

Vaporization of $\text{In}_2\text{Te}_3(\text{s})$

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The vaporization chemistry of $\text{In}_2\text{Te}_3(\text{s})$ was studied by the computer-automated simultaneous *Knudsen*-effusion and torsion-effusion method, by high-temperature mass spectrometry, and by ancillary methods. The first absolute measurements of the vapor pressure of In_2Te_3 are reported. $\text{In}_2\text{Te}_3(\text{s})$ vaporized incongruently in the temperature range 701–889 K and produced $\text{Te}_2(\text{g})$ and a solid-solution, ($X_{\text{In}} = 0.42$ and $X_{\text{Te}} = 0.58$). The standard enthalpy of the reaction at 298 K, ΔH° (298 K) by the third-law method was 136.0 ± 0.3 kJ/mol of vapor. The above solid solution vaporized incongruently and produced $\text{InTe}(\text{s})$ and a vapor which consisted of $\text{Te}_2(\text{g})$ and $\text{In}_2\text{Te}(\text{g})$. $\text{InTe}(\text{s})$ vaporized congruently in the range 701–887 K and produced $\text{Te}_2(\text{g})$ and $\text{In}_2\text{Te}(\text{g})$; the third-law ΔH_v° (298 K) was 201.5 ± 1.0 kJ/mol. These results were at variance with the literature on vaporization of In_2Te_3 where both congruent vaporization and incongruent vaporization to give $\text{InTe}(\text{s})$ are separately reported. Further, $\text{InTe}(\text{s})$ was reported to vaporize incongruently. These differences are discussed.

(*Keywords: Indium telluride, thermodynamics, vaporization chemistry; Torsion effusion; Knudsen effusion; High temperature mass spectrometry*)

Die Verdampfung von $\text{In}_2\text{Te}_3(\text{s})$

Die Chemie der Verdampfung von $\text{In}_2\text{Te}_3(\text{s})$ wurde mittels automatisierter gleichzeitiger Anwendung der *Knudsen*- und Torsions-Effusion, mittels Hochtemperaturmassenspektrometrie und entsprechenden Hilfsmethoden untersucht. Es wird über die ersten absoluten Messungen des Dampfdrucks von In_2Te_3 berichtet. $\text{In}_2\text{Te}_3(\text{s})$ verdampfte inkongruent im Temperaturbereich von 701–889 K, wobei $\text{Te}_2(\text{g})$ und eine feste Lösung mit der Zusammensetzung $X_{\text{In}} = 0.42$ und $X_{\text{Te}} = 0.58$ entstand. Die Standard-Enthalpie der Reaktion bei 298 K, ΔH° (298 K), war nach der Methode des dritten Gesetzes 136.0 ± 0.3 kJ/mol. Die erwähnte feste Lösung verdampfte inkongruent unter Bildung von $\text{InTe}(\text{s})$ und einem Dampf, der aus $\text{Te}_2(\text{g})$ und $\text{In}_2\text{Te}(\text{g})$ bestand. $\text{InTe}(\text{s})$ verdampfte im Bereich von 701–887 K kongruent unter Bildung von $\text{Te}_2(\text{g})$ und $\text{In}_2\text{Te}(\text{g})$; ΔH_v° (298 K) nach dem dritten Gesetz war 201.5 ± 1.0 kJ/mol. Diese Ergebnisse sind im Gegensatz zu Literaturangaben zur Verdampfung von In_2Te_3 , wobei sowohl kongruente als auch

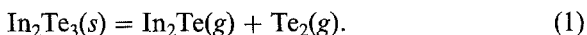
* Dedicated to Professor Dr. Kurt L. Komarek on the occasion of his 60th birthday.

inkongruente Verdampfung zu $\text{InTe}(s)$ berichtet wurden. Außerdem wurde $\text{InTe}(s)$ als inkongruent verdampfend beschrieben. Diese Abweichungen werden diskutiert.

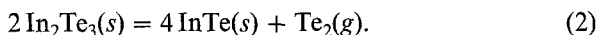
Introduction

Indium telluride, In_2Te_3 , has applications in nuclear radiation detector [1] and heterojunction devices [2]. The structure, phase equilibria, and electrical and optical properties of indium telluride have been extensively investigated. Indium telluride exists in two structures in the solid state. The high-temperature form, $\beta\text{-In}_2\text{Te}_3$, exists above $610 \pm 10^\circ\text{C}$, and is cubic with lattice constant $a = 6.613 \text{ \AA}$ [5, 6]. Its structure belongs to the space group $F\bar{4}3m$. The low-temperature phase, $\alpha\text{-In}_2\text{Te}_3$, exists below $610 \pm 10^\circ\text{C}$. The structure of $\alpha\text{-In}_2\text{Te}_3$ is controversial [7, 8]. Thermodynamic properties of $\text{In}_2\text{Te}_3(s)$ have been tabulated by *Mills* [9]. The temperature-composition phase diagram of the In—Te system has been reported [10]. There are six compounds in this system [11]; In_2Te_5 , In_3Te_5 , In_3Te_4 , and In_9Te_7 melt incongruently, and InTe and In_2Te_3 melt congruently. *Hogg* and *Sutherland* [12] have reported the composition of the phase In_9Te_7 to be In_4Te_3 . InTe is tetragonal with lattice constants $a = 8.454(2) \text{ \AA}$ and $c = 7.152(6) \text{ \AA}$. Its structure belongs to the space group $I4/mcm$ [13]. In_3Te_4 is tetragonal with lattice constants $a = 6.173 \text{ \AA}$ and $c = 12.438 \text{ \AA}$ [14].

Reports on the vaporization chemistry of $\text{In}_2\text{Te}_3(s)$ are contradictory. *Colin* and *Drowart* [15] studied the vapor-phase equilibria over $\text{In}_2\text{Te}_3(s)$ by mass spectrometry. They observed that, during the initial stages of evaporation, large amounts of Te_2 molecules evaporated and that no other atom or molecule was present. *Berger* and coworkers [16] studied the vaporization of $\text{In}_2\text{Te}_3(s)$ by mass spectrometry in the temperature range 920–1 020 K. They reported the vaporization of $\text{In}_2\text{Te}_3(s)$ to be congruent by:

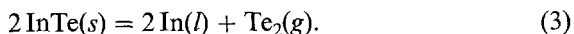


Belousov and coworkers [17] studied the vaporization of $\text{In}_2\text{Te}_3(s)$ by mass spectrometry in the temperature range 725–895 K and reported it to be incongruent by:



They reported the standard enthalpy of reaction (2) at 298 K to be $125.10 \pm 8.37 \text{ kJ/mol}$.

Santandrea and *Wiedemeier* [18] studied the vaporization of $\text{InTe}(s)$ by mass spectrometry and by the *Knudsen*-effusion method in the range 900–950 K and found it to vaporize incongruently by:



They reported the standard enthalpy of reaction (3) at 298 K to be 90.6 ± 3 kJ/mol. *Srinivasa* and *Edwards* [19] analyzed the vapor phase over $\text{InTe}(l)$ at 1106 ± 2 K. They reported the vapor phase to be comprised of $\text{In}_2\text{Te}(g)$, $\text{Te}_2(g)$ and $\text{In}_2\text{Te}_2(g)$. They analyzed the fragmentation processes and reported that In_2Te^+ fragmented to give In^+ , In_2^+ , InTe^+ and Te^+ . Their observations showed that $\text{InTe}(l)$ vaporized incongruently at 1106 ± 2 K.

Experimental

Sample Preparation

Indium wire, 99.99 percent pure, from Indium Corporation of America, and tellurium ingots, more than 99.999 percent pure, from Alfa Products, were used as starting materials. Solid samples ranging in composition from InTe to In_2Te_3 in increments of one atom percent were prepared by heating stoichiometric quantities of high-purity elements in evacuated, sealed, Vycor tubes. The samples were heated to ca. 640°C , cooled to ca. 590°C , annealed at ca. 590°C for 80–90 hours, and quenched to room temperature in water. A *Debye-Scherrer*, X-ray, powder diffractogram of each sample was made.

Preliminary Vaporization Experiments

A sample of $\text{In}_2\text{Te}_3(s)$ of known mass in a graphite *Knudsen*-effusion cell was heated under vacuum fourteen times successively at ca. 560°C . Subsequent to each heating, the crucible was cooled to room temperature and weighed. The residue was powdered, homogenized, and a representative sample was taken for analysis by powder X-ray diffraction. The remaining residue was used in the next heating.

Vapor-Pressure Measurements

Vapor pressures were measured with samples of initial composition In_2Te_3 in five sets of experiments. Four sets were done by the simultaneous *Knudsen*-effusion and torsion-effusion method [20], and will be referred to as KT1–KT4. In KT1 and KT2, vapor pressures were measured at a variety of randomly chosen temperatures in the ranges 842–896 K and 773–882 K, respectively. KT3 and KT4 were conducted isothermally; the vapor pressure of the sample was monitored as the sample effused at constant temperature. The fifth set was a high-temperature mass-spectrometric experiment labelled MS1 in which temperatures were chosen randomly in the range 701–909 K.

Simultaneous Knudsen-Effusion and Dynamic-Torsion-Effusion Studies

The apparatus [21–23], data treatment [21–23], and design of the cells [24] are described elsewhere. Three different cells, labelled C1, C2, and C3 were used. The geometric properties of the cells are given in Table 1. Column 1 identifies the cell, column 2 gives the property, and columns 3 and 4 give its value for orifices 1 and 2, respectively. All the cells had diverging right-circular-conical orifices. Recoil-force correction factors and transmission probabilities were calculated by the method of *Freeman* and *Edwards* [25]. The samples were distributed between two chambers of the cell in the same ratio as that of the two effective orifice areas [26]. Temperatures were measured with a Pt, Pt-10%-Rh thermocouple in a dummy cell identical in design and materials to the torsion-effusion cell. The two

Table 1. *Geometric properties of torsion effusion cells 1, 2, and 3*

Cell #	Parameter	Orifice 1	Orifice 2
C1	inside radius/cm	0.04915 ± 0.0002	0.04815 ± 0.0002
	length/cm	0.2095 ± 0.0008	0.2090 ± 0.0008
	moment arm/cm	0.797 ± 0.001	0.798 ± 0.001
	semiapex angle/deg	25.97 ± 0.01	27.81 ± 0.01
	inside area $\times 10^3/\text{cm}^2$	7.57 ± 0.09	7.30 ± 0.09
	transmission probability	0.8917 ± 0.0005	0.8758 ± 0.0005
	recoil-force correction factor	1.0713 ± 0.0005	1.0516 ± 0.0005
C2	inside radius/cm	0.0436 ± 0.0005	0.0413 ± 0.0005
	length/cm	0.2100 ± 0.0005	0.2100 ± 0.0005
	moment arm/cm	0.792 ± 0.001	0.808 ± 0.001
	semiapex angle/deg	28.92 ± 0.01	29.35 ± 0.01
	inside area $\times 10^3/\text{cm}^2$	5.97 ± 0.14	5.36 ± 0.13
	transmission probability	0.9000 ± 0.0005	0.9029 ± 0.0005
	recoil-force correction factor	1.0868 ± 0.0005	1.0927 ± 0.0005
C3	inside radius/cm	0.0472 ± 0.0002	0.0482 ± 0.0002
	length/cm	0.205 ± 0.001	0.208 ± 0.001
	moment arm/cm	0.803 ± 0.001	0.792 ± 0.001
	semiapex angle/deg	26.47 ± 0.01	28.51 ± 0.01
	inside area $\times 10^3/\text{cm}^2$	7.00 ± 0.06	7.30 ± 0.06
	transmission probability	0.8804 ± 0.0005	0.8976 ± 0.0005
	recoil-force correction factor	1.0575 ± 0.0005	1.0793 ± 0.0005

cells were placed symmetrically, the torsion cell above and the dummy cell below the center of the furnace and separated by ca. 2 mm.

Two Pt-10%-Ni torsion fibers, labelled A and B, were used. The torsion constants of the fibers were calibrated by the usual method of observing the period of a calibration pendulum suspended from the fiber [27].

In experiments KT1 through KT4, procedures during the vapor pressure measurements were those previously described [21-24, 26, 28].

Experiment KT1 was carried out with cell C1 and fiber A. Initially the sample was 614.73 ± 0.05 mg of In_2Te_3 , and during the course of the experiment, 123.0 ± 0.2 mg of the sample was vaporized. Experiment KT2 was carried out with cell C2 and fiber B. 641.70 ± 0.05 mg of In_2Te_3 was taken and 125.3 ± 0.2 mg of the sample was vaporized. Experiments KT3 and KT4 were carried out with cell C3 and fiber A. In experiment KT3, 62.53 ± 0.05 mg of In_2Te_3 was taken and 12.0 ± 0.1 mg of it was vaporized at 876 ± 1 K; vapor pressures were measured by torsion-effusion method only. In experiment KT4, 140.36 ± 0.05 mg of In_2Te_3 was taken and 28.5 ± 0.1 mg of it was vaporized at 879 ± 1 K.

Data Collection and Treatment

Each datum was obtained from four independent measurements; the temperature of the cell, rate of loss of mass from the effusion cell, total mass lost from the effusion cell, and the torque, Q_e , produced by the vapor effusing from the torsion-effusion cell. The methods by which the measurements were made have been described [21].

The torsion-pressures [20], P_t , were obtained from the torque with the equation:

$$P_t = 2 Q_d / (d_1 A_1 F_1 + d_2 A_2 F_2) \quad (4)$$

in which the numerical subscripts identify the orifice, d is the moment arm of the orifice, A its area, and F its recoil force correction factor [25].

The *Knudsen* pressures, P_k , were obtained from the rate of mass-loss, dg/dt , and the temperature, T , with the *Knudsen* equation:

$$P_k = (dg/dt) (2\pi RT/M^*)^{1/2} / (A_1 W_1 + A_2 W_2) \quad (5)$$

in which M^* is the assigned molecular weight of the effusing vapor and W is the transmission probability of the orifice [25]. The assigned molecular weight can be any positive real number, but in order to produce accurate *Knudsen* pressure, M^* was set equal to the molecular weight of $\text{Te}_2(g)$, 255.2.

The apparent molecular weight of the vapor was calculated with the equation:

$$M = M^* (P_k/P_t)^2. \quad (6)$$

Mass Spectrometry

A Nuclide 12-90 HT *Knudsen*-cell mass spectrometer was used. A sample of 261.75 ± 0.05 mg of In_2Te_3 was taken in a graphite *Knudsen* cell. The *Knudsen* cell was heated by radiation from electrically heated tungsten filaments and the cell and the filaments were surrounded by tantalum shields. The temperature of the *Knudsen* cell was measured with a Pt, Pt-10%-Rh thermocouple located in a well at the bottom of the *Knudsen* cell. A movable shutter was used to define the molecular beam from the *Knudsen* cell into the ionization chamber of the mass spectrometer and to discriminate against background gases. The gaseous species in the molecular beam were ionized by electrons of ca. 75 eV energy. Ion currents were amplified by an electron multiplier and measured with a vibrating-capacitor electrometer.

The sample was vaporized at temperatures selected randomly in the range 701–909 K. Ion intensities were measured as functions of temperature and time at m/e values of 128 and 130 for Te^+ , 115 for In^+ , 230 for In_2^+ , 243 and 245 for InTe^+ , 256 and 258 for Te_2^+ , and 358 and 360 for In_2Te^+ . The electron-multiplier gain at m/e of 202 (Hg^+) was measured at room temperature before and after the vaporization studies. In separate experiments, electron-multiplier gains at m/e of 258 (Te_2^+), 128 (Te^+), 115 (In^+), 230 (In_2^+), and 360 (In_2Te^+) were measured.

Ion intensities were converted to partial pressures with the equation:

$$P_i = k T \sum_j (I_j^+ / \sigma_{ij} \gamma_j f_j) \quad (7)$$

in which I_j^+ is the intensity of the j th fragment of i th precursor, σ_{ij} is the cross-section of the i th precursor ionizing to produce j th fragment, f_j is the isotopic fraction, γ_j is the electron-multiplier gain of the observed ion, T is the temperature, and k is the instrument transmission factor. Comparisons with vapor pressures measured in experiments KT1 and KT2 enabled the calculation of k . The first 8 data from experiment MS1, the vapor pressures measured during initial stages of vaporization of In_2Te_3 in experiments KT1 and KT2, and the assumption that the vapor was only $\text{Te}_2(g)$ were used to calculate k .

The atomic ionization cross-sections were from *Mann* [28]. Ionization cross-sections of In_2 , Te_2 , InTe , and In_2Te were taken to be 0.8 times the sum of those of the constituent atoms. In the absence of dependable values of ionization cross-

sections for the various fragmentation processes, the ionization cross-sections of the precursor was assumed to be independent of the subsequent fragmentation events.

Partial pressures were calculated on the basis of the following assumptions about the sources of ions. Te_2^+ and In_2Te^+ were assumed to be parents. In accordance with the observation in Group 1, one-tenth of Te_2^+ was assumed to fragment to Te^+ throughout the experiment. The rest of Te^+ and all of In^+ , In_2^+ , and InTe^+ were assumed to be fragments of In_2Te^+ .

Whenever the vapor pressures were univariant with temperature, the data were fitted by least-squares analysis, to the equation:

$$\log(X) = -AK(1/T - C) + B \quad (8)$$

where X is the vapor pressure in pascals or I^+T in ampere Kelvins, T is the temperature in Kelvins, A and B are parameters from the least-squares fit and C is the average reciprocal temperature. This choice of C made negligible the correlation between A and B from the least-squares analysis.

Thermodynamics of Vaporization

The value of ΔH° (298 K) of each vaporization reaction was determined by the second- and the third-law method [29]. *Gibbs*-energy functions for the elements and compounds, except $\text{In}_{0.71}\text{Te}(s)$, were taken from the literature [10, 27, 30], and for $\text{In}_{0.71}\text{Te}(s)$ were obtained by linear combination of those of $\text{In}_2\text{Te}_3(s)$ and $\text{InTe}(s)$. *Gibbs*-energy functions used in the present work are given in Table 2. Column 1 gives the temperature and columns 2-6 give the *Gibbs*-energy functions of $\text{In}_2\text{Te}_3(s)$, $\text{InTe}(s)$, $\text{In}_{0.71}\text{Te}(s)$, $\text{Te}_2(g)$, and $\text{In}_2\text{Te}(g)$, respectively. Those at intermediate temperatures were obtained by linear interpolation.

Table 2. *Gibbs*-energy functions

Temperature/K	$-\Phi^\circ(T)/(\text{J mol}^{-1} \text{K}^{-1})$				
	$\text{In}_2\text{Te}_3(s)$	$\text{InTe}(s)$	$\text{In}_{0.71}\text{Te}(s)$	$\text{Te}_2(g)$	$\text{In}_2\text{Te}(g)$
700	269.0	119.7	94.0	269.3	354.2
800	279.5	123.8	97.5	272.3	358.6
900	289.5	127.9	101.0	275.3	363.0
965	295.7	130.5	103.1	277.1	367.4

Results

X-Ray Analysis

X-ray analysis of samples prepared in sealed tubes showed a compound at 55 atom percent tellurium, $\text{In}_9\text{Te}_{11}$. Samples with compositions $0.55 < X_{\text{Te}} < 0.60$ were two-phase mixtures of In_2Te_3 and $\text{In}_9\text{Te}_{11}$. Samples with compositions $0.50 < X_{\text{Te}} < 0.55$ were two-phase mixtures of $\text{In}_9\text{Te}_{11}$ and InTe . Table 3 gives d -spacings of $\text{In}_9\text{Te}_{11}$, column 1 gives its d -

Table 3. *d*-Spacing of $\text{In}_3\text{Te}_4(s)$ and $\text{In}_9\text{Te}_{11}(s)$

$\text{In}_3\text{Te}_4(s)$		$\text{In}_9\text{Te}_{11}(s)$	
<i>d</i> -spacing/Å	Relative intensity	<i>d</i> -spacing/Å	Relative intensity
3.548	75	3.583	30
3.473	75	3.486	95
		3.311	85
		3.164	60
3.110	100		
3.018	40		
		2.957	95
		2.876	15
		2.812	15
		2.698	85
2.656	20		
		2.450	40
		2.343	70
2.305	10		
2.176	40		
		2.143	50
2.060	40	2.053	100
1.966	40		
		1.949	95
		1.874	70
1.858	40		
		1.811	15
1.414	20		
1.353	30		
		1.332	35
		1.292	35
1.259	30		
		1.247	35

spacings, column 2 gives its intensities, and columns 3 and 4 give the *d*-spacings and the intensities of $\text{In}_3\text{Te}_4(s)$, respectively. The *d*-spacings of $\text{In}_9\text{Te}_{11}$ did not match with those of $\text{In}_3\text{Te}_4(s)$ [14].

X-ray analysis of the residues from the preliminary vaporization experiments showed that the condensed phase ceased to be $\text{In}_2\text{Te}_3(s)$ and that a solid solution existed over the range $0.51 < X_{\text{Te}} < 0.58$.

Vapor Pressure Measurements

Values of vapor pressures measured by the simultaneous *Knudsen*-effusion and dynamic torsion-effusion method in experiments KT1 and

KT2 are listed elsewhere [31]. Figs. 1 and 2 are plots of $\log(P/Pa)$ vs. K/T from torsion and *Knudsen* measurements, respectively, in experiment KT1; Figs. 3 and 4 are the corresponding plots from KT2. In these figures, data acquired during the loss of the first 3.57 ± 0.06 and 4.2 ± 0.1 percent by mass of the sample, in experiments KT1 and KT2, respectively, are

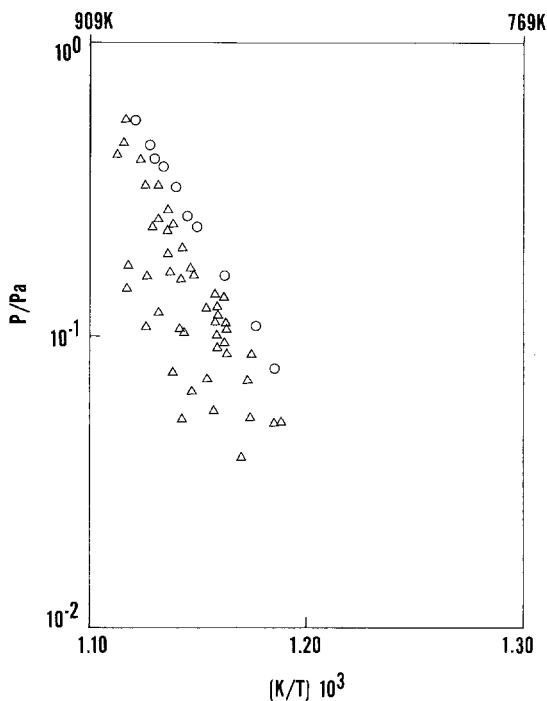


Fig. 1. Vapor pressures as functions of temperature and trends with mass lost by the sample. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe . Data are from torsion measurements in KT1

represented by open circles; they will be called Group 1. Data acquired after Group 1 will be called Group 2; they are represented by open triangles in Figs. 1 through 4. In Group 1, vapor pressures were univariant with temperature, and in Group 2, vapor pressures continuously decreased as sample effused out of the cell.

The experiments were stopped when the samples in experiments KT1 and KT2 had lost 20.0 ± 0.1 percent and 19.5 ± 0.1 percent by mass,

respectively; the residues in these experiments were found to be $\text{InTe}(s)$ by X-ray diffraction. The percentage of $\text{In}_2\text{Te}_3(s)$ by mass to be lost to form $\text{InTe}(s)$ by vaporizing only $\text{Te}_2(g)$ was calculated to be 20.8.

When the vapor pressure data in Group 1 of experiments KT1 and KT2 were fitted into equation (8), parameters given in the first 4 lines of

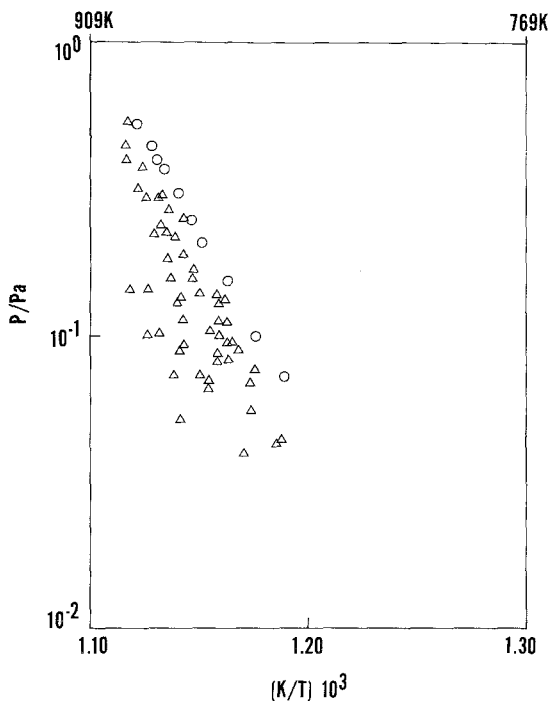


Fig. 2. Vapor pressures as functions of temperature and trends with mass lost by the sample. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe . Data are from *Knudsen* measurements in KT1

Table 4 were obtained. Column 1 gives the experiment, column 2 gives the method of vapor-pressure measurement, column 3 gives the data group, column 4 gives X , the variable which could be pressure or $I^+ T$, columns 5–7 give the values of A , B , and C , respectively, and column 8 gives the apparent molecular weight of the effusing vapor.

In the isothermal experiments, KT3 and KT4, vapor pressure remained constant till 6.5 ± 2.0 percent of the sample by mass was lost.

Subsequently, the vapor pressure decreased continuously as sample effused. The experiments were stopped when the vapor pressure was too small to be measured accurately. The vapor-pressure data from experiments KT3 and KT4 are tabulated elsewhere [31]. Fig. 5 shows the variation of vapor pressures by torsion measurements with mass remaining from KT3 and KT4.

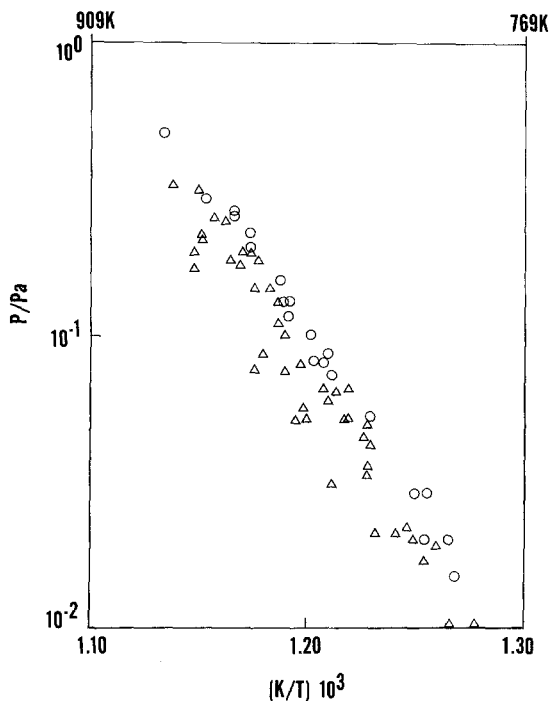


Fig. 3. Vapor pressures as functions of temperature and trends with mass lost by the sample. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe . Data are from torsion measurements in KT2

Mass Spectrometry

In the mass-spectrometric experiment, In^+ , Te^+ , In_2^+ , InTe^+ , and In_2Te^+ were observed. Ion intensities as functions of time and temperature fell in three groups, labelled 1, 2, and 3, sequentially. Figs. 6 and 7 are plots of the logarithm of $I^+ T$ vs. K/T for Te_2^+ and In^+ , respectively. In these plots data from Group 1 are represented by circles, those from Group 2 by triangles, and those from Group 3 by diamonds.

In Group 1, Te_2^+ and Te^+ intensities were univariant with temperature. The data, when fitted into equation (8), gave parameters which are shown in line 5 of Table 4. In^+ and InTe^+ were observed only twice and at temperatures above 820 K. In_2^+ and In_2Te^+ were not observed. The intensity of Te_2^+ was ca. 10 times that of Te^+ and ca. 200 times that of In^+ and InTe^+ .

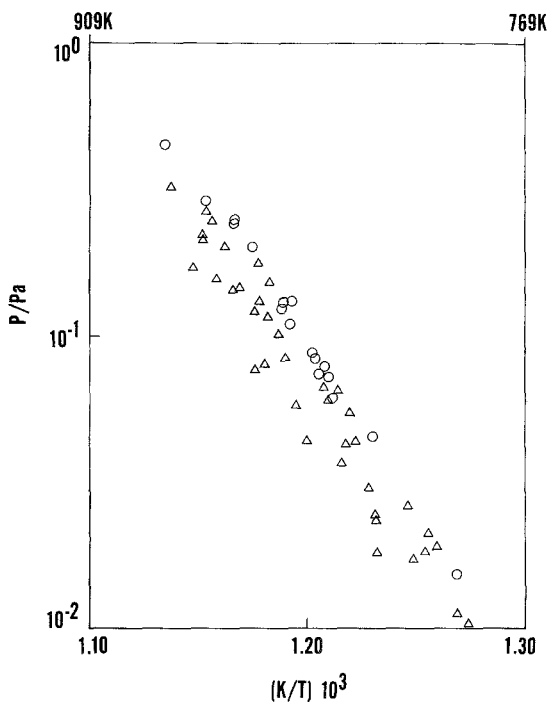


Fig. 4. Vapor pressures as functions of temperature and trends with mass lost by the sample. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe . Data are from *Knudsen* measurements in KT2.

In Group 2, intensities of all ions decreased continuously as sample effused; the intensity of Te_2^+ decreased more than that of Te^+ , In^+ , or InTe^+ .

In Group 3, intensities of In^+ , InTe^+ , Te^+ , and Te_2^+ were univariant with temperature and in the approximate respective ratio 1:1:4:10. When ion intensities and temperatures were fitted to equation (8), the parameters shown in lines 6–10 of Table 4 were obtained. In_2^+ and In_2Te^+ were each observed twice at temperatures above 850 K.

Table 4. Parameters A , B , and C in equation (8) and apparent molecular weights

Experiment	Method	Group #	X	$(A \pm \sigma_A) 10^{-4}/K$	$B \pm \sigma_B$	$C \times 10^3/K$	M
KT1	torsion	1	P_{total}/Pa	1.358 ± 0.032	-0.5726 ± 0.0064	1.146	241 ± 3
	Knudsen	1	P_{total}/Pa	1.389 ± 0.027	-0.5885 ± 0.0053	1.146	
	torsion	1	P_{total}/Pa	1.146 ± 0.061	-0.883 ± 0.014	1.188	234 ± 8
KT2	Knudsen	1	P_{total}/Pa	1.138 ± 0.041	-0.986 ± 0.013	1.199	
	Mass-	1	$IT^{++}(Te^+)/AK$	1.158 ± 0.049	-6.172 ± 0.032	1.299	
MS1	spectrometry	1	$IT^{++}(Te_s^+)/AK$	1.088 ± 0.037	-5.393 ± 0.025	1.299	
		3	$IT^{++}(Te^+)/AK$	0.98 ± 0.10	-7.064 ± 0.062	1.241	
		3	$IT^{++}(Te_s^+)/AK$	0.906 ± 0.026	-6.822 ± 0.019	1.262	
		3	$IT^{++}(In^+)/AK$	1.239 ± 0.036	-8.024 ± 0.025	1.243	
		3	$IT^{++}(InTe^+)/AK$	1.25 ± 0.15	-8.032 ± 0.074	1.215	
		1	P_{Te}/Pa	1.098 ± 0.034	-2.315 ± 0.023	1.299	
		3	P_{Te}/Pa	0.880 ± 0.041	-3.587 ± 0.025	1.241	
		3	P_{In_2Te}/Pa	1.131 ± 0.114	-4.257 ± 0.069	1.241	

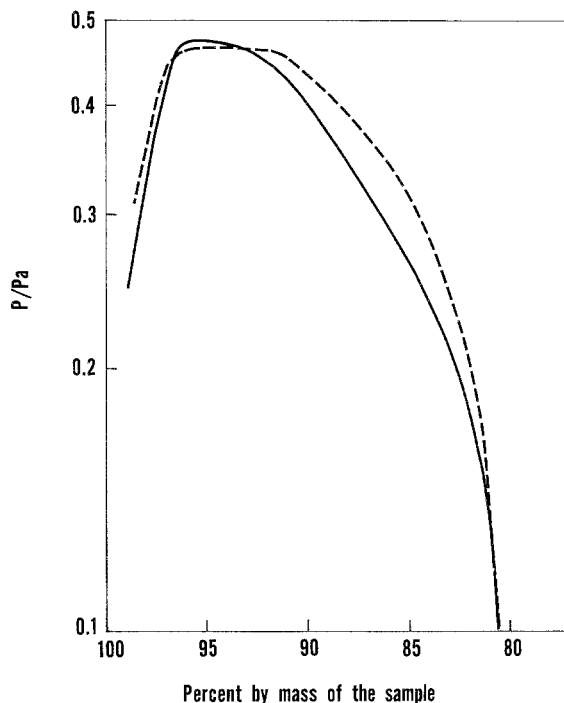


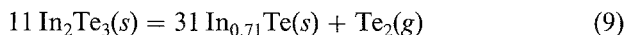
Fig. 5. Variation of torsion pressures with percent mass lost by the sample at temperatures in KT3 and KT4

When the experiment was stopped, the sample was found to have lost 90 percent of its mass. The residue was identified as $\text{InTe}(\text{s})$ by X-ray powder diffraction analysis.

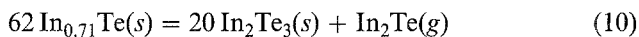
The transmission factor, k , of the mass spectrometer was found to be $(1.94 \pm 0.37) 10^{-11} \text{ Pa m}^2 \text{ A}^{-1} \text{ K}^{-1}$. The partial pressures of $\text{Te}_2(\text{g})$ and $\text{In}_2\text{Te}(\text{g})$ in Group 1 and Group 3 when fitted into equation (8) gave parameters given in the last three lines of Table 4. The vapor pressures are tabulated elsewhere [31].

Vaporization Reactions

During acquisition of data in Group 1 in experiments KT1, KT2, and MS1, vaporization of In_2Te_3 occurred by:



and



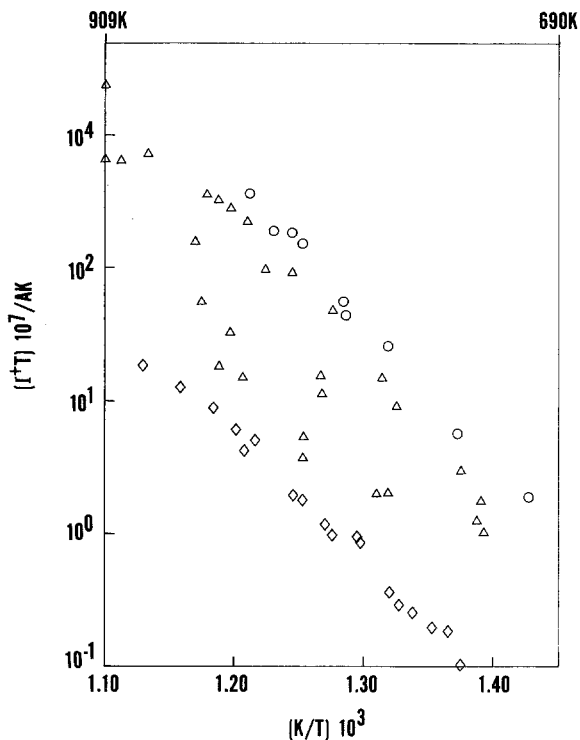


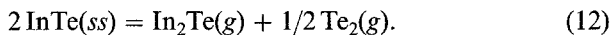
Fig. 6. Variation of $I^+ T$ with temperature and trends with time for Te_2^+ in MS1. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe

where $\text{In}_{0.71}\text{Te}(s)$ refers to the composition at the boundary of a solid solution which is in equilibrium with $\text{In}_2\text{Te}_3(s)$. The composition of this solid was assumed to be independent of temperature; the uncertainty in the subscript 0.71, and consequently, the coefficients 11, 31, 62, and 20 were $\pm 2\%$.

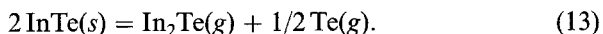
During acquisition of data in Group 2 of experiments KT1, KT2, and MS1, vaporization occurred by:



and



During acquisition of data in Group 3 of experiment MS1, vaporization occurred by:



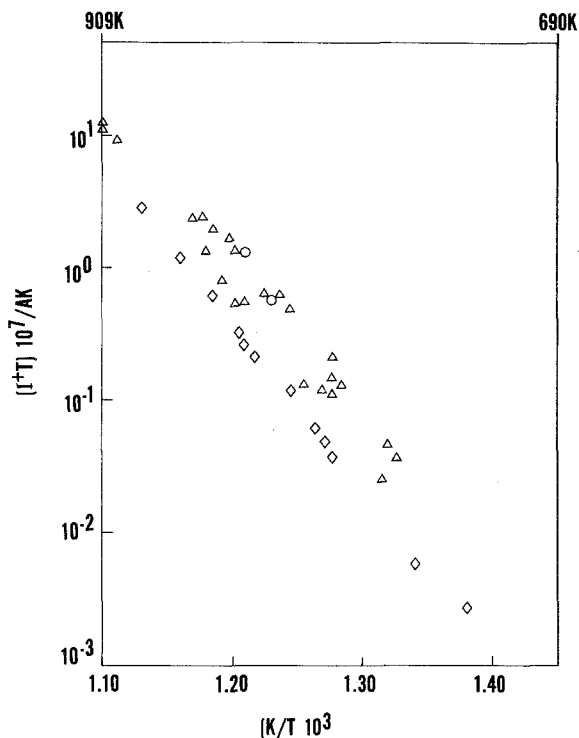


Fig. 7. Variation of $I^+ T$ with temperature and trends with time for In^+ in MS1. Initial composition of the sample: In_2Te_3 ; final composition of the sample: InTe

Thermodynamics of Vaporization

Equilibrium constants for reactions (9) and (13) were obtained with:

$$K_p = P_{\text{Te}_2}^{1/2} = P_T^{1/2} \quad (14)$$

$$K_p = P_{\text{Te}_2}^{1/2} \cdot P_{\text{In}_2\text{Te}} \quad (15)$$

Standard enthalpies of reactions (9) and (13) at 298 K obtained from equilibrium constants are given in Table 5. In Table 5, column 1 gives the experiment, column 2 gives the method of vapor-pressure measurement, column 3 gives the reaction, and columns 4 and 5 give the ΔH° (298 K) of the reaction calculated by the second-law and third-law methods, respectively.

The means of ΔH° (298 K) of vaporization reactions (9) and (13) were 136.0 ± 0.2 kJ/mol of In_2Te_3 and 201.5 ± 1.0 kJ/mol of InTe , respectively.

Table 5. *Standard molar enthalpies of vaporization reactions (9) and (13)*

Experiment	Method	Reaction	ΔH° (298 K)/kJ mol ⁻¹	
			Second-law	Third-law
KT1	<i>Knudsen</i>	9	136.7 ± 2.6	137.6 ± 0.1
	Torsion	9	133.8 ± 3.1	137.7 ± 0.1
KT2	<i>Knudsen</i>	9	113.3 ± 5.8	134.9 ± 0.2
	Torsion	9	112.4 ± 3.9	135.3 ± 0.2
MS1	Mass spectrometry	9	108 ± 11	134.7 ± 0.5
	mean	13	150 ± 15	201.5 ± 1.0

From the vapor-pressure data of *Belousov* and coworkers and *Gibbs*-energy functions from this work, ΔH° (298 K) of vaporization reaction (9) was found to be 110.5 ± 5.7 kJ/mol of In_2Te_3 . From the literature values of ΔH_f° (298 K) of $\text{InTe}(s)$, $\text{In}_2\text{Te}(g)$, and $\text{Te}_2(g)$, we calculated ΔH° (298 K) of vaporization reaction (13) to be 200.5 kJ/mol of InTe .

Discussion

This work provided the first absolute measurements of vapor pressures over samples whose initial composition was In_2Te_3 . The vapor pressures were about 30 times lower than those reported by *Belousov* et al. The vaporization of $\text{In}_2\text{Te}_3(s)$ was incongruent by reaction (9) in the temperature range 701–889 K. The solid-solution that resulted from the vaporization reaction (9) vaporized by reactions (11) and (12). The residual $\text{InTe}(s)$ vaporized congruently by reaction (13); this conclusion about the vaporization of $\text{InTe}(s)$ was supported by the observations:

1. After 90 percent by mass of In_2Te_3 was lost by evaporation, the residue was $\text{InTe}(s)$.

2. Intensities of all ions were univariant with temperature in Group 3 of experiment MS1.

3. The agreement was good between ΔH° (298 K) of reaction (13) from this work, 201.5 ± 1.0 kJ/mol, and that calculated via *Hess's* law from the literature values of ΔH_f° (298 K) of the species in reaction (13), 200.5 kJ/mol.

The conclusion that $\text{InTe}(s)$ vaporizes congruently is contradicted by the result that the calculated partial pressure of $\text{In}_2\text{Te}(g)$ was about one fourth of the partial pressure of $\text{Te}_2(g)$ in Group 3 of experiment MS1. By equation (13), one would expect partial pressures of $\text{In}_2\text{Te}(g)$ to be 2.4 times those of $\text{Te}_2(g)$. This apparent contradiction can be resolved by the following observation: During acquisition of Group 1, the vapor was

almost exclusively $\text{Te}_2(g)$. Even if we assume that the partial pressure of $\text{Te}_2(g)$ were only 2.4 times that of $\text{In}_2\text{Te}(g)$ throughout the experiment, 78.2 percent by mass of sample should have been lost as tellurium and the rest indium. This value is greater than the tellurium content of In_2Te_3 . Hence, the difference between the observed and the theoretical partial pressures were attributed to errors in ionization cross-sections and to unknown fragmentation.

The conclusion about the vaporization of $\text{In}_2\text{Te}_3(s)$ was not in agreement with that of *Berger* et al. or of *Belousov* et al. This lack of agreement arose perhaps because they failed to analyze changes in the condensed phases.

The conclusion about the vaporization of $\text{InTe}(s)$ was not in agreement with that of *Santandrea* and *Wiedemeier*. We measured vapor pressures over $\text{InTe}(s)$ in the temperature range 701–887 K and *Santandrea* and *Wiedemeier* measured in the range 900–950 K. Apparently the vaporization process changed at ca. 890 K. Such would be in line with the observation by *Srinivasa* and *Edwards* that $\text{InTe}(l)$ vaporizes incongruently at 1106 ± 2 K.

The apparent molecular weights in Group 1 from KT1 and KT2 were 241 ± 3 and 234 ± 8 , respectively, compared to the molecular weight of Te_2 , 255.2. This agreement showed that the vapor phase consisted almost completely of $\text{Te}_2(g)$.

ΔH° (298 K) of vaporization of $\text{In}_2\text{Te}_3(s)$ by the second- and the third-law methods from experiment KT1 were in good agreement. The agreement between the second- and third-law results in experiments KT2 and MS1 was poor. The poor agreement was likely due to the variation with temperature of the composition of the solid-solution in equilibrium with $\text{In}_2\text{Te}_3(s)$. Good agreement in experiment KT1 would be because the temperature range was narrow and the solid-solution boundary did not significantly vary in that range. The third-law values are more dependable because they are less sensitive to such temperature-dependent trends.

Among the indium chalcogenides, $\text{In}_2\text{S}_{2.9}(s)$ [31], $\text{In}_3\text{Se}_6(l)$ [32], and $\text{InTe}(s)$ vaporize congruently. We note that among In_2X_3 chalcogenides, the tendency to vaporize incongruently increases as the atomic number of the chalcogen increases. Tendency to vaporize incongruently increases with the ease of oxidation of the chalcogenide ion by In^{3+} . In^{3+} can more easily oxidize telluride than it can selenide or sulfide and hence, the observed trend in the vaporization behavior.

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