Triple Point Temperature of Tellurium

A. D. TEVEBAUGH[1] and E. J. CAIRNS
General Electric Research Laboratory, Schenectady, N. Y.

Literature data for the triple point of tellurium vary from 420° to 525° C. with a preponderance of values from 445° to 455° C. A value of 449.80 ± 0.05° C. for the triple point of tellurium is reported in this paper.

A RESUMÉ and evaluation of previous literature data for the triple point temperature of tellurium was published by Machol and Westrum (*4*). Published values vary from 420° to 525° C., with a preponderance of values from 445° to 455° C. The triple point temperature of tellurium as reported in this paper is in good agreement with the values reported by Machol and Westrum (*4*) and by Kracek (*3*).

EXPERIMENTAL

Semiconductor grade tellurium (99.999%) from the American Smelting and Refining Company was zone refined (five passes of the liquid zone) in a quartz boat under an atmosphere of hydrogen. A central, two-inch section (74 grams) of the resultant tellurium bar (~ 12 inches long) was transferred to a quartz section of a vacuum apparatus which contained two liquid-nitrogen traps in series between the tellurium sample and any source of grease or mercury vapor. After a vacuum of 4×10^{-6} mm. of Hg was obtained, hydrogen from heated UH_3 was added to the vacuum system to a final pressure of 76 cm. of Hg. The tellurium sample was then heated to the melting point which permitted it to run into a hot quartz dewar-shaped tube (outer jacket evacuated and sealed) which contained a thermocouple well. The tellurium (550° C.) was kept in contact with the hydrogen atmosphere for approximately three hours, and then the system was evacuated to 2×10^{-5} mm. of Hg. Hydrogen from UH_3 was again added to the system and the tellurium was kept for an additional three hours at 550° C. The tellurium sample was then held at 1×10^{-6} mm. of Hg, 550° C., for approximately 20 hours after which the quartz dewar-shaped sample tube (shown in Figure 1) was sealed by torch and removed from the vacuum system. During the latter heating period, approximately half of the tellurium sample condensed as large crystals in the cooler, upper section of the quartz container.

The zone-refined tellurium sample came into contact only with quartz which had been cleaned in c.p. grade, concentrated HF, several quartz distilled water rinses (*2*), and heated in a hydrogen atmosphere followed by heating (550° C.) under vacuum.

The triple point temperature of the above tellurium sample was determined from heating and cooling curves during which the sample was shaken in a vertical linear motion (Δh = 2 inches) at the rate of 1.33 cycles/second.

The sample was mounted inside a stationary copper tube which was heated by an electrical tube furnace in which the temperature gradient of the gas phase exterior to the copper tube was maintained within a few degrees centigrade.

A 0.010-inch diameter Pt-Pt 10% Rh thermocouple with an ice junction was used to measure the temperature of the tellurium sample. This thermocouple was calibrated (to 0.1 μv.) at the sulfur vapor (444.60° C.) and zinc (419.505° C.) points on the International Practical Temperature Scale of 1948 (which takes the triple point of water as 0.0100° C.), by the Electrical and Physical Standards Operation of the General Electric Company's Advanced Technology Laboratories.

The temperature measuring equipment consisted of a sensitive, high precision recording potentiometer with zero suppression. The full ten-inch chart span of the potentiometer corresponded to five microvolts (0.5° C. for the Pt-Pt 10% Rh thermocouple). The noise level of the measuring system was equivalent to $\pm 3 \times 10^{-3}$ °C. The recorder was calibrated against a L & N, K-3 potentiometer with calibrated standard cell (Weston unsaturated cell) and with a zener diode (Dynage Batt. Sub., 3 v. 24.44 ma.) working current supply. A description of the equipment is being prepared (*1*).

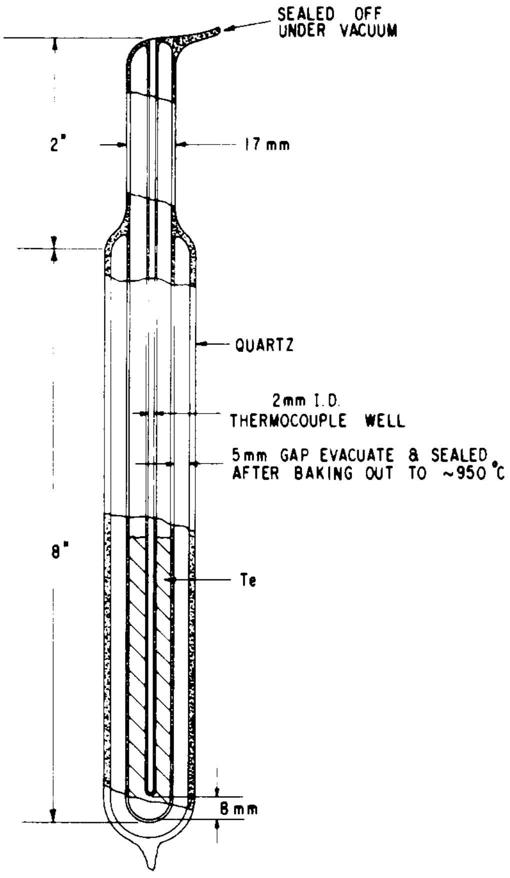

Figure 1. Zone-refined tellurium sample vacuum sealed in quartz for triple point measurement

RESULTS

Both melting and freezing point measurements were made; but since the tellurium sample supercooled 90° to 106° C., the freezing point measurements (which varied 0.06 to 0.37° C. from the melting point measurements) probably do not represent measurements at true thermodynamic

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[1] Present address; Argonne National Laboratory, Argonne, Ill.

Table I. Triple Point Temperature of Tellurium

Triple Point Temp., ° C.	Furnace Heating Rate ° C./min.	Time for Melting Point Plateau, Min.	Temp. Rise On Plateau ~95%–97% ° C.
449.8_{12}	0.16	90	0.08
449.7_{99}	0.35	60	0.20
449.9_{35}	1.0	30	0.24

Average 449.85; Most probable value = 449.80 ± 0.05° C.

equilibrium between the liquid and solid phases. Hence, only the melting point data are presented in Table I; the triple point temperatures given in Table I were determined from our data using the graphical method of Taylor and Rossini (*6*).

The plateaus for the melting point measurements (Table I) showed a gentle slope of 0.08°, 0.20°, and 0.24° C. over 95% of the plateau period for furnace heating rates of 0.16° C./min., 0.35° C./min., and 1.0° C./min., respectively. The time intervals for these plateau periods were 90, 60, and 30 minutes; the shorter time intervals are for the faster furnace heating rates.

The triple point temperature of tellurium, based on the average of all three values in Table I, is 449.85° C. The more probable value is believed to be 449.80 ±0.05° C. since for measurement # 3, the furnace heating rate may have been too fast for thermodynamic equilibrium between liquid and solid phases. The accuracy of our measurements is estimated to be ±0.05° C. The sample purity was estimated from the melting curves by the method of Mair, Glasgow, Rossini (5) to be mole fraction 0.99998, minimum. The presence of mole fraction 0.00002 of impurities would cause a freezing point error of 0.006° C.

Our values in Table I for the triple point temperature of tellurium are in good agreement with Machol and Westrum's value of 449.5 ± 0.3° C. and F.C. Kracek's value of 449.8 ± 0.2° C.

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Binary Melting Point Studies for Boron Bromide with Some Group IV Halides and for Germanium Bromide with Silicon Bromide

K. J. MILLER
Bell Telephone Laboratories, Inc., Murray Hill, N. J.

Melting point and solubility data are presented for the binary systems boron bromide–germanium bromide, boron bromide–silicon bromide, boron bromide–germanium chloride, boron bromide–silicon chloride and germanium bromide–silicon bromide. The Group IV halides with boron bromide had simple eutectics and there was no evidence of compound formation. The germanium bromide–silicon bromide system formed a continuous series of solid solutions. Comparisons of ideal and experimental solubilities have been made.

SOLID-LIQUID equilibria of the binary systems of $SnBr_4$ and of SnI_4 with BBr_3 have been studied by Adamsky and Wheeler (*1*) and the system $SiBr_4$ with BBr_3 by Nisel'son and Petrusevich (*8*). In this paper the solid-liquid equilibria of some additional Group IV tetrahalides with BBr_3 and of the $GeBr_4$-$SiBr_4$ system have been studied by determination of liquidus curves. In the BBr_3-$SiBr_4$ system the eutectic point has been more precisely determined.

EXPERIMENTAL

Materials. Electronic grade chemicals were used without further purification. The BBr_3, $GeCl_4$ and $GeBr_4$ were reported to be 99.99+%, 99.999+% and 99.99+% purity, respectively, and were obtained from Eagle-Picher Company. The $SiBr_4$ and $SiCl_4$ were reported to be 99+% and were obtained from Stauffer Chemical Co.

Procedure. Mixtures of 2 ml. total volume were prepared volumetrically from thermostated reagents, using a microsyringe calibrated in 0.02 ml. divisions. All additions were made in a dry box. Conversion from volume to weight units was made using the respective densities.

The method of determining melting points which was used was similar to that reported by Collett and Johnston (*2*). Mixtures were sealed in Pyrex tubes immediately after making them up and the melting temperature was taken when the last crystal disappeared. The sample tubes were vigorously stirred. Thermometers used were calibrated against a thermometer calibrated by the National Bureau of Standards. Melting temperatures were read with a reproducibility of ±0.1° C. A five gallon unsilvered dewar was used for the constant temperature bath and dry ice-methanol was used to obtain low temperatures. When not being measured samples were kept in the dark to minimize photochemical reactions.

Melting points were checked by time-temperature studies.