

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, K-25 PLANT, CARBIDE AND CARBON CHEMICALS COMPANY, UNION CARBIDE AND CARBON CORPORATION]

Preparation and Properties of Tellurium Tetrafluoride¹

BY J. H. JUNKINS, H. A. BERNHARDT AND E. J. BARBER

RECEIVED MAY 29, 1952

Tellurium tetrafluoride was prepared in a two-step process from elemental fluorine and tellurium. Direct combination of the elements at 200° in the presence of excess fluorine produced the hexafluoride which was subsequently reduced to the tetrafluoride with additional metal at 180°. Tellurium tetrafluoride melts at 129.6°. Its vapor pressure from room temperature to 193.8° may be described by equations (1) and (2). Above 193.8° tellurium tetrafluoride is unstable toward the hexafluoride. From the vapor pressure equations the following thermodynamic properties are calculated: $\Delta H_v = 8174$ cal. mole⁻¹; $\Delta H_s = 14,525$ cal. mole⁻¹; $\Delta S_v = 12.62$ e.u.; $\Delta H_f = 6351$ cal. mole⁻¹; $\Delta S_f = 15.77$ e.u. Tellurium tetrafluoride is consumed by metallic copper at 185° forming copper telluride and cupric fluoride. It reacts similarly with silver, less rapidly with gold, and very slowly with nickel, but not with platinum.

Introduction

Moissan,² Prideau³ and Yost⁴ observed the formation of a white solid which accompanies the main product, tellurium hexafluoride, that is formed when fluorine is passed over tellurium metal. Hartley, *et al.*,⁵ identified the crystalline compound as tellurium tetrafluoride by chemical analysis. They also observed its reactivity with glass and silicon and its instability in the presence of traces of moisture. The purpose of the present work has been to investigate the principal physical constants of the compound.

Experimental and Results

Preparation and Purification.—Tellurium metal chips were fluorinated with elemental fluorine, in a static system constructed of nickel, producing primarily gaseous tellurium hexafluoride and small quantities of the solid lower fluorides of tellurium. The highly exothermic reaction proceeded spontaneously at room temperature until the metal became coated with a layer of the lower fluorides. When the rate of reaction subsided the temperature of the reactor was increased slowly to 200° where the formation of the hexafluoride continued until the metal had been completely consumed. The product, a colorless gas, was condensed in a receiver surrounded by Dry Ice slush. Its apparent molecular weight, determined by gas density measurements, was 240 g. per mole, which compares favorably with the theoretical value of 241.6 g. per mole for tellurium hexafluoride. A mass spectrometer study of the sample confirmed the identity.

The tellurium hexafluoride was transferred in the gas phase into another reactor where it was reduced by tellurium metal chips (stoichiometric amount plus 10% excess) at 180° with absorption of heat. Over a period of 100 hours the tellurium hexafluoride was completely absorbed by the tellurium metal to form a crystalline white solid. This material sublimed from the zone of formation and deposited in a cooler region of the reduction apparatus.

A simple sublimation step in a separate apparatus was used to remove the tetrafluoride from small quantities of less volatile gray colored lower fluorides which had been formed by localized over-heating during the reduction. The total solid fluorides were heated in a zone maintained at 160° and the sublimate collected on a cold finger at 0°. The purified product was a white solid which gave a distinct X-ray diffraction pattern whose lines suggested isomorphism with uranium tetrafluoride and zirconium tetrafluoride. Analytical results shown in Table I identify the compound as tellurium tetrafluoride. These data are considered ade-

quate to discount the possibility of contamination of the TeF₄ by Te₂F₁₀. Since the compound is hygroscopic, all transfers of solid material were made in a dry-box purged with dry nitrogen to maintain a dew point of approximately -50°.

TABLE I
COMPOSITION OF SOLID TELLURIUM TETRAFLUORIDE

	Sample 1	Sample 2	Theor. for TeF ₄	Theor. for Te ₂ F ₁₀
Tellurium, %	62.12	62.00	62.67	57.32
Fluorine, %	35.91	36.17	37.33	42.68
Total	98.03	98.17	100.00	100.00

Determination of the Melting Point.—The melting point of tellurium tetrafluoride was determined from warming and cooling curves. The apparatus (Fig. 1) consisted of a hermetically sealed sample tube suspended concentrically inside a closed nickel shield. The body of the sample tube was constructed of platinum (0.010-inch wall thickness) with a nickel flare fitting welded on top to provide a simple means of closure from the atmosphere. The sample tube was supported in position by a thin nickel ring which was suspended inside the shield by three 0.007-inch platinum wires attached equally spaced about the top of the shield. Two thermocouple wells were provided, one in the bottom of the sample

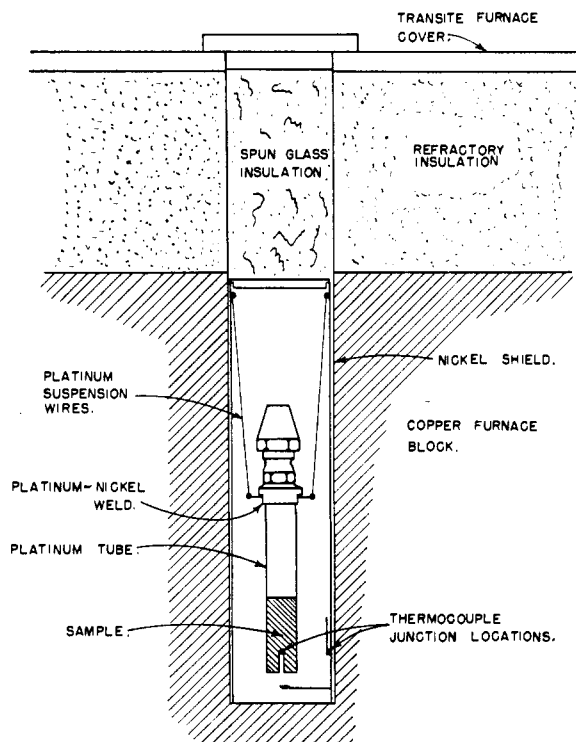


Fig. 1.—Melting point apparatus.

(1) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Company, Union Carbide and Carbon Corporation, Oak Ridge, Tennessee.

(2) Henri Moissan, *Ann. chim. phys.*, [6] **24**, 239 (1891).

(3) E. B. R. Prideau, *J. Chem. Soc.*, **89**, 320 (1906).

(4) Don M. Yost and W. H. Claussen, *THIS JOURNAL*, **55**, 885 (1933).

(5) G. A. R. Hartley, T. H. Henry and R. Whitlaw-Gray, *Nature*, **142**, 952 (1938).

tube and another attached to the inside of the shield at the sample level. Calibrated platinum, platinum-rhodium thermocouples and a Leeds and Northrup White double potentiometer were used to measure the temperatures of the sample tube and shield. The thermocouples were electrically insulated from the thermocone wells with spun glass fabric.

The tube and shield assembly was fitted in an insulated copper block which was heated by four Calrod units spaced symmetrically about the tube-shield assembly. The current to the heaters was supplied through a Variac at a predetermined constant voltage such that approximately two hours was required to pass through the melting transition. A typical plot of the warming curve data is shown in Fig. 2. The melting point of $129.6 \pm 1.0^\circ$ was obtained by extrapolating the warming curves to the intersection of tangents which represents a 100% melted condition. Although the slope of the warming curve indicated some premelting, the extrapolated value is a reasonably reliable estimate of the melting point. This fact is confirmed, within the limits of accuracy indicated, by the intersection of vapor pressure equations (1) and (2).

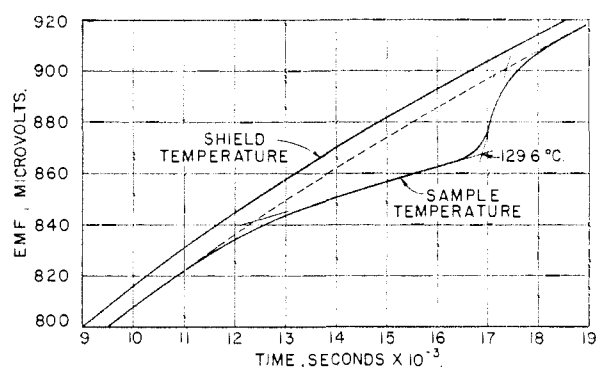


Fig. 2.—Heating curve for tellurium tetrafluoride.

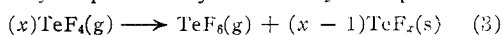
Measurement of the Vapor Pressure.—The vapor pressure of tellurium tetrafluoride was measured in a static, nickel, diaphragm-type, electrical pressure transmitter.⁶ Considerable out-gassing of the sample occurred before conditions of equilibrium were obtained. After the sample had been pumped several times at a temperature near the melting point of the compound, the vapor pressure values were reproducible from room temperature to 193.8° . The results (Fig. 3) from this temperature range, where tellurium tetrafluoride is thermally stable, were analyzed statistically and may be expressed by the equations

$$\log_{10} P_{\text{min}}(\text{solid}) = 9.0934 - 3174.3/T \quad (1)$$

$$\log_{10} P_{\text{min}}(\text{liquid}) = 5.6397 - 1786.4/T \quad (2)$$

Between 193.8 and 199.2° a sharp increase in the vapor pressure occurred. Upon cooling a residual pressure existed. This pressure was caused by a condensable material identified by mass spectrometer analysis to be tellurium hexafluoride. After the hexafluoride had been pumped off, the remaining tellurium tetrafluoride yielded vapor pressure data entirely compatible with that obtained before part of the sample had disproportionated.

When the temperature of disproportionation was reached the second time, it was observed from time versus pressure data, at a fixed temperature, that the disproportionation was a rate process. After 30 hours at 199.2° the system reached an equilibrium pressure of 750 mm. The mechanism of the process may be qualitatively described by the expression



where x is 2 or 3, or a combination of the two.

As the temperature was increased above 200° the apparent vapor pressure increased very slowly, even less than would be expected from the gas law effect alone. The measurements in this temperature range do not represent the vapor pressure of any one compound, but rather the sum of the partial pressures of the lower fluorides and the hexafluoride. As the temperature was increased, the tendency

(6) J. H. Junkins, R. L. Farrar, Jr., E. J. Barber and H. A. Bernhardt, *THIS JOURNAL*, **74**, 3464 (1952).

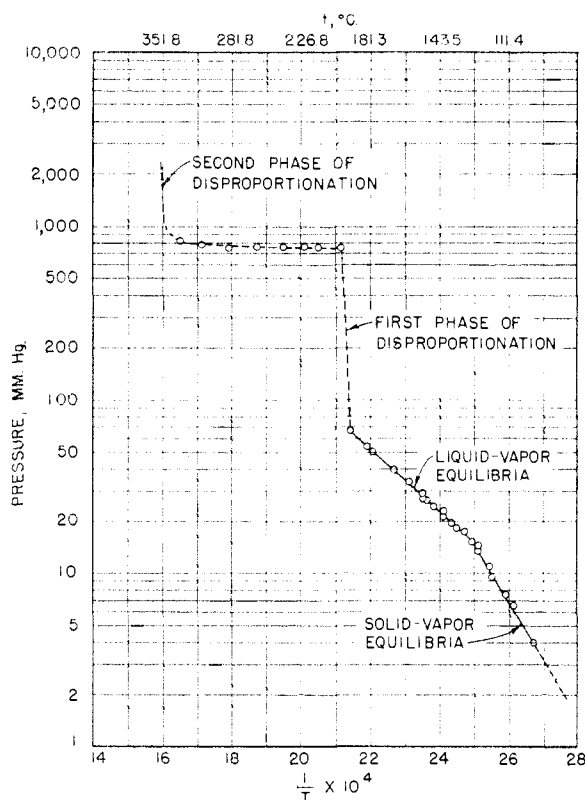
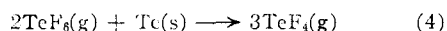


Fig. 3.—Vapor pressure of tellurium tetrafluoride.

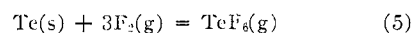
of these partial pressures to increase was opposed by more rapid chemical reactions in which part of the tellurium tetrafluoride and tellurium hexafluoride were consumed in forming relatively non-volatile lower fluorides. The formation of these fluorides was confirmed by analytical results obtained from side reaction studies.

At 333° there was a second upward discontinuity in the vapor pressure curve as the products of the first phase of the disproportionation themselves decomposed giving more hexafluoride and either a still lower fluoride or elemental tellurium.

Previous workers⁷ have mentioned the great stability of these fluorides, with respect to dissociation into the elements. The observed instability of tellurium tetrafluoride toward the hexafluoride and the metal, however, is to be expected, since the reaction



is endothermic. On the other hand the hexafluoride would not be expected to be thermally unstable toward the elements because the combination



is highly exothermic, 300 kcal. mole⁻¹.

Thermodynamic Properties.—The estimation of certain physical constants is based on the Clausius-Clapeyron equation. Assuming ideal behavior of the gas and neglecting the volume of the solid or liquid, the integrated form is the equation of a straight line, the slope of which is numerically equal to $-\Delta H/R$.

$$\Delta H = -(\text{slope of the line} \times 2.303 \times 1.987) \quad (6)$$

Substituting slope values from the vapor pressure equations (1) and (2).

$$\Delta H_v = 1786.4 \times 2.303 \times 1.987 = 8174 \text{ cal. mole}^{-1} \quad (7)$$

$$\Delta S_v = \Delta H_v/T = 8174/647.5 = 12.62 \text{ e.u.} \quad (8)$$

(7) D. M. Yost and Horace Russell, Jr., "Systematic Inorganic Chemistry," Prentice-Hall, Inc., New York, N. Y., 1944, p. 297

$$\Delta H_s = 3174.3 \times 2.303 \times 1.987 = 14,525 \text{ cal. mole}^{-1} \quad (9)$$

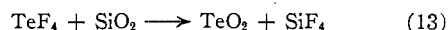
$$\Delta H_t = \Delta H_s - \Delta H_v = 14,525 - 8174 = 6351 \text{ cal. mole}^{-1} \quad (10)$$

$$\Delta S_t = \Delta H_t/T = 6351/402.8 = 15.77 \text{ e.u.} \quad (11)$$

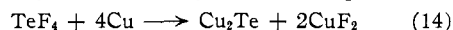
Chemical Behavior.—Tellurium tetrafluoride is unstable in the presence of traces of water.⁵



and is completely consumed by glass or silica⁵ containers at 200°.



It also reacts with copper at the same temperature. The products of this reaction were identified by chemical analyses and X-ray diffraction patterns.



Silver is attacked similarly, but the reactions with gold and nickel are very slow. Platinum appears to be inert at temperatures below 300°.

OAK RIDGE, TENNESSEE

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, AND RADIATION LABORATORY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Solubility of Hydrous Germanous Oxide and the Potential of the Germanous Oxide-Germanic Oxide Couple

BY WILLIAM L. JOLLY¹ AND WENDELL M. LATIMER

RECEIVED JULY 7, 1952

The solubility of the brown form of hydrous GeO has been determined as $2 \pm 1 \times 10^{-4}$ mole per liter. From potential measurements, $\text{GeO}(\text{yellow}) = \text{GeO}(\text{brown})$, $\Delta F^\circ = -7.2$ kcal./mole and $\text{GeO}(\text{brown}) + \text{H}_2\text{O} = \text{GeO}_2 + 2\text{H}^+ + 2e^-$, $E^\circ = 0.118 \pm 0.010$ volt at 25°.

Freshly prepared hydrous germanous oxide (precipitated with alkali in the cold) is yellow, and it stays this color if stored under water at room temperature. But if an aqueous suspension of the yellow oxide is boiled, or if it is treated with aqueous hydrochloric acid, the color changes to dark brown.

Solubility of Germanous Oxide. Preparation of Brown GeO.—Germanous hydroxide was precipitated by adding aqueous ammonia to a hydrochloric acid solution of +2 germanium. The precipitate was washed thoroughly with water by repeated centrifugation and decantation and then an aqueous suspension of the material was boiled for about 45 minutes in an inert atmosphere. A final centrifugation yielded a brown paste of hydrous GeO.

Solubility Measurements.²—The hydroxide was equilibrated with the solvent (water or aqueous hydrochloric acid) at 25°. A filtered sample of the supernatant solution was titrated with standard permanganate, using iodide as an indicator.

An average of $2 \pm 1 \times 10^{-4}$ molar was obtained for the solubility of brown germanous hydroxide in water. The solubility in aqueous hydrochloric acid is less than 0.01 molar for hydrochloric acid concentrations less than 4 *M* HCl, and increases rapidly for concentrations beyond 4 *M* HCl.

Everest and Terrey³ found germanous hydroxide to be insoluble in alkaline solutions and hence discredited the report of Hantzsch,⁴ who postulated "germano-formic acid." They measured the solubility of the hydroxide in water and found a solubility of 5.0×10^{-3} molar. Their method of analysis consisted of oxidizing the +2 germanium in solution to germanic acid and then titrating this acid after addition of glycerol. (Any germanic acid already present or formed by air oxidation of the germanous hydroxide would have led to high results.) Everest and Terrey apparently used the yellow form of GeO in their investigation.

The GeO, GeO₂ Electrode.—From the spontaneous conversion of yellow GeO to brown GeO, the yellow form is obviously thermodynamically unstable with respect to the brown form. The following cell was studied for the purpose of

obtaining a quantitative measure of the instability: $\text{GeO}(\text{yellow})$, GeO_2 , 0.0025 *M* HCl, $\text{GeO}(\text{brown})$, GeO_2 . The hydrochloric acid concentration in this cell was low enough so that the yellow GeO changed very slowly to the brown form. The two electrodes consisted of noble metal wire spirals packed with pastes of GeO and GeO_2 . In Table I, the observed e.m.f. of the cell is given as a function of time from preparation of the cell. From the initial cell potential, ca. 0.155 volt, we calculate $\Delta F^\circ = -7200$ cal./mole for the following two-electron reaction: $\text{GeO}(\text{yellow}) = \text{GeO}(\text{brown})$. As was expected, the cell potential dropped gradually with time, because of spontaneous conversion of the yellow GeO to brown GeO.

Two more cells were prepared and observations made concurrently. Both were of the type— GeO , GeO_2 , *x M* HCl, Hg_2Cl_2 , Hg, but one contained yellow GeO initially and the other contained brown GeO.

TABLE I
CELL VOLTAGES

Time, hours	<i>E</i> , volts	Time, hours	<i>E</i> , volts
1.0	0.155	43.5	0.098
3.0	.156	47.5	.090
6.8	.129	117	.064
21.5	.122		

Cell Materials and Experimental Procedure.—Double distilled mercury was washed with nitric acid and rinsed well with water. U. S. P. mercurous chloride was washed by decantation with water. The hydrochloric acid solutions were prepared by appropriate dilution of stock solutions, which had been standardized by titration of weighed amounts of mercuric oxide by the iodo-mercurate method. In one case, the hydrochloric acid was prepared by diluting some constant boiling acid. The molalities and activity coefficients were calculated from the data of Harned and Owen.⁵ Whenever the electrolyte was changed, the cell was rinsed very thoroughly by draining and adding the fresh electrolyte. This rinsing was repeated at hourly intervals until the cell potential changed less than a millivolt. The most dilute solution of HCl was used first, and the most concentrated last. Therefore one would expect the first run with the cell containing the yellow GeO to be in disagreement with the later runs, where the HCl concentration was sufficient to rapidly convert the GeO to the stable form.

(5) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943.

(1) Taken from a thesis presented by William L. Jolly for partial satisfaction of the requirements for the Ph.D. degree, University of California, 1952.

(2) For experimental details, the reader is referred to University of California Radiation Laboratory Report 1638, "Some Problems in the Chemistry of Germanium," January, 1952.

(3) D. A. Everest and H. Terrey, *J. Chem. Soc.*, 2282 (1950).

(4) A. Hantzsch, *Z. anorg. Chem.*, **30**, 316 (1902).