A KNUDSEN CELL–MASS SPECTROMETER STUDY OF THE VAPORIZATION OF CESIUM TELLURIDE AND CESIUM TELLURITE *

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(Received 1 July 1988)

ABSTRACT

Vapour pressures of cesium telluride, Cs_2Te, and of cesium tellurite, Cs_2TeO_3, were measured as a function of temperature from 600 to 1000 °C using a Knudsen cell technique with a quadrupole mass spectrometer as the detector for gaseous species. Standard enthalpies of vaporization were measured for Cs, Te, Te_2, Te_3, CsTe and Cs_2Te from Cs_2Te, and for Cs from Cs_2TeO_3. All were in the range of 147 ± 9 kJ mol^{-1}. Absolute vapour pressures were measured using silver as a standard. From these vapour pressures, standard Gibbs energies of vaporization for Cs and Te were 99.7 and 110.0 kJ mol^{-1} from Cs_2Te, and 116.9 and 133.4 kJ mol^{-1} from Cs_2TeO_3. The values for Cs_2Te are in good agreement with thermodynamic measurements reported recently.

Difficulties in calibrating the mass spectrometer prevented the accurate determination of absolute vapour pressures for species with molecular weight much above 300.

INTRODUCTION

For any loss-of-coolant accident in a nuclear reactor, the most volatile and hazardous fission products are the noble gases, cesium and iodine. The release of semi-volatile fission products such as tellurium is also a hazard [1]. Tellurium is not only a hazard by itself, but also in combination with cesium. Thus a knowledge of the volatility of cesium–tellurium compounds, such as cesium telluride, Cs_2Te, and cesium tellurite, Cs_2TeO_3, is useful for predicting the behaviour of both cesium and tellurium.

Volatilities, or vapour pressures, can be calculated directly if sufficient thermodynamic data (such as standard Gibbs energies of formation) are available, although in such cases direct experimental verification is desirable. In the case of Cs_2Te, standard Gibbs energies of formation are available over a range of temperatures [2]. These values were determined by a

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* Issued as AECL-9673

transpiration technique, which assumes that Cs_2Te vaporizes congruently as Cs_2Te molecules. No account could be taken of possible dissociation into constituent atoms and diatomic species, such as Cs_2, Te_2 or CsTe. Standard enthalpies [3] and heat capacities of formation [4] have been measured recently, but few data are available on the volatility of Cs_2TeO_3 [5].

This paper describes an experimental examination of the volatility of Cs_2Te and Cs_2TeO_3 using the Knudsen cell–mass spectrometer technique. The mass spectrometer gives a good indication of the species present in the gas phase [6] and, in principle, the method is quantitative.

EXPERIMENTAL

Materials

The Cs_2Te and Cs_2TeO_3 were supplied by Cerac Inc. of Milwaukee, WI, as products C-1185 and C-1186, respectively. Both were 99.9% pure and were shipped under argon. The Cs_2Te was greyish in colour but, when heated under vacuum, took on a yellowish-green colour. The silver metal was Aldrich Chemical Company Gold Label grade, 99.9999% pure. Bis(pentafluorophenyl) phenylphosphine (Ultramark 443), used for quantitative calibration of the mass spectrometer, was obtained from PCH Research Chemicals, Gainsville, FL, and perfluorotributylamine (FC 43), used as a mass marker, was obtained from Scientific Instrument Services, Pennington, NJ.

Apparatus and procedures

The Knudsen cell–mass spectrometer was built around a Finnigan model 3200 quadrupole mass spectrometer. It was controlled by a PDP11 computer using software written especially for this application.

The Knudsen cell assembly was constructed from a standard two inch (50 mm) Conflat tee fitted with cooling coils on its exterior surface. A Conflat section fitted with a rotatable shaft was mounted on the upper flange of the tee, and a thin flat plate mounted assymetrically on the edge of this shaft acted as a beam flag, or shutter. The upper surface of this section was mounted directly on the mass spectrometer, just below, and in line with, the electron gun. The two side arms of the tee served as connections to a diffusion pump and a cold cathode pressure gauge, respectively. The flange at the lower end of the tee provided a demountable support for the Knudsen cell and contained electrical feed-throughs for the resistance heater and a calibrated chromel-alumel thermocouple.

The crucible for the Knudsen cell was supported on a ceramic pedestal, which defined the vertical position of the cell in the tee. The horizontal

position was defined by two ceramic discs, which centred the crucible in the tee. The crucible was machined from a bar of tantalum, and in its outer walls, there were vertical holes to accommodate the resistance-wire ribbons serving as heaters. The Knudsen cell itself was machined from fused alumina. It had an alumina cap with a 0.5 mm tapered hole.

Before each run, the Knudsen cell, crucible, bottom flange and associated parts were thoroughly cleaned. The alumina Knudsen cell was first soaked in an HF/HNO_3 solution, then rinsed and dried. The ceramic parts were sandblasted, after which all the pieces were ultrasonically cleaned, rinsed with methanol and acetone and oven-dried. The assembly was then put together and mounted back on the bottom of the tee. During this operation, the mass spectrometer analyzer and the assembly were flushed with dry nitrogen. The system was evacuated, heated to 900°C for an hour or two and then cooled.

At this point, the bottom flange was removed, again employing a dry nitrogen flush, and the Knudsen cell was loaded with the sample in an argon-flushed dry box. The assembly was put together and replaced on the tee. The cell temperature was brought to about 150°C and evacuated overnight at this temperature to drive off excess water.

Before a typical temperature run was carried out, the Knudsen cell was adjusted to the desired temperature and allowed to stabilize for at least 15 minutes. A mass spectrum was then obtained at 40 eV, one with the beam flag closed and one with the beam flag open. The temperature was changed
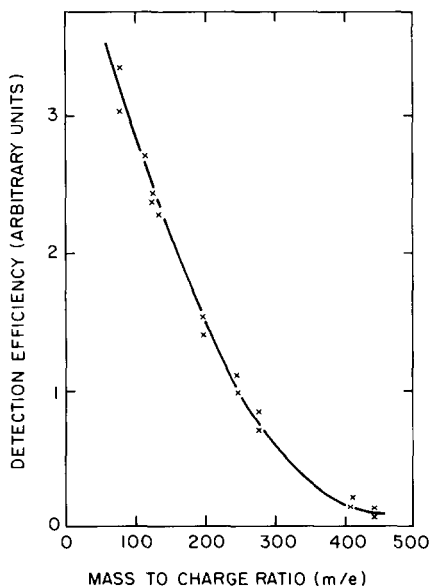

Fig. 1. Calibration of Finnigan model 3200 quadrupole mass spectrometer for ion transmission using Ultramark 443.

and the process repeated. When silver standards were run to determine appearance potentials, similar procedures were followed, except the sample had to be heated to about 1000°C under vacuum to remove the oxide layer. Occasionally, sandblasting of the silver surface was necessary.

Perfluorotributylamine (FC 43) was used to calibrate the mass scale of the mass spectrometer. Another calibration was necessary to calibrate the response of the quadrupole mass spectrometer quantitatively; therefore, mass spectra were obtained for bis(pentafluorophenyl)phenylphosphine (Ultramark 443). Intensities were compared with those obtained by the manufacturer on an AEI MS-30 with a source temperature of 200°C and an ionization energy of 70 eV. The relative intensities of given masses were then used to construct a calibration curve of relative sensitivity against mass number (Fig. 1).

RESULTS

Mass spectra

Typical mass spectra of the vapour emitted from Knudsen cells containing Cs_2Te and Cs_2TeO_3 are shown in Figs. 2 and 3, respectively. These uncorrected spectra show cesium and tellurium atoms as the most prominent
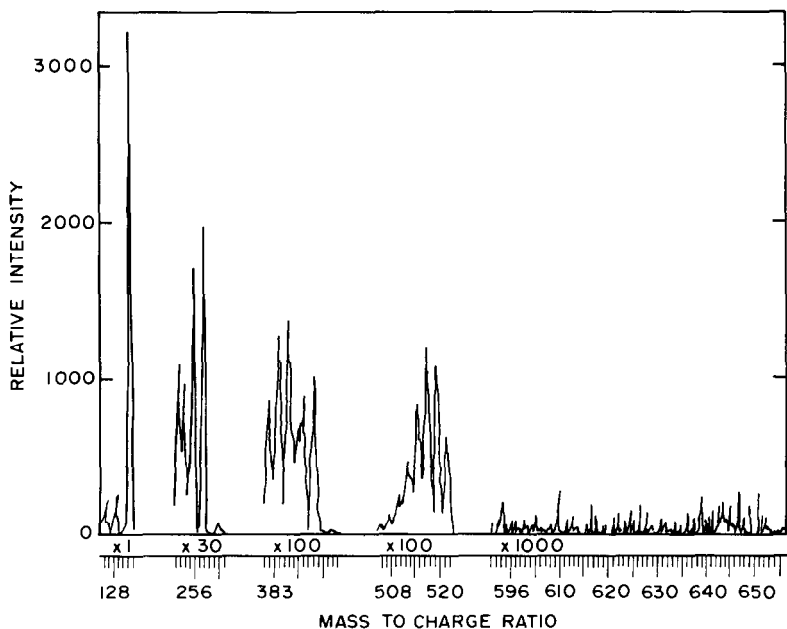

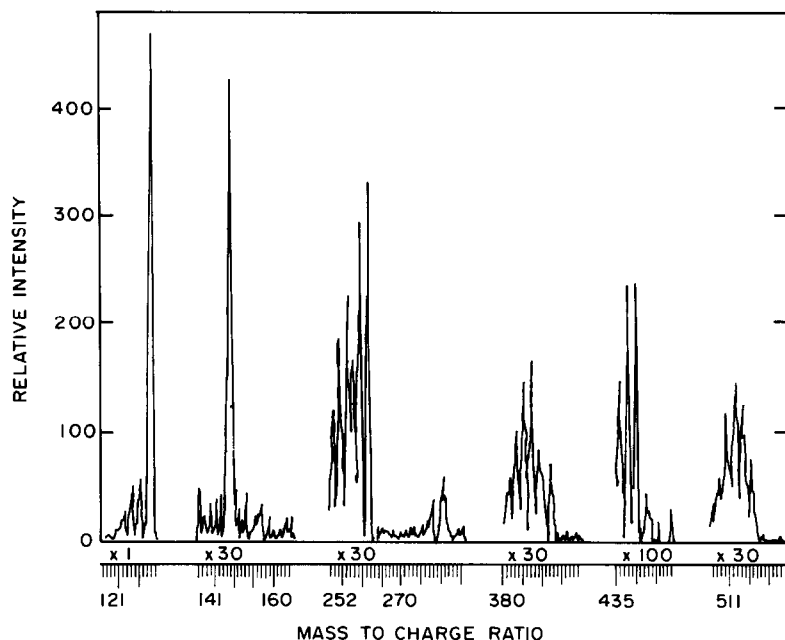Fig. 2. Raw mass spectrum for Cs_2Te at 873°C.

Fig. 3. Raw mass spectrum for Cs_2TeO_3 at $887^\circ C$.

features. There are also some diatomic species present such as Cs_2, Te_2 and CsTe and some oxygenated species from Cs_2TeO_3. Ions corresponding to the molecular species Cs_2Te and Cs_2TeO_3 are not especially prominent. A mass spectrum of the vapour from pure Cs_2Te synthesized at the Netherlands Energy Research Foundation, and supplied by Professor E.H.P. Cordfunke, was qualitatively similar to that shown in Fig. 2.

The uncorrected mass spectra show the intensities of positive ions produced by the interaction of 40 eV electrons with the chemical species in the vapour emitted from the Knudsen cell. Ions may arise from direct ionization of atoms and molecules according to the equations

$$Cs + e^- \rightarrow Cs^+ + 2e^- \tag{1}$$

$$Cs_2Te + e^- \rightarrow Cs_2Te^+ + 2e^- \tag{2}$$

or the fragmentation of a molecule may occur, giving an ion and an undetected neutral fragment as, for example, in the following equation

$$Cs_2Te + e^- \rightarrow Cs^+ + CsTe + 2e^- \tag{3}$$

Thus the peaks in the uncorrected mass spectra cannot be identified unambiguously with atomic and molecular products without some knowledge of the relative importance of processes such as the one described by eqn. (3). In other words, the mass spectrum of each component should be known.

One method for distinguishing between processes such as reactions (2) and (3) is to measure the appearance potential of the produced fragment.

TABLE 1

Appearance potentials for Cs_2Te

T (°C)	Appearance potential (eV)
673	4.4 ± 1.4
681	5.5 ± 1.0
753	4.8 ± 1.0
795	3.3 ± 1.0
833	3.5 ± 1.0

First, silver appearance potentials were determined as a function of temperature to verify the voltage scale and to make small corrections. They agreed with the known ionization potentials to within ± 0.05 eV [7]. Table 1 shows appearance potentials for species from Cs_2Te at various temperatures. Generally, the scatter in these results is very high. This is rather surprising in view of the precision with which the appearance potentials of the silver standards were determined. The scatter is so high that proper discrimination between processes (1) and (2) is very difficult; nevertheless, there are some indications as to which process is important.

If process (1) is the dominant one, then the energy required is simply the ionization potential of the cesium atom, or 3.894 eV [7]. This should then be the appearance potential at mass 133. On the other hand, if process (3) were dominant, the appearance potential of that peak would be the ionization potential of the cesium atom plus the bond dissociation energy of the Cs–TeCs bond. The latter was estimated to be about 2–3 eV using two different methods: one method was to consider the available thermodynamic data; the other was to use correlations to estimate the bond length, followed by an electrostatic calculation of the bond energy. Thus, if process (1) were dominant, we would expect appearance potentials of about 3.9 eV, whereas if process (3) were dominant, we would expect about 6.5 eV. Although the scatter is large, the data presented in Table 1 clearly favours process (1), the ionization of cesium atoms, as the source of Cs^+.

Enthalpies of vaporization

Enthalpies of vaporization were obtained from the variation of the intensities, I, of their respective mass peaks with temperature. Data were obtained from both Cs_2Te and Cs_2TeO_3. Because the partial pressures of the species present in the Knudsen cell are proportional to the areas, or intensity I, of one of their mass spectra peaks and to the absolute temperature, T, the enthalpy of the vaporization, $\Delta_s^g H^{\ominus}$, is given by the following equation [6]:

$$\Delta_s^g H^{\ominus} = -RT \frac{\partial \ln(IT)}{\partial(1/T)} \qquad (4)$$
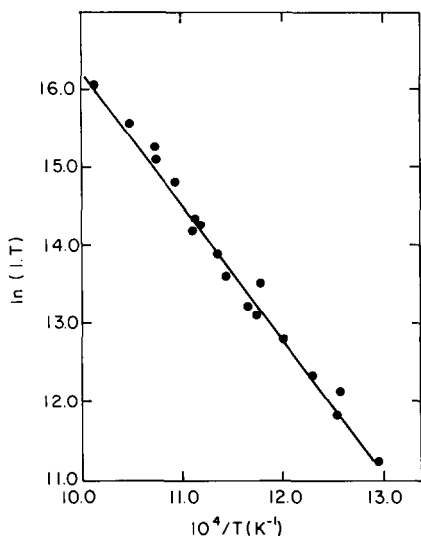
Fig. 4. Data for peak intensity from Cs_2Te as a function of temperature, plotted so as to obtain the enthalpy of vaporization, which, in this case, is $+146$ kJ mol^{-1}.

Enthalpies obtained this way are referred to as Second Law Enthalpies [8]. A typical plot of the $\ln(IT)$ for Cs^+ against reciprocal temperature is given in Fig. 4 for Cs_2Te vaporization. The slope corresponds to an enthalpy of vaporization of 146 kJ mol^{-1}. The enthalpies of vaporization measured in this work are listed in Table 2 for species from Cs_2Te and Cs_2TeO_3. The similarity of many of the values for the Cs_2Te species suggests a common origin for many of these products.

Gibbs energies of vaporization

As noted above, enthalpies of vaporization can be obtained by measuring relative changes in intensity as a function of temperature. To measure Gibbs energies of vaporization, however, it is necessary to measure the absolute

TABLE 2

Second Law Enthalpies of vaporization

Species	$\Delta_s^g H^{\ominus}(Cs_2Te)$ (kJ mol^{-1})	$\Delta_s^g H^{\ominus}(Cs_2TeO_3)$ (kJ mol^{-1})
Cs	146	142
Te	136	–
Te_2	145	–
Te_3	141	–
CsTe	152	–
Cs_2Te	160	–

TABLE 3

Ionization cross section employed

Species	σ $(10^{-20}$ J m$^2)$	Species	σ $(10^{-20}$ J m$^2)$
Ag	5.05	O	1.27
Cs	10.78	CsO	9.0
Te	7.09	Cs$_2$O	14.9
Te$_2$	10.6	Cs$_2$TeO$_3$	15.3
Te$_3$	13.3	Cs$_2$Te	18.0
		CsTe$_2$	15.6
CsTe	13.4	Cs$_2$Te$_2$	20.1

vapour pressures in the cell. A number of methods are available to calibrate the instrument to do this [9]. We compared peak areas with those from pure silver whose vapour pressure is accurately known over the temperature range. After measurements of peak areas of both the silver standard and the sample, it is necessary to correct the intensities of the sample peaks for isotopic purity, for differences in the ionization cross section, for varying detector sensitivity and for the ion transmission characteristics of the mass spectrometer itself [9].

The basic formula for the pressure, P, of species i is

$$P_i = P_{Ag} \frac{I_i T_i}{I_{Ag} T_{Ag}} \frac{\sigma_{Ag}}{\sigma_i} \frac{\gamma_{Ag}}{\gamma_i} \frac{\rho_{Ag}}{\rho_i} \frac{E_{Ag}}{E_i - AP_i^{g_i}} \tag{5}$$

where I is the intensity (area) of the mass spectrum peaks; σ is the ionization cross section; γ is the detector sensitivity; ρ is the instrument sensitivity; g is the isotopic abundance weighting factor; E is the electron

TABLE 4

Vapour pressures over Cs$_2$Te at 873°C

Species	P (mPa)	$\Delta_s^g G^\ominus$ (kJ mol^{-1})
Cs	2880	99.7
Te	980	110.7
Te$_2$	280	121.9
Te$_3$	440	117.6
CsTe	580	115.0
Cs$_2$Te	350	119.7
CsTe$_2$	690	113.3
Cs$_2$Te$_2$	1140	108.5

TABLE 5

Vapour pressures over Cs_2TeO_3 at $887\,^\circ C$

Species	P (mPa)	$\Delta_s^g G^\ominus$ (kJ mol^{-1})
Cs	550	116.9
Te	99	113.4
Te$_2$	85	135.0
Te$_3$	210	126.3
CsTe	130	130.8
Cs$_2$Te	112	132.2
Cs$_2$Te$_2$	650	115.3
CsO	38	142.6
Cs$_2$O	8	157.3
Cs$_2$TeO$_3$	230	125.4

energy, which was usually 40 V; and AP$_i$ is the appearance potential. Atomic ionization cross sections were taken from the compilation of Mann [10]. There are a number of ways of constructing molecular ionization cross sections from the atomic cross sections, but we used the recent method of Kordis and Gingerich [11]. The values of atomic and molecular ionization cross sections actually used are listed in Table 3. According to conventional practice, detector sensitivity was assumed to vary inversely with the square root of the molecular weight. The measurement of appearance potentials and instrument sensitivity factors were calculated from standard tables of the isotopes. At the higher masses, where the spectra overlap considerably, the peak area for any given species was determined by the stripping technique. Absolute vapour pressures measured in this fashion are given in Tables 4 and 5. They show a large preponderance of dissociated products, such as Cs, Te and CsTe.

Deposits

Surface deposits were scraped off the beam flag and the walls of the chamber after Cs$_2$Te runs at $900\,^\circ C$. These were analyzed by X-ray diffraction for crystal structure, and for elemental composition. The X-ray diffraction patterns did not match those calculated for Cs$_2$Te from the unit cell dimensions reported by Prins and Cordfunke [12]. X-ray fluorescence analyses of material from the chamber wall indicated that the deposit consisted of particles enriched with cesium on their outer surfaces, but with an overall Cs/Te ratio of about 1.0. Similarly, the material from the beam flag had a Cs/Te ratio of 0.85. Thus the condensed material shows a definite deficiency of cesium compared to the original Cs$_2$Te.

DISCUSSION

For Cs_2Te, our results given in Table 4 indicate that, at 1500 K, atomic cesium and other fragment species are the abundant species in the gas phase. Molecular Cs_2Te seems to be present in rather smaller amounts.

Recently [2–4], Cordfunke and collaborators have measured vapour pressures, enthalpies and heat capacities of vaporization for Cs_2Te. From these data and from thermodynamic data for the elemental cesium and tellurium, along with their dimers [12], the gas phase equilibrium concentrations of Cs, Te, Cs_2, Te_2 and Cs_2Te can be calculated at any reasonable temperature [13]. The results of such calculations are given in Fig. 5 together with our experimental results from Table 4. Our experimental results for cesium, tellurium and the corresponding dimers are in reasonable agreement with the predicted partial pressures; however, the result for cesium telluride is far too low.

At this point it is not possible to state unequivocally the cause of the discrepancy between the experimental and theoretical values for the Cs_2Te vapour pressures. The calculations do not take into account CsTe and its dimer, so it is possible that the vapour phase composition is more complicated than previously assumed. On the other hand, our problems with calibrating the mass spectrometer for absolute intensities at the higher masses means that our errors may be very large in this region. Furthermore, the appearance potential data is of such poor quality that we cannot rule out
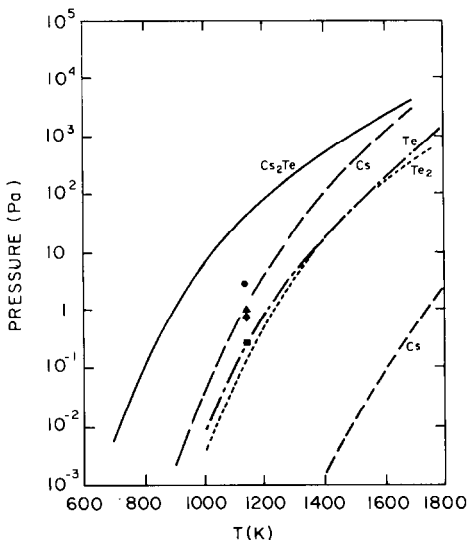

Fig. 5. Experimental and calculated vapour pressures from Cs_2Te. The lines are calculated for Cs_2Te (———), Cs (——— ———), Te (- — - — -), Te_2 (- - - - - -) and Cs_2 (— — —). The points are experimental for Cs (●), Te (▲), Cs_2Te (◆) and Te_2 (■).

the possibility that fragment ions may be contributing significantly to our spectra. Also, using the techniques available to us, it was not possible to load and mount the Knudsen cell in as inert an environment as might be wished. Thus oxygen contamination may be affecting our results.

Very little thermodynamic information is available for cesium tellurite. By analogy with the cesium telluride, it is likely that measured cesium and tellurium vapour pressures, along with those of the dimers, are reasonably reliable; however, our estimates of the vapour pressures of larger species may be greatly in error.

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