraction of BrF_3 ; the decontamination factor for Te was 1700. The HETP in the 2nd column was 4.5–6.3 in. There was evidence of the formation of a nonvolatile complex between BrF_3 and a Te fluoride, such as Te_2F_{10} , but the complex was not identified. The app. and methods of analysis are described in detail. J. C. Brosheer

NSA 11:7408

7408 ANL-5560
Argonne National Lab., Lemont, Ill.
CHEMICAL ENGINEERING DIVISION SUMMARY REPORT [FOR] JANUARY, FEBRUARY, AND MARCH 1956.
May 2, 1956. Decl. Feb. 12, 1957. 139p. Contract W-31-109-eng-38. \$0.80(OTS).

Measurements of radioactive carryover were made on the Borax III boiling reactor. Mass transfer in a continuous-flow mixing chamber was investigated; additional light scattering data were obtained. The evaluation of Ni in fluorinated and hydrofluorinated fused salts was continued. Corrosion rates of several metals and alloys in BrF_3 – UF_6 systems and gaseous F_2 were measured. The radiochemical properties and volatilization of fission product fluorides (TeF_6) were investigated. Studies were continued on the preparation, handling, and thermal stability of PuF_6 . Uranium tetrafluoride produced from ore concentrate was fluorinated in a fixed-bed reactor to produce volatile UF_6 . Melt-refining of spent EBR fuel pins and the corrosive effects of molten U on alumina and Ta were investigated. Additional studies were conducted

on the extraction of Pu from U with liquid Mg, and the subsequent distillation of the Mg to recover the Pu. Several methods of inert gas purification were tested. Procedures are described for the direct assay of Mo and Ru in ternary U alloys by x-ray emission. (For preceding period see ANL-5529.) (C.W.H.)

NSA 15:7412

7412 (TID-11398) KINETICS OF URANIUM AND FISSION PRODUCT FLUORIDE ADSORPTION BY SODIUM FLUORIDE. Final Report to January 1959. J. H. Krause and J. D. Potts (Houdry Process Corp. Research and Development Labs., Linwood, Penna.). Apr. 18, 1960. 50p. For Oak Ridge National Lab. Contract W-7405-eng-26, Subcontract 2010. (60-OCR-1). OTS.

Results of a program to measure the kinetics of adsorption and desorption of volatile metal fluorides by sodium fluoride are described. Most effort was concentrated on uranium hexafluoride, while other fluorides such as those of silicon, molybdenum, tellurium, ruthenium, and iodine were examined briefly. (J.R.D.)

57:16089

Fused salt-fluoride volatility process with irradiated urania decayed 15–30 days. G. I. Cathers, R. L. Jolley, and H. F. Soard (Oak Ridge Natl. Lab., Oak Ridge, Tenn.). *U.S. At. Energy Comm. ORNL-3280*, 29 pp.(1962). U from irradiated UO_2 fuel, decayed 15–30 days, was highly decontaminated from short-lived fission products by the fused salt-fluoride volatility process. The disappearance of the radioactive I, Te, Nb, Ru, Zr, and Mo in the fused salt dissoln. step indicated that pptn. or volatilization and condensation at the top of the dissoln. reactor occurred with little material being carried from the vessel. Dissoln. rates for irradiated UO_2 clad in Zircaloy-2, used as feed material, were approx. the same as those obtained with unirradiated material. M. M. de Maine

NSA 17:39179

39179 (ORNL-3452(p.26-50)) FLUORIDE VOLATILITY PROCESSING. (Oak Ridge National Lab., Tenn.).

Observations made in the course of attempting to prepare TeF_6 , a volatile fission product fluoride present in processing short-decayed fuel, indicated that it is readily reduced by nickel at less than 300°C. Thus, in the fused-salt fluorination step much of this fission product is retained on the relatively cool upper walls of the fluorination reactor. In studying the absorption of TeF_6 in 10% aqueous KOH, a 12% TeF_6 mixture in fluorine was passed through two 20-in.-long x 1 in.-dia columns, in series, packed with 0.25-in. Alundum Berl saddles with an absorption of 46, 68, and 67% of the tellurium, respectively, at 25, 50, and 70°C.

NSA 18:14118

14118 (TID-7677(p.102-24)) EXPERIENCE IN TRAPPING IODINE-131 AND OTHER FISSION PRODUCTS RELEASED FROM IRRADIATED AGR-TYPE FUEL ELEMENTS. D. A. Collins, R. Taylor, and W. D. Yuille (Gt. Brit. National Inst. for Research in Nuclear Science. Rutherford High Energy Lab., Harwell, Berks, England).

I^{131} and other fission products were released from irradiated stainless steel-clad uranium dioxide under conditions relevant to potential accidents in the Advanced Gas-Cooled Reactor. Measurements were made of the penetration of I^{131} , Te^{132} , Cs^{137} , and Sr^{90} , released in the above manner, through a trapping system consisting of an

7.0 NUCLEAR TECHNOLOGY AND TELLURIUM HEXAFLUORIDE (Contd.)

absolute filter, followed by a 4-in. deep bed of charcoal and a final absolute filter, in series. No significant penetrations were observed except in the case of I^{131} in the form of alkyl iodides. Some small fraction of the iodine released from the irradiated fuel is in this form and investigations showed some conditions in which this form can be produced from iodine initially present in other forms. Experiments with macroscopic amounts of methyl iodide, representing the above form of iodine, showed that it is only delayed on activated charcoal at temperatures up to 100°C, but part of it can be permanently retained at 200°C. Oxidizing catalysts showed some promise of effectively retaining methyl iodide, but the presence of carbon monoxide interfered. (auth)

NSA 19:4247

4247 (ORNL-3627(p.29-72)) FLUORIDE VOLATILITY PROCESSING. (Oak Ridge National Lab., Tenn.).

Development of a molten-salt fluoride-volatility process is described which consists basically of dissolution of the metal (or oxide) by hydrofluorination in a molten salt, volatilization of U from the melt as UF_6 by contacting the salt with gaseous fluorine, and the purification of the product UF_6 from contaminants by passing the impure gas stream through beds of NaF and MgF_2 pellets. The first fuel processed at ORNL by the molten-salt fluoride-volatility process was the molten salt from the Aircraft Reactor Experiment. The next effort was the development of a process for use with alloys of Zr and highly enriched U. A few years ago, the study of the application of the process to Al-U alloy fuels began; this work was prompted by the large potential load of such fuels to be processed. In addition, some work has been done on developing processes for fuels containing zirconia-urania, thoria-urania, beryllia-urania, and stainless steel. Studies were also made aimed at the volatilization and recovery of U and Pu from low-enrichment fuels. Work on the molten-salt fluoride-volatility process for Zr-U alloy fuels is nearly complete, and its application to Al-U alloy fuels is being studied. In the future, process development efforts will emphasize the application of the molten-salt fluoride-volatility approach to low-enrichment fuels. Also, a proposal was made to install a fluidized-bed fluoride-volatility pilot plant in Building 3019, primarily for studies on stainless-steel- or zirconium-clad UO_2 . (auth)