

Characterization of Silver Tellurite

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Silver tellurite (Ag_2TeO_3) was prepared from an aqueous solution and also by oxidation of Ag_2Te in air at 973 K. Pure, stoichiometric Ag_2TeO_3 was obtained by recrystallization from an ammoniacal solution. The phase crystallized from aqueous media (α) is orthorhombic, while the high-temperature preparation is monoclinic (β). The α -phase is metastable and transforms irreversibly to the β -phase above 573 K. DTA studies showed that Ag_2TeO_3 melts congruently at 857 K. The phase diagram in the composition region of Ag_2TeO_3 - TeO_2 was determined. It showed a eutectic at 710 K and 70 mole% TeO_2 of the Ag_2O - TeO_2 system. The isothermal section at 700 K of the ternary phase diagram of Ag - Te - O system was constructed from the results of this study. The free energy of formation of Ag_2TeO_3 is >-65 kcal/mole. This upper limit of stability indicates that it cannot form in a nuclear reactor. Freezing behavior of Ag_2O - TeO_2 melt showed a tendency to glass formation in the composition range of 61-72 mole% TeO_2 . Freezing of the melt also appears to produce "tellurite," the naturally occurring mineral form of TeO_2 . © 1989 Academic Press, Inc.

1. Introduction

One of the inputs to the calculations of release behavior of fission products to the environment under accidental conditions is the chemical state of tellurium in an operating nuclear reactor. The chemical state in turn is determined to a first approximation by the chemical equilibrium resulting from the interactions of all elements present in the fuel-fission product-clad complex. Hence, the possible interactions of tellurium with another fission product, namely silver, in the ubiquitous presence of oxygen in the conventional fuels was explored.

The present work is restricted to the characterization of silver tellurite (Ag_2TeO_3), one of the three ternary compounds in the Ag - Te - O system, as a part of our

broader goal of constructing the ternary phase diagram of the system. The preparation of Ag_2TeO_3 from aqueous solutions was described in literature and was characterized as amorphous (1). Consequently no X-ray diffraction pattern of this phase was reported until recently (2). Certain characteristics recorded by Lenher and Wolesensky (1) suggested six forms of Ag_2TeO_3 as shown schematically in Fig. 1.

The present investigation was directed at knowing the nature of the various forms of Ag_2TeO_3 , crystallographic as well as thermodynamic, in the context of the Ag - Te - O phase diagram.

2. Experimental

Ag_2TeO_3 was prepared from aqueous solutions of AgNO_3 and Na_2TeO_3 . Na_2TeO_3 solution was prepared according to the pro-

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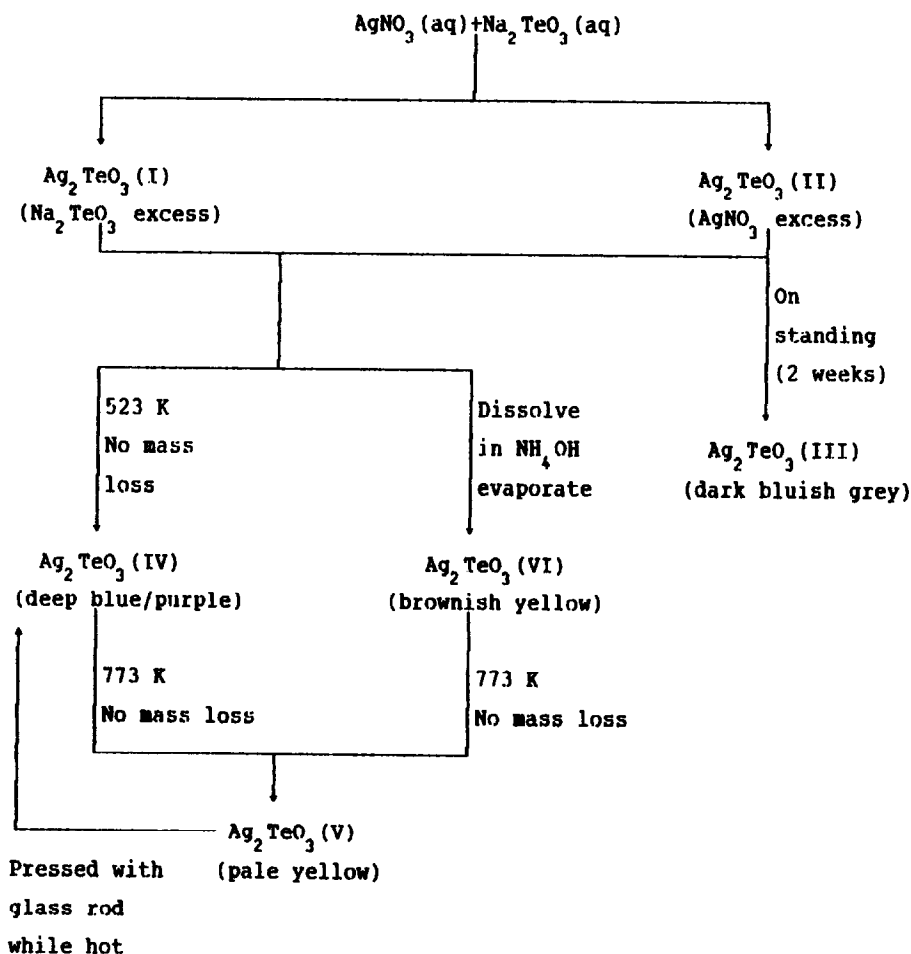


FIG. 1. Schematic description of various forms of Ag_2TeO_3 , as observed by Lenher and Wolesensky (1).

cedure given by Brauer (3). It was divided into two parts. One part was added to AgNO_3 solution. To the other part, AgNO_3 solution was added. In each case the amount added was 5% less than the stoichiometric amounts. This simulated the conditions of Lenher and Wolesensky (1). The flocculent precipitate was filtered, washed, and air dried. The precipitates from solutions with excess Na_2TeO_3 and excess AgNO_3 are labeled I and II, respectively, in Fig. 1. The precipitates were subjected to dissolution in ammonia solution,

batch heating in air, X-ray powder diffraction (XRD), thermogravimetry (TG), and differential thermal analysis (DTA).

XRD photographs were taken with a Debye-Scherrer powder camera and $\text{CuK}\alpha$ radiation.

TG and DTA runs were taken in flowing argon as well as in air. The particulars about the setup of the thermobalance and the DTA apparatus are given in Refs. (4) and (5), respectively.

Thermogravimetry was carried out in silver and/or platinum crucibles at a heating

rate of 4°/min to monitor mass losses of Ag₂TeO₃ samples in air and argon and to attempt the preparation of Ag₂TeO₃ by heating a mixture of Ag₂CO₃ + TeO₂ and a mixture of Ag + TeO₂ and Ag₂Te in air to confirm the existence of Ag₂TeO₃ in the equilibrium diagram of the Ag-Te-O system.

The DTA experiments were carried out in platinum sample holders and the heating rate was optimized at 10°/min. The temperature sensor was made of chromel/alumel thermocouple. The apparatus was calibrated with K₂Cr₂O₇ (melting, 671 K), Li₂SO₄ (phase transition, 848 K), and TeO₂ (melting, 1006 K).

DTA was used to locate the phase transition and melting temperatures of Ag₂TeO₃ and also to determine the phase diagram in the region Ag₂TeO₃-TeO₂. The composition change in the Ag₂TeO₃-TeO₂ region was carried out by gradual addition of small amounts of TeO₂ to Ag₂TeO₃ and melting them *in situ*. In the TeO₂-rich side Ag₂TeO₃ was added to TeO₂. At least three heating-cooling cycles were carried out in the DTA runs for each composition.

Preliminary studies indicated that TeO₂ did not react with platinum. This was concluded by heating a mixture of Pt powder and TeO₂ at 1000 K for 7 days and examining it by XRD. Further, repeated DTA experiments and subsequent cleaning showed negligible weight losses of the Pt crucibles. Preliminary experiments also indicated that Ag₂Te reacted with Pt and TeO₂ formed a low-temperature eutectic with Ag.

3. Origin of Chemicals

The starting materials were Ag and Te (99.99%, Chemistry Division, BARC), AgNO₃ and Na₂CO₃ (GR, 99.9%, Sarabhai Chemicals, India), TeO₂ (99.999%, Kochlight, UK), Li₂SO₄ (99.0%, Analar, BDH, India), and K₂Cr₂O₇ (99.9%, Analar, Glaxo Laboratories, India).

Ag₂Te was prepared by melting silver

foils and tellurium ingots together in stoichiometric ratio in an evacuated and sealed silica tube to a maximum temperature of 1273 K.

Ag₂CO₃ was prepared by mixing solutions of AgNO₃ and Na₂CO₃. The pale yellow precipitate of Ag₂CO₃ was filtered, washed, and air dried.

4. Results

4.1. The Aqueous Preparations

The dried samples were buff colored and neither changed color on storing up to 2 years, but all samples became dark after being powdered and exposed to air. Heating in air at 523 K failed to produce form IV of Fig. 1. Precipitates I and II readily dissolved in NH₄OH (25 w/w NH₃). The freshly precipitated sample gave dark brown crystals (form VI) while crystals obtained from the solution of dried precipitate were pale in color.

No weight change was detected for samples I, II, and VI by thermogravimetry up to 773 K either in air or in argon. XRD results of the samples I, II, and VI dried at room temperature gave identical patterns (phase α) which remained unaltered even on exposure to air for 2 years. This pattern changed when the samples were heated above 573 K and cooled to room temperature (phase β). The *d* values of these phases are given in Table I. The crystal systems and the lattice parameters were determined using the computer program TREOR-4 (6). Phase α is orthorhombic with $a = 0.777 \pm 0.001$ nm, $b = 0.760 \pm 0.002$ nm, and $c = 0.530 \pm 0.001$ nm; phase β is monoclinic with $a = 1.02 \pm 0.06$ nm, $b = 0.53 \pm 0.03$ nm, $c = 0.65 \pm 0.04$ nm, and $\beta = 89.84 \pm 0.09^\circ$.

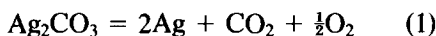
4.2. High-Temperature Preparations of Ag₂TeO₃

The attempt to prepare Ag₂TeO₃ by heating equimolar mixtures of Ag₂CO₃ and TeO₂

TABLE I
X-RAY DIFFRACTION PATTERNS OF
PHASES α AND β

Phase α			Phase β		
<i>d</i> (nm)	<i>I</i>	<i>h k l</i>	<i>d</i> (nm)	<i>I</i>	<i>h k l</i>
0.1438	m	5 2 0	0.1222	w	3 4 1
0.1478	m	2 2 3	0.1236	w	0 4 2
0.1541	w	0 4 2	0.1256	w	7 2 1
0.1587	vw	0 2 3	0.1402	vw	6 2 1
0.1623	w	2 4 1	0.1423	m	7 0 1
0.1711	m	3 3 1	0.1457	vw	7 0 0
0.1771	m	4 1 1	0.1473	m	3 0 4
0.1895	w	2 2 2	0.1499	m	2 3 2
0.1968	w	2 3 1	0.1530	vw	-3 3 1
0.2414	s	2 2 1	0.1568	vw	0 3 2
0.2596	m	3 0 0	0.1578	vw	-3 3 0
0.2694	w	2 2 0	0.1634	w	0 0 4
0.2856	vs	1 2 1	0.1661	w	4 0 3
			0.1729	m	5 0 2
			0.1756	s	1 3 0
			0.1905	m	5 1 0
			0.1943	m	5 0 1
			0.2442	s	-2 1 2
			0.2475	vs	0 2 1
			0.2717	v	1 1 2
			0.2805	s	0 1 2
			0.2849	vs	-3 1 0
			0.2876	s	3 1 0

in a thermobalance showed that the mass loss corresponded to the decomposition

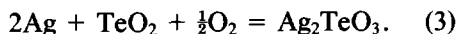


and was complete below 623 K.

The formation of Ag_2TeO_3 would have been indicated by smaller mass loss. On the other hand when finely powdered Ag_2Te or a mixture of $\text{Ag} + \text{TeO}_2$ in the molar ratio of 2:1 were heated in air in silica crucibles at 723 K for 14 days, the samples melted partially and showed weight gains, indicating incomplete formation of Ag_2TeO_3 , according to the expected reactions



and



This was confirmed from the XRD of the products as shown in Table II.

Thermogravimetric runs with these products and fresh reactants extended to higher temperatures showed further mass gain required for the completion of reactions (2) and (3).

The results of mass gain experiments are summarized in Table II. The TG in column 1 indicates that the reaction was carried out in a thermobalance. The initial composition in column 3 indicates whether the starting material was Ag_2Te , $\text{Ag} + \text{TeO}_2$, or a partially oxidized mixture. The final value of x was calculated on the assumption that the mass gain has been solely due to the absorption of oxygen.

It is seen from Table II that Ag_2TeO_3 is formed in a molten state when Ag_2Te is oxidized in air at 973 K. When heated to a higher temperature the mass gain is probably offset by a concurrent mass loss due to vaporization of free TeO_2 which is formed at a lower temperature according to the reaction



In the preoxidized sample, however, most of the TeO_2 having already reacted, the loss due to volatilization was not measurable.

TABLE II
RESULTS OF OXIDATION OF Ag_2Te AND
 $2\text{Ag} + \text{TeO}_2$ IN AIR

Sample	Temperature (K) and other conditions	x in Ag_2TeO_x		Phases identified by XRD
		Initial	Final	
$2\text{Ag} + \text{TeO}_2$	723	2.00	2.59	$\text{Ag} + \text{TeO}_2 + \beta$
Silica crucible	14 days, air			partly melted
Ag_2Te	723	0.00	2.32	$\text{Ag} + \text{TeO}_2 + \beta$
Silica crucible	14 days, air			partly melted
$\text{Ag}_2\text{TeO}_{2.32}$	1113	2.32	3.00	XRD could not be
TG, silver cup	2 hr, air			done because the
Ag_2Te	up to	0.00	2.51	molten mass could
TG, silver cup	1073, air			not be separated
Ag_2Te	973	0.00	3.00	from the container
TG, silver cup	3 hr, air			

4.3. Phase Transitions in Ag_2TeO_3

Results of DTA experiments on the samples I, II, and VI which showed some variations are summarized in Table III. Columns 2 and 3 of Table III show an irreversible exothermic peak at about 583 K and a reversible endothermic peak at 715 K. Columns 5 and 6 indicate that the peak at 583 K seen in sample (I) corresponds to $\alpha \rightarrow \beta$ transition. Therefore Ag_2TeO_3 precipitated from aqueous solutions is metastable, though it could be retained on heating at 543 K for 40 hr. All samples heated up to temperatures between 588 and 693 K and subsequently cooled slowly ($10^\circ/\text{min}$) to room temperature during the DTA experiments, when examined by XRD, corresponded to the β phase (column 6 of Table III). This shows that at room temperature the equilibrium phase of Ag_2TeO_3 is β . The peak at 715 K would normally indicate the existence of a high-temperature phase. To detect any such high-temperature phase, one sample of Ag_2TeO_3 was fast cooled in the DTA apparatus from 821 K. This showed only the β phase. Attempts were made to quench the high-temperature phase in ice. One sample in α -form and another in β -form were quenched in ice from 733 K. The former showed pale yellow and the latter showed deep brown color, but both

showed XRD patterns of the β phase (see column 7 of Table III). The absence of the peak in sample VI, which was crystallized by slow evaporation of NH_3 from an ammonical solution, points toward the possibility that the peaks in samples I and II might belong to the eutectic in the Ag_2TeO_3 - TeO_2 region due to a slight contamination of TeO_2 (see Section 4.5).

4.4. Melting of Ag_2TeO_3

DTA experiments showed another peak at 857 K which has been attributed to melting as suggested from the visual observation of the sample. Inspection of the DTA peak of Ag_2TeO_3 in air and argon shows sharpness in the case of VI and a long initial trail and an asymmetry for samples I and II. Also, irreproducibility was observed in the latter samples in the heating cycles when DTA was carried out in argon; for example, sometimes a small hump appeared preceding the main peak. The phases identified from the room-temperature XRD patterns of the frozen melts are given in column 8 of Table III.

XRD of the frozen melts from DTA runs of Ag_2TeO_3 (I) and (II) in argon showed one or two extra lines other than the β phase. These lines are also found in the frozen melt of $\text{Ag}_2\text{TeO}_3 + \text{TeO}_2$ in air containing

TABLE III
RESULTS OF DTA EXPERIMENTS WITH SAMPLES I, II, AND VI

Sample	Exothermic peak at 583 K	Endothermic peak at 715 K	Melting peak	Phases identified			
				Starting material	Cooled from above 583 K	Quenched from above 715 K	Frozen melts
I	Yes	Yes	Broad 847 K	α	β	β	β^a
II	No	Yes	Broad 847 K	α	β	β	β^b
VI	No	No	Sharp 857 K	α	β	β	β

^a One extra line.

^b Three extra lines.

86% TeO₂ as well as in the reaction product of a mixture of Ag + TeO₂ heated in an evacuated and sealed silica tube at 845 K for 7 days. These extra lines are ascribed to a phase which appears to be *tellurite*, the naturally occurring orthorhombic modification of TeO₂. Further, Ag₂TeO₃ (I), when heated to 763 K in air or quenched from 693 K shows the presence of α -TeO₂ in addition to β . These observations reinforce the question of whether the melting of Ag₂TeO₃ is congruent or incongruent and/or sample VI is stoichiometric while I and II are rich in TeO₂. One possible mode of incongruent melting is a peritectic, whereas, in the case of congruent melting of Ag₂TeO₃, one would expect a eutectic reaction in the region of Ag₂TeO₃-TeO₂. Hence, the phase diagram in this region was investigated with the help of DTA.

4.5. Phase Diagram of Ag₂TeO₃-TeO₂ System

DTA runs in the composition range Ag₂TeO₃-TeO₂ of the Ag₂O-TeO₂ system showed a eutectic at 710 K for all compositions. The variation of the peak heights with composition indicates that the eutectic composition is about 70 mole% TeO₂. The compositions of 51.9, 55.6, 59.2, 95.9, and 99.3% TeO₂ showed in addition to the invariant peak another broad peak which is attributed to the liquidus. For the compositions between 61.6 and 86.3 mole% TeO₂ the liquidus appears as a shoulder to the invariant peak. The temperatures corresponding to the maximum in the DTA peaks in the heating cycles are taken as the liquidus temperatures and are given in Table IV for various compositions.

The composition was calculated from the initial composition and the added weights of TeO₂ or Ag₂TeO₃ as the case may be. Ag₂TeO₃ was assumed to be stoichiometric and thus equivalent to 0.5 mole fraction of Ag₂O and TeO₂ each in the Ag₂O-TeO₂ phase diagram. In order to validate the cal-

TABLE IV
LIQUIDUS TEMPERATURES IN THE
Ag₂TeO₃-TeO₂ REGION OF THE
Ag₂O-TeO₂ PHASE DIAGRAM

Composition (mole% TeO ₂)	Liquidus temperature (°C)
50.0	584
51.9	567
55.6	559
59.2	533
61.6	513
62.2	506
64.3	507
68.7	—
70.7	—
72.7	492
75.5	519
76.4	546
86.3	641
95.9	718
99.3	718

culated compositions the DTA runs were extended beyond the melting point of TeO₂ in the second cycle. Lack of any peak at the melting point of TeO₂ ensured that no unreacted TeO₂ remained and thus a homogeneous melt was obtained. It was further ensured that the compositions did not change during the experiment by weighing the DTA crucible before and after the experiment. The uncertainty in the temperature of transition is estimated as $\pm 3^\circ$ for the eutectic and $\pm 10^\circ$ for the liquidus. The phase diagram is presented in Fig. 2.

On the TeO₂-rich side, no solid solubility of Ag₂O in TeO₂ is shown because of the fact that the invariant peak at 710 K was just discernible for the composition containing 0.7 mole% Ag₂O. This shows that solid solubility of Ag₂O in TeO₂ is less than 1 mole%. The Ag₂O-rich side of the phase diagram could not be studied because of the high dissociation pressure of Ag₂O (7). An attempt to prepare melt compositions richer in Ag₂O was made by heating a mix-

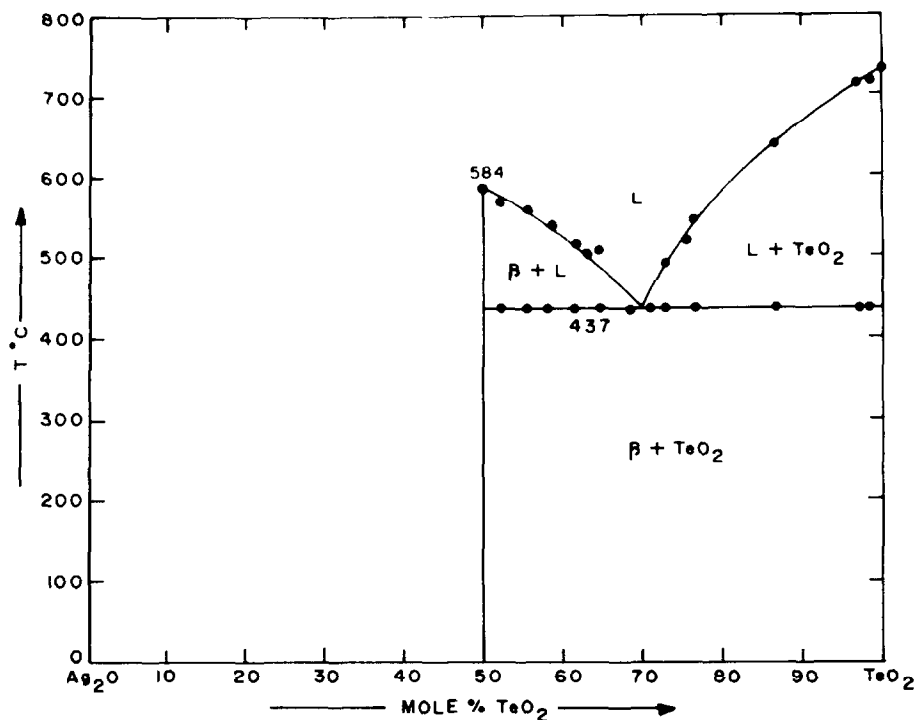


FIG. 2. Phase diagram of the system Ag₂O-TeO₂.

ture of Ag₂CO₃ and Ag₂TeO₃. It was observed that at 703 K, Ag₂CO₃ decomposed to Ag. Further heating to 873 K did not show any weight gain. The nonexistence of a peritectic, the nondeviation from the stoichiometry Ag₂TeO₃ until at least 973 K in air or argon, the existence of a eutectic in Ag₂TeO₃-TeO₂ range, and the comparison of the shapes of the DTA peaks suggest that the melting of Ag₂TeO₃ is congruent but the stoichiometric composition is obtained only for sample VI. Samples I and II contain excess TeO₂ either within the same homogeneous phase or as a contaminating phase. The latter supposition seems to be true. Sample I mixed with Ag and heated in air should make the 715 K peak disappear and it did, when small amounts of Ag flakes were added to Ag₂TeO₃ (I) and melted together in the DTA crucible in air. The melting peak also became gradually sharper and larger and the XRD of the frozen melt did

not show any extra line. Further, the peak appeared when sample VI mixed with a small amount of TeO₂ was subject to DTA.

Some interesting freezing behavior was observed in the DTA experiments of Ag₂TeO₃-TeO₂ system. Almost all samples tended to supercool but the extent of supercooling was unpredictable. The composition of 61.6, 64.3, and 72.7 mole% did not show any DTA peak while cooling down to the room temperature. In the subsequent heating cycle the sample showed an exothermic peak closely followed by an endothermic peak corresponding to the eutectic. The frozen eutectic could be maintained for at least 72 hr at room temperature. This was indicative of glass formation. In the cooling process the latent heat of fusion was stored which was released in the heating cycle.

The formation of the tellurite phase discussed in Section 4.4 finds additional support in the cooling behavior of Ag₂TeO₃-

TeO₂ melts which showed a small exothermic spike during freezing. This is remarkable because attempts to synthesize this phase had failed in the past (8, 9), although it has been demonstrated that synthesis of the tellurite phase from aqueous solution is possible (10, 11).

4.6. The Ternary System Ag-Te-O

The isothermal section at 700 K of the ternary phase diagram of the Ag-Te-O system could be constructed from the foregoing results in conjunction with the data for the binary system Ag-Te (12), Te-O (13), and Ag-O (14) and is presented in Fig. 3. In addition to Ag₂TeO₃, two more ternary compounds, Ag₃Te₂O₇ (15) and Ag₆TeO₆ (16, 17), have been reported in the literature. These compounds have not been represented in the present diagram because they are assumed to be unstable at 700 K (16).

The results of Table II clearly establish that Ag₂Te does not coexist with Ag₂TeO₃ whereas Ag, TeO₂, and Ag₂TeO₃ (β) coexist together. This is in contradiction with the coexistence of Ag₂Te, Ag₂TeO₃, and TeO₂ assumed by Ref. (18). Tie lines joining various phases in the Ag-Te binary follow automatically according to the rules of construction of the phase diagram.

4.7. Free Energy of Formation of Ag₂TeO₃

From the phase diagram of Fig. 3 and results of Table II it is seen that reaction (3) proceeds at P_{O₂} = 0.2 atm.

This implies

$${}^f\Delta G^0(\text{Ag}_2\text{TeO}_3) < [{}^f\Delta G^0(\text{TeO}_2) + \frac{1}{2}\Delta\bar{G}_{\text{O}_2}] \quad (5)$$

Further, one notes that the reaction

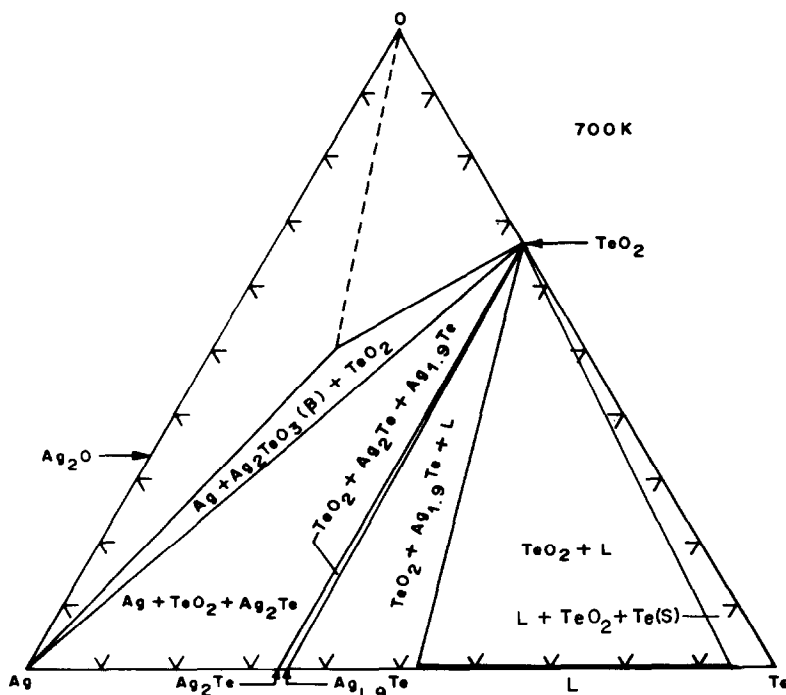
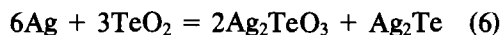


FIG. 3. Isothermal section of the phase diagram of the system Ag-Te-O at 700 K.

does not proceed in the right-hand direction or, in other words, Ag_2Te does not coexist with Ag_2TeO_3 . This implies

$${}^f\Delta G^0(\text{Ag}_2\text{TeO}_3) > \frac{1}{2}[3{}^f\Delta G^0(\text{TeO}_2) - {}^f\Delta G^0(\text{Ag}_2\text{Te})]. \quad (7)$$

Taking ${}^f\Delta G^0(\text{TeO}_2) = -47.5$ kcal/mole and ${}^f\Delta G^0(\text{Ag}_2\text{Te}) = -12.4$ kcal/mole at 700 K from Mills (19)

$$-65 < {}^f\Delta G^0(\text{Ag}_2\text{TeO}_3) < -49 \quad \text{in kcal/mole.} \quad (8)$$

5. Conclusion

Ag_2TeO_3 can be prepared from an aqueous solution and at high temperature. The phase crystallized from the aqueous media (α) is orthorhombic. The high-temperature preparation is monoclinic (β). The former (α) is metastable and transforms irreversibly to the latter (β). The stoichiometric compound is obtained by recrystallization from the ammoniacal solution by slow evaporation of NH_3 and melts congruently at 857 K. A high-temperature phase was suspected but could not be detected. At and perhaps below 700 K, Ag_2TeO_3 coexists with Ag and TeO_2 . Its free energy of formation at 700 K is > -65 kcal/mole, giving an upper limit of stability toward the decomposition to Ag and TeO_2 somewhere between that of IrO_2 and OsO_2 toward the respective metals. Hence, the possibility of its formation in a nuclear reactor can be ruled out. There is a eutectic between Ag_2TeO_3 and TeO_2 at 710 K and 70 mole% TeO_2 of the $\text{Ag}_2\text{O}-\text{TeO}_2$ system. The melt around 60–70 mole% TeO_2 could be stored at room temperature at least 72 hr, pointing toward glass formation and promising to be a good thermal storage medium (20). The melt composition of Ag_2TeO_3 is stable in air at least to 1073 K.

The ternary diagram above 700 K appears to become much more complicated because of low-temperature eutectics and

tendencies toward glass formation in the system.

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