



Vaporization studies on elemental tellurium and selenium by Knudsen effusion mass spectrometry



R. Viswanathan*, R. Balasubramanian, D. Darwin Albert Raj, M. Sai Baba, T.S. Lakshmi Narasimhan

Fuel Chemistry Division, Chemistry Group, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

ARTICLE INFO

Article history:

Received 6 December 2013

Received in revised form 3 March 2014

Accepted 6 March 2014

Available online 17 March 2014

Keywords:

Vaporization of tellurium

Vaporization of selenium

Thermochemistry

Tellurium clusters

Selenium clusters

ABSTRACT

Vaporization studies on elemental tellurium and selenium were conducted by Knudsen effusion mass spectrometry in the temperature range of 590–690 K and 380–480 K, respectively.

The ionic species Te_i^+ ($i = 1-7$) and Se_i^+ ($i = 1-9$) were detected in the mass spectra over these two condensed phases. Measurement of ion intensities were performed as a function of electron impact energy and as a function of temperature (at different electron impact energies) for identifying the gaseous precursor species as well as for determining the partial pressure–temperature relations and sublimation enthalpies for these species. While the major species over elemental tellurium was confirmed to be $\text{Te}_2(\text{g})$ (with all other gaseous species $\text{Te}_3\text{--Te}_7$ put together constituting less than 5%), the major species over elemental selenium was found to be $\text{Se}_6(\text{g})$, closely followed by $\text{Se}_5(\text{g})$ (with other gaseous species $\text{Se}_2\text{--Se}_4$ and $\text{Se}_7\text{--Se}_9$ put together also moderately constituting $\sim 25\%$). From the partial pressures, the thermodynamic data for the sublimation reactions $i \text{ Te(s)} = \text{Te}_i(\text{g})$ and $i \text{ Se(s)} = \text{Se}_i(\text{g})$ were deduced by second- and third-law methods. The atomization enthalpies of tellurium and selenium clusters were also deduced by using the recommended enthalpies of formation of monomeric species. Comparison of the findings obtained in the present study with those in previous studies revealed general agreement with regard to major species $\text{Te}_2(\text{g})$ and $\text{Se}_6(\text{g})$, but still some differences to be resolved with regard to minor species in both systems.

© 2014 Published by Elsevier B.V.

1. Introduction

The study of vaporization of elemental tellurium was first taken up by us in 1984 as a prelude to measurements on binary metal–tellurium systems [1–4], which are of relevance to Fuel Cladding Chemical Interactions [5] in mixed-oxide fueled fast breeder nuclear reactors. Dimeric tellurium species, $\text{Te}_2(\text{g})$, was the major gaseous species identified over elemental tellurium [6] and also over many M–Te systems [4], and thus, measurement on elemental tellurium served the purpose of pressure calibration in most of our Knudsen effusion mass spectrometric measurements (KEMS) on M–Te systems. However, the fact that the other gaseous species $\text{Te}_i(\text{g})$ ($i = 3-7$) also are present in the equilibrium vapor phase over Te(s) enthused us to conduct a very detailed KEMS investigation of elemental tellurium, a volatile and reactive element generated during fission in nuclear reactors. Having

known that the fellow chalcogen selenium, another element of interest to nuclear industry [7], also forms clusters in the vapor phase with Se_6 as the major species, we were motivated to undertake a similar detailed KEMS investigation on solid selenium also. A survey of literature, including the recent comprehensive book on selenium [7], reveals that for both systems, there still exists only one study each on solid phases, that covers a reasonably large temperature range. This acted as an incentive for us to present now the results of our extensive measurements performed on solid tellurium and selenium long time ago (during 1984–85; at high and low electron energies), but after evaluating the selenium results with the new thermal functions deduced from the most recent compilation [7]. Furthermore, the only previous report of these measurements are just as part of a Ph.D thesis (work on tellurium) [8] or as a presentation in an international meeting as a brief two page extended abstract (work on both tellurium and selenium) [9]. Additional motivating factor for this article is that since only a small number of laboratories presently use KEMS [10], an investigation of the type conducted by us (on tellurium and selenium clusters) is best reported now so that it could revive interest in such studies, which have been more in vogue until twenty years ago.

* Corresponding author. Tel.: +91 9994529509; fax: +91 44 27480065.

E-mail addresses: rvis1953@gmail.com, rvis@igcar.gov.in (R. Viswanathan), rbs@igcar.gov.in (R. Balasubramanian), darwinalbertraj1953@gmail.com (D. Darwin Albert Raj), msb@igcar.gov.in, msai@igcar.gov.in (M. Sai Baba), tslak@igcar.gov.in (T.S. Lakshmi Narasimhan).

The information on elemental tellurium and selenium has been reviewed by Mills [11] and by Grønvold et al. in 1994 [12]. The information on elemental selenium has been reviewed as recently as in 2005 [7]. From these reviews, one infers that the simultaneous mass-loss and torsion effusion measurements by Niwa and Sibata [13] gave the first indication that $\text{Te}_2(\text{g})$ is the principal vapor species over tellurium and that Se_6 and also Se_5 both qualify to be the principal vapor species over selenium [14]. Since torsion effusion results are not affected by the nature of the vapor species, we have used in the present study the total vapor pressure obtained by Niwa and Sibata [13,14] along with the ion intensities measured by us to deduce pressure calibration constants in situ in each run.

The above-mentioned reviews [11,12] also refer to many kind of vaporization studies, but in this paper, we will restrict the reference to mainly the KEMS studies.

In the case of tellurium, the investigation by Neubert [15] is by far the most complete mass spectrometric work reported yet. With the exception of Te^+ , all the ions identified in the mass spectra Te_i^+ ($i = 1-7$) were treated as parent ions and the partial pressures of $\text{Te}_i(\text{g})$ ($i = 2-7$) were computed from the ion intensities measured at a small but equal electron energy (3 eV) above the respective appearance energies of the ions. The authors employed external pressure calibration procedure (using silver or lead) to deduce p - T relations in the temperature range of 600–720 K. The present study, as mentioned already, seeks to use total vapor pressure obtained in the torsion effusion investigation for pressure calibration. Furthermore, it also seeks to measure ion intensities at a constant high electron energy of 44 eV (past the maximum in the ionization efficiency) as well as at low electron energies, varying from 9.6 to 11.3 eV for different ions. While in the case of major vapor species $p(\text{Te}_2)$, our value was $\sim 50\%$ higher than Neubert's, the disagreement in the values of partial pressures of other species was much higher, by a factor of 2–5. That the most likely reason for this discrepancy could be the difference in pressure calibration procedures and that in the values ionization cross sections is what one would infer from the considerable decrease in disagreement seen between the equilibrium constants for homogeneous gas phase reactions. These aspects will be discussed in more detail in this paper.

In the case of selenium, there are at least four studies to our knowledge which exist for solid phase. Goldfinger and Jeunehomme [16] performed mass spectrometric measurements on coarsely squashed crystals taken in graphite crucibles in the temperature range of 450–510 K. They did not give relative compositions, but inferred that species $\text{Se}_i(\text{g})$ ($i = 2-8$) are present in the vapor phase with Se_7 and Se_8 being in the order of 10%, and species lower than hexa-atomic (Se_6) being of the same order of magnitude (so as to yield mean molecular weight equivalent to that of hexamer). Fujisaki et al. [17] performed measurements in the temperature range 375–460 K at 40 eV. Their special arrangement for ionization was that the ionizing electron beam passed through the vapor inside the effusion cell instead of the conventional arrangement that electron beam crosses the vapor species after they effuse out of the Knudsen cell. This apparatus, however, did not allow measurement of absolute partial pressures, but only the relative abundances of species $\text{Se}_i(\text{g})$ ($i = 5-9$) with respect to $\text{Se}_6(\text{g})$. According to these authors, the ions Se_i^+ ($i = 1-4$) are formed solely due to fragmentation of $\text{Se}_6(\text{g})$. Almost at the same time, Berkowitz and Chupka [18] also performed measurements on elemental selenium as well as on selenides of Sr, Cd, and Hg. They employed both free and Knudsen cell vaporization in addition to a variant of what the authors term as 'double oven approach' (for HgSe). These authors sought to use the information on various gas phase equilibria over the selenides to eventually deduce the partial pressures of 5 gaseous species, Se_i ($i = 2$ and 5–8) at

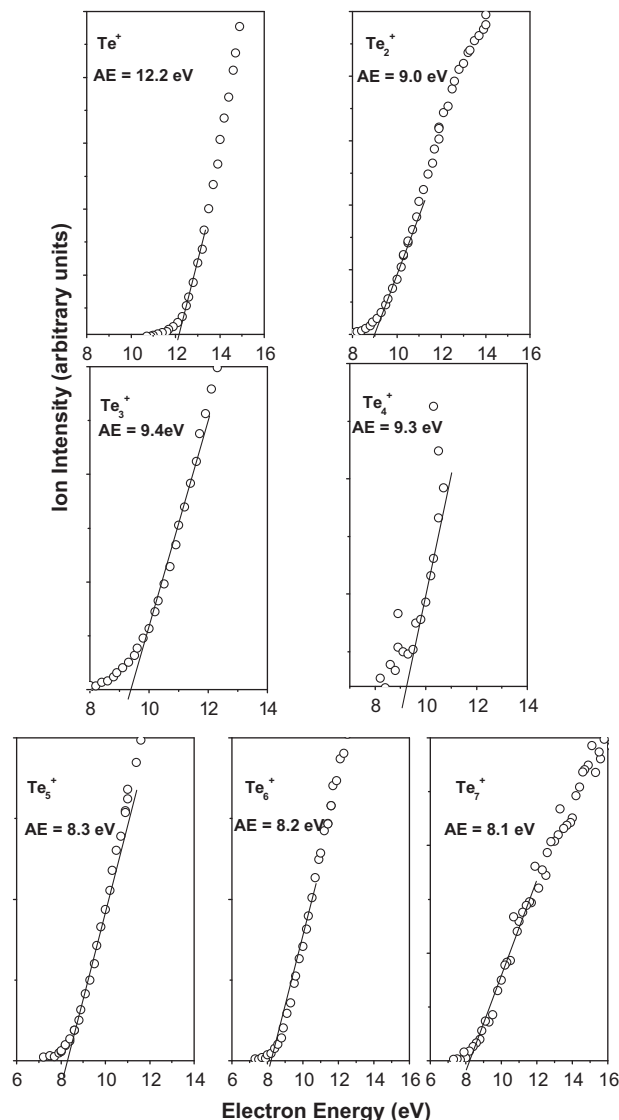


Fig. 1. Ionization efficiency curves for ions Te_i^+ ($i = 1-7$).

$T = 469$ K. The contributions are in the order: $\text{Se}_8 < \text{Se}_2 < \text{Se}_7 < \text{Se}_5 \leq \text{Se}_6$. Grimley et al. [19] used angular distribution mass spectrometry to identify 6 gaseous species Se_i ($i = 2$ and 4–8) and by combining with second-law ion intensity measurements, deduced the mole fractions of these species at $T = 483$ K. The contributions are in the order: $\text{Se}_8 < \text{Se}_4 < \text{Se}_2 < \text{Se}_7 \ll \text{Se}_6 \leq \text{Se}_5$. Huang et al. [20] performed vacuum balance rate of mass-loss measurements using Knudsen and Langmuir crucibles in the temperature range covering both solid and molten selenium. However, since their mass spectrometric measurements, again with both Knudsen and Langmuir crucibles, corresponded to molten selenium (in a narrow temperature range), they combined the mass-loss and mass spectrometric data only for molten selenium and reported partial pressures of 7 gaseous species Se_i ($i = 2-8$) only for molten selenium at $T = 500$ K. The contributions are in the order: $\text{Se}_8 < \text{Se}_2 \approx \text{Se}_3 < \text{Se}_4 < \text{Se}_7 < \text{Se}_5 \leq \text{Se}_6$. Yamdagni and Porter [20] used single and double-oven type Knudsen effusion cells in their mass spectrometric measurements to study molten selenium. Though they did not give any relative compositions, they concluded that the vapor phase contains 5 gaseous species, Se_i ($i = 2, 5-8$). They also performed simultaneous mass-loss torsion effusion measurements,

the results from which enabled them to state that the mean molecularity of the vapor species is between 5 and 6. That is, both Se_6 and Se_5 could be of comparable abundance. The present study was conducted in the temperature range of 390–490 K, and pressure calibration again was sought to be performed by using torsion effusion total pressure data. Three series of measurements are performed: (1) at high electron energy of 44 eV; (2) at low electron energy of 13.2 eV; and (3) at still lower, but not all at same electron energy for all species. These measurements revealed a good picture of fragmentation effects for Se_2^+ . In general, there is reasonable consistency amongst different mass spectrometric results, considering the complexity of the vapor phase. These aspects will be described in this paper.

Besides p – T relations, we also seek to report sublimation reaction enthalpies for $\text{Te}_i(\text{g})$ and $\text{Se}_i(\text{g})$ as well as atomization enthalpies of these species. Where possible, comparisons with previously reported results are made.

2. Experimental

The vaporization experiments presented in this paper were performed essentially with the same Knudsen effusion mass spectrometer (VG micromass 30 BK, U.K.) that has been described in detail in our recent papers [22,4] except that the present study corresponded to the time when some of the operations were to be performed manually and not through computer. Knudsen cells having a knife edged orifice of ≈ 0.5 mm diameter were used to contain the samples of powders of tellurium (Koch-Light Laboratories, U.K., purity: >99.7 mass%) and selenium (Leico industries, U.S.A., purity: 99.999%). The Knudsen cell was placed inside a cylindrical outer cup made of tantalum and closed with a tight fitting lid made of tungsten having a 3 mm diameter circular hole, collinear with the Knudsen cell orifice. The outer cup having three equidistant holes at its base (diameter: 2 mm and depth 6 mm) was slipped into three 'supporting rods', one of which was a stainless steel sheathed chromel-to-alumel thermocouple, employed for measurement of temperature. Heating of the 'Knudsen cell furnace' was effected by radiation from two independent tungsten filaments encircling it. During the time of these measurements (1984–85), the temperature regulation was achievable only in power control mode, with manual adjustment of power required to be done at times whenever the temperature went beyond ± 1 °C (that is beyond ± 0.04 mV of the targeted thermocouple output). Ionization of the molecular beam effusing out of the Knudsen cell was effected by electron-impact, the emission current of electrons maintained at 50 or 100 μA . To cover the mass range up to Te_7^+ (m/z of the most abundant isotope = 896) and Se_5^+ (m/z of the most abundant isotope = 712), the ion-acceleration voltage was kept at 3 kV. The mass separation of ions was effected by a 30.5 cm radius magnetic analyzer with 90° sector angle, while the ion intensities were measured by a secondary electron multiplier, the first dynode of which was kept at 2.5 or 3 kV. A 'molecular beam shutter', which provides the means of deducing the net ion intensities arising from the ionization of vapor species that effused out from within the Knudsen cell was being operated manually at the time of these measurements.

The thermocouple calibration was performed against the melting temperature of silver while the calibration of the ionizing electron energy scale was performed by determining the apparent appearance energies (AE) for In^+ , Hg^+ , Ag^+ , Ar^+ and He^+ and by ascertaining the linear relationship between AE and the known first ionization energies (IE) [23]. The ionization efficiency measurements for the ions observed in the mass spectrum of vapor over $\text{Te}(\text{s})$ and $\text{Se}(\text{s})$ were performed by maintaining the temperature constant at ~ 690 K and ~ 480 K, respectively. Our

Table 1

The parameters pertinent to electron-impact ionization of $\text{Te}_i(\text{g})$. Appearance energies (AE) of Te_i^+ and ionization cross section σ ratios at $E = 44$ eV and $E < (\text{AE} + 2.5 \text{ eV})$.

<i>i</i>	AE/eV	$[\sigma(\text{Te}_i, 44 \text{ eV})/\sigma_{\text{max}}(\text{Te})]$		E/eV	$[\sigma(\text{Te}_i, E)/\sigma_{\text{max}}(\text{Te})]$	
		Set-A ^a	Set-B ^b		Set-C ^c	Set-D ^d
2	9.0	1.50	1.44	11.3	0.128	0.123
3	9.4	2.11	1.76	11.3	0.142	0.119
4	9.3	2.73	2.04	9.6	0.029	0.022
5	8.3	3.36	2.28	10.5	0.297	0.201
6	8.2	3.99	2.49	10.5	0.373	0.233
7	8.1	4.62	2.69	10.5	0.456	0.266

^a Calculated according to Eq. (3), proposed and used by Neubert [15] in his measurements of tellurium clusters at $E = (\text{AE} + 3 \text{ eV})$.

^b Calculated according to Eq. (4), proposed by Rosinger et al. [24] as being valid for measurements at 75 eV and used by them in their measurements of sulfur clusters at 12 eV, after multiplying by $(12 \text{ eV} - \text{AE})/(75 \text{ eV} - \text{AE})$.

^c Calculated by multiplying Set-A value by $(E - \text{AE})/(3 \text{ AE})$.

^d Calculated by multiplying Set-B value by $(E - \text{AE})/(3 \text{ AE})$.

Table 2

Partial pressure – temperature relations for $\text{Te}_i(\text{g})$ ($i = 2$ –7) over $\text{Te}(\text{s})$. $T/K = 590$ –690 K. $T_{\text{mean}} = 640$ K.

<i>i</i>	$\log[p(\text{Te}_i)/\text{Pa}] = -[A/(T/K)] + B$		$p(\text{Te}_i)/\text{Pa}$ at $T = 640$ K
	A^a	B^a	
<i>Set-A^b: E = 44 eV</i>			
2	7957 ± 77	12.44 ± 0.12	1.0
3	9966 ± 121	13.64 ± 0.19	1.2×10^{-2}
4	10,405 ± 164	13.23 ± 0.26	9.3×10^{-4}
5	9830 ± 362	13.67 ± 0.57	2.0×10^{-2}
6	10,150 ± 428	12.67 ± 0.68	6.4×10^{-4}
7	11,181 ± 704	13.03 ± 1.10	3.7×10^{-5}
<i>Set-B^c: E = 44 eV</i>			
2	7958 ± 77	12.44 ± 0.12	1.0
3	9967 ± 122	13.70 ± 0.19	1.3×10^{-2}
4	10,406 ± 164	13.33 ± 0.26	1.2×10^{-3}
5	9831 ± 361	13.81 ± 0.57	2.8×10^{-2}
6	10,151 ± 428	12.85 ± 0.68	9.8×10^{-4}
7	11,182 ± 703	13.25 ± 1.10	6.0×10^{-5}
<i>Set-C^d: E < (AE + 2.5 eV)</i>			
2	7782 ± 84	12.16 ± 0.13	1.0
3	9364 ± 119	12.95 ± 0.19	2.1×10^{-2}
4	10,443 ± 116	13.21 ± 0.18	7.9×10^{-4}
5	9493 ± 116	13.08 ± 0.18	1.8×10^{-2}
6	10,110 ± 143	12.55 ± 0.22	5.6×10^{-4}
7	11,538 ± 178	13.57 ± 0.28	3.5×10^{-5}
<i>Set-D^e: E < (AE + 2.5 eV)</i>			
2	7781 ± 84	12.16 ± 0.13	1.0
3	9363 ± 119	13.00 ± 0.19	2.4×10^{-2}
4	10,442 ± 116	13.32 ± 0.18	1.0×10^{-3}
5	9492 ± 116	13.22 ± 0.18	2.5×10^{-2}
6	10,109 ± 143	12.73 ± 0.22	8.6×10^{-4}
7	11,537 ± 178	13.78 ± 0.28	5.6×10^{-5}

^a Uncertainties quoted are standard deviations.

^b Deduced with Set-A σ ratios given in Table 1.

^c Deduced with Set-B σ ratios given in Table 1.

^d Deduced with Set-C σ ratios given in Table 1.

^e Deduced with Set-D σ ratios given in Table 1.

usual procedure was to measure ion-intensities by decreasing the electron energy from 70 eV, at larger intervals of 2–5 eV up to ~ 35 eV and at closer intervals of 0.4 eV in the region below the ion-intensity maximum. This permitted us to deduce not only appearance energies (by linear extrapolation method) but also the energies where dissociative ionization (that is, fragmentation) would be minimum. Measurements of ion-intensities as a function of temperature were done subsequently. Ion intensities used for calculation of partial pressures were those measured after at least one hour of reaching the first temperature (usually the highest temperature) and 20 min of reaching subsequent lower temperatures. At the end of each run, the sample was taken to the highest temperature once again in order to ascertain that the sensitivity of the mass spectrometer remained constant through out the run. In each run, the focusing parameters and the Knudsen alignment (the position of the Knudsen cell orifice with respect to the ion source entrance slit) were first optimized to obtain maximum ion intensity for the most abundant ion, Te_2^+ for $\text{Te}(\text{s})$ and Se_2^+ for $\text{Se}(\text{s})$. As mentioned in the introduction, two series of temperature dependence measurements (590–690 K) were conducted on elemental tellurium, each series consisting of three runs, the first series at a constant electron energy of 44 eV and the second series at low electron energies, value for each ion being less than 2.5 eV above appearance energy, and selected after examining the respective ionization efficiency curve. In the case of selenium, three series of temperature dependence measurements were conducted (380–480 K), again, each series consisting of three runs. The first series of runs were conducted at 44 eV, the second series at 13.2 eV, and the third series at still lower electron energies, value for each ion selected after examining the respective ionization efficiency curve.

3. Results and discussion

3.1. Elemental tellurium

3.1.1. Partial pressures

The ions Te_i^+ ($i = 1$ –7) were detected in the mass spectrum of the equilibrium vapor over $\text{Te}(\text{s})$. They were identified by their mass, shutter effect, and by comparison of the net intensity of peak corresponding to each m/z with the calculated relative isotopic abundances. Fig. 1 shows portions of the ionization efficiency

Table 3Comparison of partial pressures and mole fractions of $\text{Te}_i(\text{g})$ obtained in this study with those reported previously by Neubert [15].

<i>i</i>	$p(\text{Te}_i)$ at $T = 640 \text{ K}$					$x(\text{Te}_i) = p(\text{Te}_i)/p(\text{Te}_i)$ at $T = 640 \text{ K}$				
	Present study ^a				Neubert ^c	Present study				Neubert
	Set-A	Set-B	Set-C	Set-D ^b		Set-A	Set-B	Set-C	Set-D ^b	
2	1.0	1.0	1.0	1.0	0.67	0.97	0.96	0.96	0.95	0.98
3	1.2×10^{-2}	1.3×10^{-2}	2.1×10^{-2}	2.4×10^{-2}	6.0×10^{-3}	1.1×10^{-2}	1.3×10^{-2}	2.0×10^{-2}	2.3×10^{-2}	8.8×10^{-3}
4	9.3×10^{-4}	1.2×10^{-3}	7.9×10^{-4}	1.0×10^{-3}	1.9×10^{-4}	8.8×10^{-4}	1.1×10^{-3}	7.6×10^{-4}	9.6×10^{-4}	2.7×10^{-4}
5	2.0×10^{-2}	2.8×10^{-2}	1.8×10^{-2}	2.5×10^{-2}	7.0×10^{-3}	1.9×10^{-2}	2.7×10^{-2}	1.7×10^{-2}	2.4×10^{-2}	1.0×10^{-2}
6	6.4×10^{-4}	9.8×10^{-4}	5.6×10^{-4}	8.6×10^{-4}	1.6×10^{-4}	6.1×10^{-4}	9.3×10^{-4}	5.4×10^{-4}	8.2×10^{-4}	2.3×10^{-4}
7	3.7×10^{-5}	6.0×10^{-5}	3.5×10^{-5}	5.6×10^{-5}	1.6×10^{-5}	3.5×10^{-5}	5.6×10^{-5}	3.3×10^{-5}	5.4×10^{-5}	2.3×10^{-5}
$\sum p(\text{Te}_i)$	1.1	1.1	1.0	1.0	0.68					

^a Reproduced from Table 2.^b Recommended in the present study. Measurements at $E < (\text{AE} + 2.5 \text{ eV})$.^c Deduced from the p - T relations given in the paper.**Table 4**Comparison of equilibrium constants for reactions $\text{Te}_i(\text{g}) = (i/2) \text{Te}_2(\text{g})$ ($i = 3-7$) at $T = 640 \text{ K}$, $p^\circ = 101,325 \text{ Pa}$.

<i>i</i>	$K^\circ = [p(\text{Te}_2)/p^\circ]^{1/2} / [p(\text{Te}_i)/p^\circ]$	
	This study	Neubert [15]
3	1.3×10^{-1}	2.9×10^{-1}
4	9.8×10^{-3}	2.4×10^{-2}
5	1.2×10^{-6}	1.6×10^{-6}
6	1.1×10^{-7}	1.9×10^{-7}
7	5.4×10^{-9}	4.8×10^{-9}

curves from which the appearance energies (AE) for each ion was determined. The estimated error on AE values is $\pm 0.5 \text{ eV}$. For each ion, the maximum intensity was observable at an electron energy, E_{max} , close to 4 times the respective AE. The AE of Te^+ (12.2 eV) was much higher than the known ionization energy of $\text{Te}(\text{g})$ (9.01 eV [23]) indicating that Te^+ was formed only by dissociative ionization. The low AE values of other ions were taken to indicate that they were all generated by simple ionization, especially at $E < (\text{AE} + 2.5 \text{ eV})$. A constant value of $I(\text{Te}^+)/I(\text{Te}_2^+)$ was obtained at 44 eV at all temperatures, an observation taken to infer that the main contributor to $I(\text{Te}^+)$ was $\text{Te}_2(\text{g})$.

The partial pressures, $p(\text{Te}_i)$, of the neutral species, Te_i ($i = 2-7$) at any temperature, T , were derived from the ion intensities, $I(\text{Te}_i^+)$, measured at that temperature and by employing the following relation:

$$p(\text{Te}_i) = k \cdot I(\text{Te}_i^+) \cdot T / \{ [\sigma(\text{Te}_i, E) / \sigma_{\text{max}}(\text{Te})] \cdot \eta(\text{Te}_i^+) \cdot \gamma(\text{Te}_i^+) \} \quad (1)$$

Table 5Comparison of second- and third-law enthalpies for sublimation reactions, $\text{Te}(\text{s}) = \text{Te}_i(\text{g})$.

<i>i</i>	$\Delta_{\text{sub}} H_m^\circ(\text{Te}_i(\text{g}), 298.15 \text{ K})$				
	Present study			Neubert [15]	
	Second-law ^a	Third-law ^a	Recommended ^b	Second-law ^b	Third-law ^b
2 ^c	156.6 ± 1.6	161.7 ± 0.5		163.6 ± 4	162.8 ± 4
2 ^d	154.6 ± 1.6	161.9 ± 0.5	158.0 ± 6.6	161.1 ± 4	164.0 ± 4
3 ^e	190.5 ± 2.3	197.1 ± 0.9	193.8 ± 7.5	207.1 ± 10	203.3 ± 6
4 ^e	214.3 ± 2.2	227.6 ± 1.0	221.0 ± 11.6	214.6 ± 8	235.6 ± 2
5 ^e	199.7 ± 2.2	185.6 ± 2.5	192.7 ± 12.8	207.1 ± 8	190.4 ± 8
6 ^e	214.3 ± 2.7	207.9 ± 2.5	211.1 ± 10.3	236.8 ± 10	213.4 ± 8
7 ^e	244.7 ± 3.4	228.2 ± 3.3	236.5 ± 15.9	223.8 ± 25	231.4 ± 8

^a Errors quoted are standard deviations.^b Errors quoted are estimated values (presumably in the case of Neubert also).^c Auxiliary thermodynamic functions given by Mills [11] used.^d Auxiliary thermodynamic functions given by Grønvold et al. [12] used.^e Auxiliary thermodynamic functions estimated by Neubert [15] used.

where k is the pressure calibration constant, $\sigma(\text{Te}_i, E)$ is the ionization cross section of the species, Te_i , at electron energy E , $\sigma_{\text{max}}(\text{Te})$ is the maximum ionization cross section for Te , $\gamma(\text{Te}_i^+)$ is the relative electron multiplier response, and $\eta(\text{Te}_i^+)$ is the relative abundance of the isotope measured. While $\gamma(\text{Te}_i^+)$ was assumed to be inversely proportional to square root of the mass number of the ion whose intensity was measured, $\eta(\text{Te}_i^+)$ was calculated from the isotopic distribution for Te . The pressure calibration constant k was computed for each temperature of measurement by employing the total pressure P_{tot} given by Niwa and Sibata [13] and the following relation:

$$P_{\text{tot}} = \sum p(\text{Te}_i) = k \cdot \sum [I(\text{Te}_i^+) \cdot T / \{ [\sigma(\text{Te}_i, E) / \sigma_{\text{max}}(\text{Te})] \cdot \eta(\text{Te}_i^+) \cdot \gamma(\text{Te}_i^+) \}] \quad (2)$$

The mean value of k for each run was calculated and used subsequently to compute the partial pressures according to Eq. (1).

Following empirical relations were considered for deducing R_i , the ratio $[\sigma(\text{Te}_i)/\sigma(\text{Te})]$ valid for $E \geq E_{\text{max}}$:

$$R_i \text{ (at } E \geq E_{\text{max}}) = [\sigma(\text{Te}_i)/\sigma(\text{Te})] = i \left\{ 1 - [(i-1)/i]^i \right\} \quad (3)$$

$$R_i \text{ (at } E \geq E_{\text{max}}) = [\sigma(\text{Te}_i)/\sigma(\text{Te})] = 1.44(i/2)^{1/2} \quad (4)$$

While Eq. (3) is the simplified form of the relation used by Neubert [15] in his study of tellurium clusters, Eq. (4) is of the form used by Rosinger et al. [24] in their study of sulfur clusters. Since E_{max} for all ions were less than 44 eV, the ratios deduced by using Eqs. (3) and (4) were directly used for measurements at 44 eV. In the case of measurements at low electron energies, the values of R_i were modified by using the following approximation suggested by Drowart [25]:

$$R_i \text{ (at } E \leq E_{\text{max}}) = R_i \text{ (at } E \geq E_{\text{max}}) \cdot [(E - \text{AE}) / (E_{\text{max}} - \text{AE})]_i \quad (5)$$

The idea of using $[\sigma(\text{Te}_i, E)/\sigma_{\text{max}}(\text{Te})]$ in Eqs. (1) and (2) and of deducing it through equations of type 3–5 is that absolute values of $\sigma(\text{Te}_i, E)$ or $\sigma_{\text{max}}(\text{Te})$ are not required to be used. Since E_{max} for each ion was $\sim 4\text{AE}$, Eq. (5) got reduced to:

$$R_i \text{ (at } E \leq E_{\text{max}}) = R_i \text{ (at } E \geq E_{\text{max}}) \cdot [(E - \text{AE}) / (3 \cdot \text{AE})]_i \quad (6)$$

Table 1 gives the values of AE obtained by us and the values of R_i deduced in accordance with the above description. For the sake of clarity, the values of R_i have been designated as Set-A and Set-B (44 eV) and as Set-C and Set-D (low eV). The R_i values of Set-A are relatively higher than those of Set-B, and similarly the R_i values of Set-C are relatively higher than those of Set-D. Table 2 gives the least-squares-fitted partial pressure–temperature relations and the values of $p(\text{Te}_i)$ at the mid-temperature, 640 K, of the investigation. Comparison of $p(\text{Te}_i)$ s obtained in Set-A and Set-C or of those obtained in Set-B and Set-D will reveal that the $p(\text{Te}_i)$ s deduced from measurements at 44 eV and at low electron energies agree

Table 6Auxiliary thermodynamic functions used for the sublimation reactions, $\text{iTe(s)} = \text{Te}_i(\text{g})$.

<i>i</i>	$\Delta_f[H_m^\circ(T) - H_m^\circ(298.15 \text{ K})]^a (\text{kJ mol}^{-1})$	$\Delta_f\{[G_m^\circ(T) - H_m^\circ(298.15 \text{ K})]/T\}^b (\text{J mol}^{-1} \text{ K}^{-1})$	
	at <i>T</i> = 650 K	at <i>T</i> = 600 K	at <i>T</i> = 700 K
2 ^c	−7.6	−156.3	−154.5
2 ^d	−5.0	−157.5	−156.3
3 ^e	−11.3	−184.9	−176.0
4 ^e	−14.4	−207.3	−195.6
5 ^e	−18.0	−169.6	−155.4
6 ^e	−20.8	−177.7	−160.9
7 ^e	−23.8	−187.9	−168.7

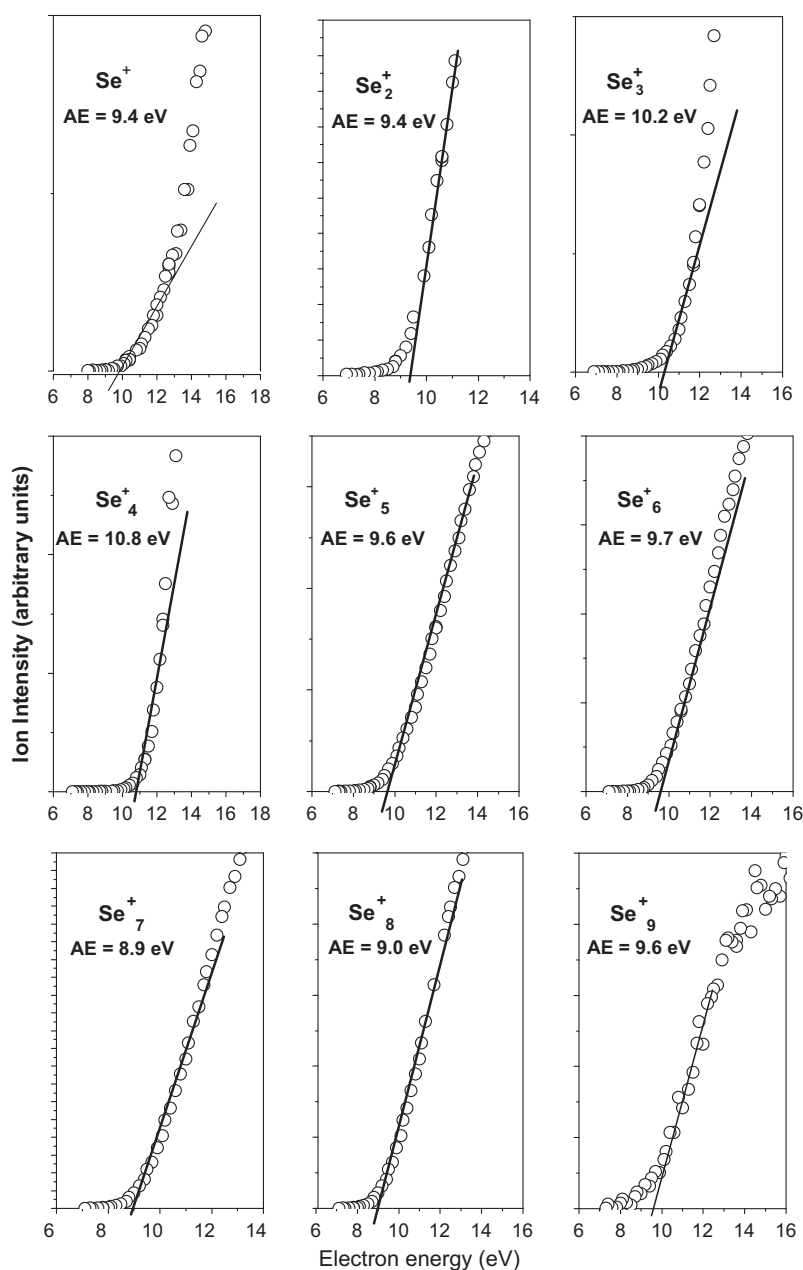
^a Enthalpy increments employed to convert second-law $\Delta_f H_m^\circ(T_{\text{mean}}/K)$ to $\Delta_f H_m^\circ(298.15 \text{ K})$. $\Delta_f H_m^\circ(T_{\text{mean}}/K)$ was computed from the slope of the $\log(p)$ vs. $1/T$ relations.^b Gibbs free energy functions employed to deduce third-law $\Delta_f H_m^\circ(298.15 \text{ K})$.^c Data from Mills [11].^d Data from Grønvold et al. [12].^e Estimated by Neubert [15].**Fig. 2.** Ionization efficiency curves for ions Se_i^+ ($i = 1-9$).

Table 7
Comparison of Mass spectra, $100 \times [I(\text{Se}_i^+)/I(\text{Se}_2^+)]$, obtained in this work with those by others.

i	This work ^a				Fujisaki et al. [17]		Goldfinger and Jeunehomme [16]		Grimley et al. [19]	Berkowitz and Chupka [18]	Yamdagni and Porter [21]
	Low eV	13.2 eV	44 eV	40 eV	70 eV		18 eV		75 eV	75 eV	
	T = 480 K				T = 448 K		Se T = 473 K HgSe T = 484 K		T = 483 K	T = 544 K	T = 600 K
1	0.04	0.11	14.2	21.5	16.3	20.3	1.7	34.9	19.5		
2	100	100	100	100	100	100	100	100	100		
3	86.3	68.3	53.4	50.9	45.6	32.8	71.9	31.2	23.2		
4	190	126	56.7	68.7	86.1	67.0	64.9	16.4	14.4		
5	983	733	185	129	154.8	82.5	117.3	31.7	37.7		
6	1809	1396	319	306.7	396.8	525	189.8	36.3	41.3		
7	393	451	84.4	70.6	52.0	80	46.7	11.5	15.4		
8	63.2	81.0	15.0	14.4	9.4	25	8.2	1.9	2.1		
9	1.46	0.99	0.16	0.1	–	–	–	–	–		

^a $I(\text{Se}_2^+)$ at 44 eV is 13.2 times that at 13.2 eV and 37.8 times that at low electron energy.

Table 8
Partial pressure – temperature relations^a for $\text{Se}_i(\text{g})$ ($i = 2\text{--}9$) deduced by combining the results from three runs over $\text{Se}(\text{s})$.

i	No. of points	Temperature range		$\log[p(\text{Se}_i)/\text{Pa}] = A/(T/\text{K}) + B$	
		T1/K	T2/K	–A	B
Series 1 ^a : Measurements at low electron energies $E_i/\text{eV} \leq (AE_i + 1.2)$					
2	23	400	480	7555 ± 146	13.72 ± 0.33
3	26	400	480	7608 ± 88	13.77 ± 0.20
4	26	400	480	7341 ± 62	13.88 ± 0.14
5	32	380	480	7964 ± 54	15.53 ± 0.13
6	33	380	480	7277 ± 62	14.38 ± 0.15
7	27	390	480	8045 ± 62	15.28 ± 0.14
8	23	410	480	7901 ± 83	14.19 ± 0.19
9	12	450	480	8196 ± 704	12.94 ± 1.5
Series 2; Set-1 ^b : Measurements at 13.2 eV					
2	21	410	480	7680 ± 116	14.23 ± 0.26
3	28	390	480	7818 ± 70	14.41 ± 0.16
4	31	380	480	7323 ± 52	13.70 ± 0.10
5	33	380	480	7897 ± 64	15.39 ± 0.15
6	33	380	480	7348 ± 47	14.51 ± 0.11
7	30	380	480	8093 ± 76	15.41 ± 0.18
8	23	400	480	8213 ± 99	14.91 ± 0.22
9	11	440	480	9214 ± 574	15.17 ± 1.2
Series 2; Set-2 ^c : Measurements at 13.2 eV					
2	21	410	480	7676 ± 116	14.27 ± 0.26
3	28	390	480	7817 ± 71	14.32 ± 0.16
4	31	380	480	7323 ± 52	13.49 ± 0.12
5	33	380	480	7897 ± 64	15.40 ± 0.15
6	33	380	480	7348 ± 47	14.51 ± 0.11
7	30	380	480	8093 ± 75	15.54 ± 0.18
8	23	400	480	8213 ± 99	15.01 ± 0.22
9	11	440	480	9205 ± 574	15.17 ± 1.24
Series 3 ^c : Measurements at 44 eV					
2	28	390	480	7432 ± 66	14.25 ± 0.15
3	32	380	480	7689 ± 73	14.45 ± 0.17
4	32	380	480	7184 ± 51	13.37 ± 0.12
5	32	380	480	7905 ± 59	15.32 ± 0.14
6	33	380	480	7300 ± 44	14.26 ± 0.10
7	30	390	480	7969 ± 50	15.06 ± 0.12
8	26	410	480	8083 ± 77	14.51 ± 0.18
9	12	430	480	9528 ± 1492	15.44 ± 3.2

^a Computed by using $\sigma(\text{Se}_i)/\sigma(\text{Se}) = [1.44 (i/2)^{1/2}] [(E_i - AE_i)/(E_{i,\text{max}} - AE_i)]$; $E_{i,\text{max}} = 4 AE_i$.
^b Computed by using $\sigma(\text{Se}_i)/\sigma(\text{Se})$ according to the equation given above but with $E_i = 13.2$.
^c Computed by using $\sigma(\text{Se}_i)/\sigma(\text{Se}) = 1.44 (i/2)^{1/2}$.

reasonably well with each other, especially if one considers that no fragmentation correction was applied for measurements at 44 eV. This observation could be taken to indicate the reliability of our measurements and the mutual compatibility of ion intensities with the relations employed to deduce ionization cross section ratio

R_i . The uncertainties in the coefficients of the p – T relations in Set-C and Set-D are either the same or lower than for Set-A and Set-B, which is taken to indicate good electron energy control of the ion-source, so very important for measurements at low electron energy.

Table 3 compares the $p(\text{Te}_i)$ s determined in this study with those deducible from the p – T relation given by Neubert [15]. The mole fractions deduced from the $p(\text{Te}_i)$ s are also given in the same table. Qualitatively, the findings of the two studies are consistent: (1) that the vapor phase is almost wholly due to $\text{Te}_2(\text{g})$; and (2) that the relative abundances of minor species decrease in the following order: $(\text{Te}_3 \approx \text{Te}_5) > (\text{Te}_4 \approx \text{Te}_6) > \text{Te}_7$. Meaningful quantitative comparison of partial pressures from this study with those from Neubert are with Set-A and Set-C values, since they have a common basis of computation of ionization cross sections. It is readily seen that the $p(\text{Te}_i)$ s obtained in the present study are higher than those reported by Neubert – by about 50% for the predominant vapor species, $\text{Te}_2(\text{g})$ (mole fraction of which is ~ 0.95) and by a factor of 2–5 for the other minor species. Since the discrepancy is not uniform for all vapor species, we believe that besides the difference in pressure calibration procedures employed in the two studies, neglect of the term $[(E_{\text{max}} - AE)]_i$ by Neubert, and some unknown factor (associated with measurements at electron energies that lie in the steep rising linear portion of ionization efficiency curves) could be the reason. That in the present study the $p(\text{Te}_i)$ s at 44 eV and low electron energy agree reasonably well leads us to believe that our results are more reliable. We, however, seek to recommend Set-D values in the present study based on the reasoning that (1) the empirical relation (4) yields ionization cross section ratios in accord with those selected by Drowart [26] for sulfur clusters or selenium clusters: $\sigma(\text{S}_8)/\sigma(\text{S}) = 2$ and $\sigma(\text{Se}_6)/\sigma(\text{Se}) = 2$; (2) Set-B and Set-D values agreeing reasonably well, uncertainties associated with fragmentation are likely to be minimal in measurements at low eV (that is in Set-D). An uncertainty of 20% was assumed in the value of total vapor pressure used for pressure calibration. Accordingly, uncertainty in recommended $p(\text{Te}_2)$ was estimated as 20%, and the uncertainty in partial pressures of minor species could be higher, even to an extent of a factor of 2, in view of their very low abundances and approximations involved in the ionization cross sections.

It is gratifying to note that the $p(\text{Te}_2)$ deduced in the present study (using the total vapor pressure value of Niwa and Sibata for pressure calibration) is in excellent agreement with the results of Langmuir free sublimation experiment by Korneeva et al. [27]. The apparent $p(\text{Te}_2)$ at $T = 640$ K deducible from the p – T relation given by Korneeva et al. is 1.0 Pa, and the corrected $p(\text{Te}_2)$ is ~ 0.95 Pa. We sought to deduce equilibrium constants for the following gas-phase reactions:

Table 9Partial pressures, $[p(\text{Se}_i)/\text{Pa}]$ ($i = 2-9$) at $T_{\text{mean}} = 430$ K, computed from p - T relations given in Table 8.

i	AE _{i} of Se_i^+ (eV)	E_i of Se_i^+ (eV)	$p(\text{Se}_i)/\text{Pa}$ at E_i^a	$p(\text{Se}_i)/\text{Pa}$ at 13.2 eV		$p(\text{Se}_i)/\text{Pa}$ at 44 eV ^d
				Set 1 ^b	Set 2 ^c	
2	9.4	10.6	1.41×10^{-4}	2.34×10^{-4}	2.62×10^{-4}	9.25×10^{-4}
3	10.2	11.3	1.19×10^{-4}	1.69×10^{-4}	1.38×10^{-4}	3.70×10^{-4}
4	10.8	11.3	6.43×10^{-4}	4.67×10^{-4}	2.88×10^{-4}	4.60×10^{-4}
5	9.6	10.6	1.02×10^{-3}	1.06×10^{-3}	1.08×10^{-3}	8.64×10^{-4}
6	9.7	10.6	2.86×10^{-3}	2.64×10^{-3}	2.64×10^{-3}	1.92×10^{-3}
7	8.9	9.7	3.72×10^{-4}	3.88×10^{-4}	5.24×10^{-4}	3.37×10^{-4}
8	9.0	9.7	6.54×10^{-5}	6.46×10^{-5}	8.26×10^{-5}	5.16×10^{-5}
9	9.6	10.6	7.58×10^{-7}	5.52×10^{-7}	5.79×10^{-7}	1.91×10^{-7}

^a Computed from the p - T relations given in Table 8, Series 1.^b Computed from the p - T relations given in Table 8, Series 2, Set 1.^c Computed from the p - T relations given in Table 8, Series 2, Set 2.^d Computed from the p - T relations given in Table 8, Series 3.**Table 10**Comparison of partial pressures $[p(\text{Se}_i)/\text{Pa}]$ measured in this study^a with previous mass spectrometric studies.

i	$T = 469$ K				$T = 500$ K				$T = 473$ K	
	This work			Berkowitz and Chupka [18]	This work			Huang et al. [20]	Keller et al. ^b [28]	
	Low eV	13.2 eV ^c	44 eV		Low eV	13.2 eV ^c	44 eV			
2	4.10×10^{-3}	7.16×10^{-3}	2.53×10^{-2}	6.12×10^{-3}	4.07×10^{-2}	7.41×10^{-2}	2.43×10^{-1}	5.78×10^{-2}	3.57×10^{-3}	
3	3.53×10^{-3}	5.50×10^{-3}	1.14×10^{-2}		3.58×10^{-2}	5.94×10^{-2}	1.19×10^{-1}	6.08×10^{-2}	4.07×10^{-6}	
4	1.69×10^{-2}	1.22×10^{-2}	1.13×10^{-2}		1.58×10^{-1}	1.13×10^{-1}	1.00×10^{-1}	1.11×10^{-1}	9.82×10^{-6}	
5	3.54×10^{-2}	3.56×10^{-2}	2.92×10^{-2}	3.34×10^{-2}	4.00×10^{-1}	3.94×10^{-1}	3.24×10^{-1}	9.52×10^{-1}	3.07×10^{-2}	
6	7.31×10^{-2}	6.96×10^{-2}	5.00×10^{-2}	4.90×10^{-2}	6.70×10^{-1}	6.52×10^{-1}	4.61×10^{-1}	1.22	1.50×10^{-1}	
7	1.34×10^{-2}	1.43×10^{-2}	1.19×10^{-2}	1.30×10^{-2}	1.55×10^{-1}	1.67×10^{-1}	1.34×10^{-1}	3.55×10^{-1}	4.03×10^{-2}	
8	2.20×10^{-3}	2.50×10^{-3}	1.89×10^{-3}	1.93×10^{-3}	2.44×10^{-2}	3.05×10^{-2}	2.21×10^{-2}	2.94×10^{-2}	3.62×10^{-3}	
9	2.91×10^{-5}	3.34×10^{-5}	1.33×10^{-5}		3.60×10^{-4}	5.55×10^{-4}	2.40×10^{-4}			
$\Sigma p(\text{Se}_i)^d$	1.49×10^{-1}	1.47×10^{-1}	1.41×10^{-1}	1.03×10^{-1}	1.48	1.49	1.40	2.79	2.28×10^{-1}	

^a The values attributed to this work were deduced from the $p(\text{Se}_i)$ - T relations valid for $T \leq 480$ K. That is, by extrapolation slightly beyond the melting temperature of 493 K.^b Mass spectrometry coupled to a solid state galvanic cell (and not a conventional Knudsen effusion mass spectrometric study).^c Computed from the p - T relations given in Table 8 for Series 2, Set-1.^d Total vapor pressure.

$$\text{Te}_i(\text{g}) = (i/2)\text{Te}_2(\text{g}) \quad (7)$$

Table 4 gives the results deduced from our recommended $p(\text{Te}_i)$ s at $T = 640$ K and those from Neubert also. There is reasonably good agreement between the two studies, unlike in $p(\text{Te}_i)$ s. It might be that different kinds of errors including the random ones combine in such a way that overall discrepancy has got reduced to within a factor of 2. The value of K° recommended by Mills [11] (9.3×10^{-7} for $i = 5$) is very close to the value obtained in the present study.

3.1.2. Sublimation enthalpies

The standard molar enthalpies for the following reactions were evaluated by second- and third-law methods:

$$i\text{Te}(\text{s}) = \text{Te}_i(\text{g}) \quad (8)$$

where $i = 2-7$. Table 5 gives the results. Having recommended Set-D partial pressures, only the enthalpy values corresponding to Set-D partial pressures are given. The values from Set-A, Set-B, and Set-C partial pressures were also very close to these values. The second-law enthalpy value at $T_{\text{mean}} = 640$ K was deduced from the coefficient A in the recommended p - T relation and converted to $T = 298$ K. The third-law enthalpy given in Table 5 is the mean of third-law values deduced from $p(\text{Te}_i)$ at each temperature. The recommended enthalpy value at $T = 298$ K is the mean of second- and third-law values. The required auxiliary thermal functions employed in second- and third-law evaluations (enthalpy increments and Gibbs free energy functions), were taken from Grønvold et al.

[12] for $i = 2$ and from Neubert [15] for $i = 3-7$. These are given in Table 6.

In Table 5, we have also given the values corresponding to the study of Neubert [15] for comparison. The agreement between second- and third-law values for $i = 2$ is good in both studies, but admittedly better for Neubert's data. The difference between the second- and third-law values is larger than 10 kJ mol^{-1} for Te_4 , Te_5 , and Te_7 in the present work whereas difference of such magnitude was seen for Te_4 , Te_5 , and Te_6 in Neubert's results. Consistent with the fact that the partial pressures obtained in the present study are higher, the third-law values from the present study are slightly higher (by $\sim 2-8 \text{ kJ mol}^{-1}$). The uncertainties in recommended values of the present study were deduced by error propagation by considering the statistical uncertainties in second- and third-law values as well as those that would arise due to possible errors in temperatures, partial pressures, and auxiliary functions (all estimated).

3.2. Elemental selenium

3.2.1. Partial pressures

The ions Se_i^+ ($i = 1-9$) were detected in the mass spectrum of the equilibrium vapor over $\text{Se}(\text{s})$. These ions were also identified in the same way as were Te_i^+ . Fig. 2 shows portions of the ionization efficiency curves from which the appearance energy (AE) for each ion was determined. The estimated error on AE values is ± 0.5 eV. Low values of AE for all ions were taken to indicate that at low electron energies (that is, not very far from their AEs), simple ionization of $\text{Se}_i(\text{g})$ ($i = 1-9$) would occur. The AEs of Se_3^+ and Se_4^+ are slightly

Table 11Comparison of mole fractions, $x(\text{Se}_i)$, measured in this study^a with previous mass spectrometric studies.

<i>i</i>	<i>T</i> = 483 K				<i>T</i> = 500 K				<i>T</i> = 473 K	
	This work			Grimley et al. [19] 18 eV	This work			Berkowitz and Chupka ^c [18]	Huang et al. [20]	Keller et al. ^d [28]
	Low eV	13.2 eV ^b	44 eV		Low eV	13.2 eV ^b	44 eV			
2	2.75×10^{-2}	4.92×10^{-2}	1.78×10^{-1}		2.75×10^{-2}	4.97×10^{-2}	1.74×10^{-1}	4.90×10^{-2}	2.08×10^{-2}	1.56×10^{-2}
3	2.40×10^{-2}	3.86×10^{-2}	8.27×10^{-2}	3.00×10^{-2}	2.41×10^{-2}	3.98×10^{-2}	8.45×10^{-2}	1.20×10^{-3}	2.18×10^{-2}	1.79×10^{-5}
4	1.10×10^{-1}	7.97×10^{-2}	7.64×10^{-2}	$<2 \times 10^{-2}$	1.06×10^{-1}	7.59×10^{-2}	7.19×10^{-2}		4.01×10^{-2}	4.30×10^{-5}
5	2.53×10^{-1}	2.53×10^{-1}	2.19×10^{-1}	4.60×10^{-1}	2.70×10^{-1}	2.64×10^{-1}	2.32×10^{-1}	3.58×10^{-1}	3.42×10^{-1}	1.35×10^{-1}
6	4.73×10^{-1}	4.57×10^{-1}	3.41×10^{-1}	4.00×10^{-1}	4.51×10^{-1}	4.37×10^{-1}	3.27×10^{-1}	4.27×10^{-1}	4.37×10^{-1}	6.57×10^{-1}
7	9.66×10^{-2}	1.04×10^{-1}	8.87×10^{-2}	6.00×10^{-2}	1.04×10^{-1}	1.12×10^{-1}	9.48×10^{-2}	1.40×10^{-1}	1.27×10^{-1}	1.77×10^{-1}
8	1.56×10^{-2}	1.86×10^{-2}	1.45×10^{-2}	1.00×10^{-2}	1.65×10^{-2}	2.04×10^{-2}	1.58×10^{-2}	2.42×10^{-2}	1.06×10^{-2}	1.59×10^{-2}
9	2.15×10^{-4}	2.86×10^{-4}	1.26×10^{-4}		2.38×10^{-4}	3.70×10^{-4}	1.73×10^{-4}			

^a The values attributed to this work were deduced from the $p(\text{Se}_i)$ – T relations valid for $T \leq 480$ K.^b Computed from the p – T relations given in Table 8 for Series 2, Set-1.^c Deduced by us by employing the equilibrium constant – temperature relations given by the authors for sublimation to $\text{Se}_6(\text{g})$; for various homogeneous gas phase reactions involving $\text{Se}_6(\text{g})$ and $\text{Se}_i(\text{g})$ ($i = 2, 5, 7, 8$); and the reaction involving $\text{Se}_3(\text{g})$ and $\text{Se}_2(\text{g})$.^d Deduced by us from the partial pressures given by the authors and listed in Table 10 also.

higher, but since clear negative breaks were not observed in Se_5 or Se_6 (unlike that in Te_2^+ at around the AE of Te^+), we assigned Se_3^+ and Se_4^+ as parent ions at low electron energies. Three series of temperature dependence measurements were undertaken, one at very low electron energies, $E \leq (\text{AE} + 1.2 \text{ eV})$, at slightly higher but constant electron energy of 13.2 eV, and at high electron energy of 44 eV. The ion intensity of Se^+ was very low for convenient measurements at many temperatures and also was not as steady as other ions. Therefore, they were not considered for evaluating partial pressures or thermodynamic quantities.

Table 7 compares the mass spectrum obtained in this work with those reported in other studies. For each ion, the mean of ion intensities measured in three runs at $T = 480$ K (the highest temperature of our investigation), corrected for relative isotope abundances and relative detective gains, is given in this table. The mass spectra of vapor over solid selenium are consistent despite the differences in the electron energies: Se_6^+ is the most abundant ionic species and Se_5^+ closely following it. The results from this work shown at three levels of electron energies show increasing effect of fragmentation with increase in electron energy. The measurements of Berkowitz and Chupka [18] and Yamdagni and Porter [21], both over molten selenium and at 75 eV, yielded Se_2^+ as the major ion, apparently indicating very high level of fragmentation.

Like for elemental tellurium, the pressure calibration was performed again by using the total vapor pressure determined by Torsion effusion method [14], and hence the equation pertinent to $p(\text{Se}_i)$ is similar to Eq. (2) used for deducing $p(\text{Te}_i)$. For ionization cross sections, Eq. (3) was not employed since for tellurium, it was done only to enable comparison with the results of Neubert [15] who proposed the relation. Eqs. (4) to (6) were put to use for evaluation, Eq. (4) for measurements at 44 eV as well as 13.2 eV, and Eq. (6) at low electron energies as well as 13.2 eV. Thus, measurements at 13.2 eV provided the means of comparing the results of evaluations with two sets of ionization cross section ratios. Table 8 gives the least-squares-fit p – T relations for Se_i ($i = 2$ –9) deduced from the ion intensities measured at different electron energies. Table 9 enables a comparison of $p(\text{Se}_i)$ values at $T = 430$ K (the mean temperature of our investigation) deduced from the p – T relations given in Table 8. One infers that for $i = 4$ –8, the partial pressure values deduced from measurements at different electron energies are in reasonable accord with each other. Even for $i = 2, 3$, and 9, while the values corresponding to low electron energies and 13.2 eV agree reasonably, the values corresponding to 44 eV are too high for $i = 2$ and 3 and too low for $i = 9$. The most likely reason for such results at 44 eV is fragmentation, although why only Se_9

and not Se_8 and Se_7 also were low is not clear. We seek to recommend the values of $p(\text{Se}_i)$ corresponding to low electron energies based on the reasoning that fragmentation would be minimum and that the values at 13.2 eV (both sets of ionization cross section ratios) are not very different from them.

Tables 10 and 11 compare the results from this study with those reported by others, Table 10 dealing with partial pressures, and Table 11 dealing with relative mole fractions. As for partial pressures, Huang et al. [20] and Berkowitz and Chupka [18] gave their results in tabular form at $T = 500$ K and 469 K, respectively, and we deduced our values from the p – T relations given in Table 8. With the exception of Se_3 and Se_4 , the results from different studies can be reconciled as being reasonably consistent, considering the complexity involved in determining the partial pressures of cluster species. As for mole fractions, we have for comparison the results from Grimley et al. [19] also, which place Se_5 slightly ahead of Se_6 unlike all other studies in which Se_6 holds the top position, although Se_5 closely follows it. The results for the species Se_2 , Se_3 , and Se_4 reveal inconsistencies amongst various studies, although reasonable agreement with our results exists for Se_2 with those of Berkowitz and Chupka [18]; for Se_3 with those of Grimley et al. [19] and Huang et al. [20]; and for Se_4 with Huang et al. In general, it may be stated that the values of mole fractions obtained in this study agree more uniformly with those of Huang et al. than with others. In the last column of Tables 10 and 11 are given the results corresponding to an investigation which is not a conventional KEMS study [28]. It consisted of a solid state galvanic cell $\text{Pt, Ag/AgI/Ag}_2\text{Se, Pt}$, built into the effusion cell of a mass spectrometer. The results from this investigation place Se_6 at the top (but much higher than do those from any other study) and place Se_7 subsequently (even slightly higher than Se_5). Overall, the composition follow in this order: $\text{Se}_6 > \text{Se}_7 \approx \text{Se}_5 > \text{Se}_8 \approx \text{Se}_2 \gg \text{Se}_3 \geq \text{Se}_4$. There is reasonable consistency amongst the values of $\sum p(\text{Se}_i)$ from different studies, but it is only a mask for some serious discrepancy in $p(\text{Se}_i)$ s or $x(\text{Se}_i)$ s.

3.2.2. Sublimation enthalpies

The partial pressures of $\text{Se}_i(\text{g})$ were evaluated by second- and third-law methods to deduce sublimation enthalpies corresponding to the reactions:



where $i = 2$ –9. Table 12 gives the results. The required auxiliary thermal functions were deduced by using the pertinent C_p – T

Table 12Results of second- and third-law evaluation of $p(\text{Se}_i)$ s from three runs corresponding to measurements at different electron energies.

<i>i</i>	$\Delta_r H^\circ(298.15 \text{ K})/(\text{kJ mol}^{-1})$ for $i \text{ Se(s)} = \text{Se}_i(\text{g})$					
	Low $E_i (E_i \leq \text{AE}_i + 1.2)$		$E_i = 13.2 \text{ eV}^a$		$E_i = 44 \text{ eV}$	
	II law	III law	II law	III law	II law	III law
2	146.1 ± 2.8	142.7 ± 0.2	148.6 ± 2.2	140.7 ± 0.1	143.7 ± 1.3	135.9 ± 0.1
3	148.9 ± 1.7	151.5 ± 0.1	152.8 ± 1.3	150.1 ± 0.1	150.2 ± 1.4	147.3 ± 0.1
4	144.2 ± 1.2	140.8 ± 0.1	146.6 ± 1.0	142.0 ± 0.1	140.9 ± 1.0	142.1 ± 0.1
5	156.0 ± 1.0	145.8 ± 0.2	154.7 ± 1.2	145.8 ± 0.2	154.9 ± 1.1	146.4 ± 0.1
6	143.0 ± 1.2	137.1 ± 0.1	144.4 ± 1.0	137.4 ± 0.1	143.4 ± 1.0	138.5 ± 0.1
7	158.1 ± 1.2	151.2 ± 0.6	158.9 ± 1.5	151.1 ± 0.1	156.5 ± 1.0	151.7 ± 0.1
8	156.0 ± 1.6	156.4 ± 0.1	161.8 ± 1.9	156.2 ± 0.1	159.1 ± 1.5	157.1 ± 0.1
9 ^b	156.9 ^c ± 13.5		176.4 ± 11.0		182.4 ± 29.0	

^a Deduced from partial pressures corresponding to Series 2, Set 1.^b Values are given at $T_m = 465 \text{ K}$, 460 K , and 455 K , respectively at low eV, 13.2 eV, and 44 eV.^c $\Delta_r H^\circ(298.15 \text{ K})$ is estimated to be $161.1 \text{ kJ mol}^{-1}$ by using $\Delta_r [H_m^\circ(T) - H_m^\circ(298)]$, based on a least-squares fit of $\Delta_r [H_m^\circ(T) - H_m^\circ(298)]$ against i (for Se_3 – Se_8).**Table 13**Auxiliary thermal functions employed in the second-law^a and third-law^b evaluation of enthalpies for $i \text{ Se(s)} = \text{Se}_i(\text{g})$ ($i = 2$ – 8)^c.

<i>T/K</i>	Se(s)	Se ₂ (g)	Se ₃ (g)	Se ₄ (g)	Se ₅ (g)	Se ₆ (g)	Se ₇ (g)	Se ₈ (g)
$[H_m^\circ(T) - H_m^\circ(298)]/(\text{kJ mol}^{-1})$								
380	2.10	3.42	4.50	6.35	8.38	10.40	12.36	14.32
400	2.62	4.25	5.61	7.93	10.45	12.98	15.41	17.86
420	3.15	5.08	6.73	9.51	12.53	15.55	18.48	21.41
440	3.69	5.90	7.85	11.10	14.62	18.14	21.55	24.96
460	4.23	6.72	8.98	12.70	16.72	20.73	24.63	28.53
480	4.77	7.54	10.10	14.30	18.82	23.33	27.71	32.11
$[S_m^\circ(T) - S_m^\circ(298)]/(\text{J mol}^{-1} \text{ K}^{-1})$								
380	6.21	10.13	13.32	18.80	24.81	30.82	36.61	42.42
400	7.55	12.26	16.17	22.85	30.13	37.41	44.44	51.49
420	8.85	14.28	18.90	26.71	35.21	43.71	51.91	60.15
440	10.09	16.20	21.51	30.42	40.07	49.72	59.06	68.43
460	11.29	18.02	24.01	33.97	44.73	55.49	65.90	76.35
480	12.45	19.76	26.41	37.38	49.20	61.01	72.47	83.96
$S_m^\circ(298)/(\text{J mol}^{-1} \text{ K}^{-1})$								
298	42.09	247.38	308.9	340.6	398.3	428.5	487	526.2

^a Second-law: $\Delta_r H_m^\circ(298)] = \Delta_r H_m^\circ(T_{\text{mean}})] - \Delta_r [H_m^\circ(T) - H_m^\circ(298)]$; $\Delta_r H_m^\circ(T_{\text{mean}})]/(\text{kJ mol}^{-1}) = (-A)8.3143 \times 10^{-3} \ln(10)$; A is the coefficient of the least-square-fit relation $\log(p) = A/T + B$.^b Third-law: $\Delta_r H_m^\circ(298)] = -T \{8.3143 \times 10^{-3} \ln[(p/\text{Pa})/(101325 \text{ Pa})] + \Delta_r \text{GEF}\}$; $\text{GEF} = [H_m^\circ(T) - H_m^\circ(298)]/T - [S_m^\circ(T) - S_m^\circ(298)] - S_m^\circ(298)$.^c Taken from Ref. [7]. $[H_m^\circ(T) - H_m^\circ(298)]$ and $[S_m^\circ(T) - S_m^\circ(298)]$ values were computed from the recommended molar heat capacity-temperature relations.

relations and the $S_m^\circ(298)$ values given in the recently brought out book on chemical thermodynamics of selenium [7]. Absence of thermal functions for Se_9 did not permit us perform a third-law evaluation, which would have been desirable in view of the fact that for Se_9 , only very few number of points could be collected in each run. Table 13 gives the values of thermal functions used by us in our evaluations. That the agreement between second- and third-

law values is reasonably satisfactory indicates absence of any serious temperature dependent error in our measurements or auxiliary functions. Table 14 gives third-law enthalpy values for all temperatures in one run. There is no trend in enthalpy values with temperature for any species. Therefore, we seek to recommend mean of second- and third-law values corresponding to measurements at low electron energy.

Table 15 compares the sublimation enthalpies obtained in this work with those available in literature. Apart from the present study, only the results of Huang et al. [20] are from partial pressures of all species directly measured. The authors, however, confessed that their temperature range of measurements is small and that their main objective was to compare Langmuir and Knudsen pressures and enthalpy changes and not to obtain highly reliable enthalpy values. The results of Fujisaki et al. [17] were not from partial pressures but from plots of $\log(\text{IT})$ vs. $1/T$ us. The agreement with our results seem to be best in this case. Thus these are the only two mass spectrometric studies that appear to have covered a good temperature range, and the present study appears to be the only one that gives the p – T relations directly deduced from ionic species representing the neutral species.

3.3. Atomization enthalpies of tellurium, selenium, and sulfur clusters

Atomization enthalpy is a thermodynamic property that is believed to be of fundamental interest – to obtain a good understanding of bonding in clusters. Such information has been presented by Berkowitz and Chupka [18] and Keller et al. [28] for selenium, Neubert [15] for tellurium, and Rosinger et al. [24] for sulfur clusters. Since monomeric species were not measured on all the three systems (S or Se, or Te), it was necessary to take from literature [12] enthalpy of formation of monomer, which in turn was to be deduced by using dissociation energy of dimeric species, spectro-

Table 14Third-law enthalpies $\Delta_r H_m^\circ(298)/(\text{kJ mol}^{-1})$ for $i \text{ Se(s)} = \text{Se}_i(\text{g})$ at different temperatures in run 1 at low electron energy.

<i>T/K</i>	<i>i</i> = 2	<i>i</i> = 3	<i>i</i> = 4	<i>i</i> = 5	<i>i</i> = 6	<i>i</i> = 7	<i>i</i> = 8
480	142.4	151.2	140.2	145.1	136.8	150.7	156.7
470	142.6	151.7	140.8	145.1	136.7	150.9	156.5
460	142.9	151.5	140.5	145.2	136.6	150.8	156.0
450	142.9	151.7	140.8	145.3	136.7	150.9	156.4
440	143.5	151.7	141.0	145.4	136.8	150.9	155.9
430	142.7	151.3	140.6	145.2	136.6	151.0	156.2
420	142.7	150.8	140.5	145.4	136.7	150.9	156.9
410		151.4	141.1	146.5	137.3	151.7	155.9
400				147.1	138.5		
390				146.8	138.3		
380				146.1	136.7		
Mean	142.8 ± 0.4	151.4 ± 0.3	140.7 ± 0.3	145.8 ± 0.7	137.1 ± 0.7	151.0 ± 0.3	156.3 ± 0.4

Table 15Comparison of enthalpies (kJ mol^{-1}) for $i \text{ Se}(s, l) = \text{Se}_i(g)$ from different studies.

<i>i</i>	This work ^a <i>T</i> = 298 K	Berkowitz and Chupka ^b [18] <i>T</i> = 298 K	Fujisaki et al. ^c [17] <i>T</i> = 418 K	Huanag et al. ^d [20] <i>T</i> = 500 K	Selenium Book ^e [7] <i>T</i> = 298 K	Keller et al. ^f [28] <i>T</i> = 0 K
2	144.4 ± 3.3	143.1 ± 3.3	144.2 ± 2.9	153.1 ± 7.1	141.1 ± 3.0	145.02
3	150.2 ± 2.1	160.7 ± 6.3	147.5 ± 1.9	144.3 ± 4.2	178 ± 10	184.5
4	142.5 ± 2.1		141.7 ± 1.9	142.7 ± 3.8	163 ± 12	190.8
5	150.9 ± 5.2	169.5 ± 6.3	151.6 ± 1.6	163.6 ± 4.2	144.4 ± 4.3	143.9
6	140.1 ± 3.2	157.3 ± 6.3	141.9 ± 1.7	157.7 ± 3.3	136.1 ± 3.8	140.2
7	154.7 ± 2.7	173.6 ± 6.3	160.6 ± 1.9	177.0 ± 3.8	150.2 ± 4.5	151.5
8	156.2 ± 2.0	186.2 ± 6.3	166.9 ± 2.8	182.8 ± 3.3	156.8 ± 3.0	160.7
9	161.1 ± 13.5					

^a Mean of second- and third-law values from low electron energy measurements except for Se_9 , which is second-law value.^b Direct information obtained for Se_6 and the rest by combining this information with those for gas phase equilibria involving $\text{Se}_6(g)$.^c Computed by us from the slopes of the $\log(I^*T)$ vs. $1/T$ given by the authors.^d Deduced by us by combining the enthalpy of vaporization given by the authors (that is, for liquid selenium) with enthalpy of fusion of solid selenium = 9.6 kJ mol^{-1} determined by Berkowitz and Chupka.^e Enthalpy of formation recommended in this book.^f Enthalpy of vaporization, presumably obtained by third-law. Mass spectrometric measurements with an effusion cell built into a solid state galvanic cell.**Table 16**Comparison of atomization enthalpy per atom, $\Delta_{at}H_i^\circ/i$, and the increment in atomization enthalpy, $\Delta_{at}H_i^\circ - \Delta_{at}H_{i-1}^\circ$ for tellurium, selenium, and sulfur clusters.

<i>i</i>	$\text{Te}_i(g)$		$\text{Se}_i(g)$		$\text{S}_i(g)$	
	Neubert [15]	This work	Berkowitz and Chupka [18]	Keller et al. [28]	This work	Rosinger et al. [24]
<i>Atomization enthalpy $\Delta_{at}H_i^\circ/(kJ mol^{-1})$</i>						
2	261.0	260.9	332.1	329.1	330.8	425.7
3	431.7	434.6	552.1	526.6	562.6	695.3
4	611.2	616.8		757.4	807.9	978.5
5	868.0	854.6	1018.6	1041.3	1037.2	1260.4
6	1057.2	1045.6	1268.4	1282.1	1285.6	1544.2
7	1249.5	1229.7	1489.7	1507.8	1508.6	1819.1
8			1714.7	1735.7	1744.7	2107.0
9					1977.4	
<i>Atomization enthalpy per atom $(\Delta_{at}H_i^\circ/i)/(kJ mol^{-1})$</i>						
2	130.5	130.5	166.1	164.5	165.4	212.9
3	143.9	144.9	184.0	175.5	187.5	231.8
4	152.8	154.2		189.3	202.0	244.6
5	173.6	170.9	203.7	208.3	207.4	252.1
6	176.2	174.3	211.4	213.7	214.3	257.4
7	178.5	175.7	212.8	215.4	215.5	259.9
8			214.3	217.0	218.1	263.4
9					219.7	
<i>Increment in atomization enthalpy $(\Delta_{at}H_i^\circ - \Delta_{at}H_{i-1}^\circ)/(kJ mol^{-1})$</i>						
3	170.7	173.7	220.0	197.6	231.8	269.6
4	179.5	182.3		230.7	245.3	283.2
5	256.8	237.8		283.9	229.2	281.9
6	189.2	191.1	249.8	240.7	248.4	283.9
7	192.3	184.1	221.3	225.7	223.0	274.9
8			225.0	227.8	236.1	287.9
9					232.7	

scopic data for which are available. Neubert has compared the results corresponding to all three systems and noted that (1) atomization enthalpy decreases from sulfur to tellurium: $\Delta_{at}H^\circ(\text{S}_5) > \Delta_{at}H^\circ(\text{Se}_5) > \Delta_{at}H^\circ(\text{Te}_5)$; (2) atomization enthalpy per atom, $(\Delta_{at}H_i^\circ/i)$, increases with *i* (from 1 to 5) and then remains nearly constant; and (3) increment of atomization enthalpy, $\Delta_{at}H_i^\circ - \Delta_{at}H_{i-1}^\circ$ shows a maximum at *i* = 5 for Te and Se and at *i* = 5, 6, 8 for sulfur. Table 16 gives information related to atomization enthalpies for sulfur, selenium, and tellurium clusters. While agreeing with Neubert's [15] first remark that atomization enthalpy decreases from sulfur to tellurium, we feel that it might be more appropriate to make following statements: (1) atomization enthalpy per atom increases with *i*, but the increase is at much slower rate where *i* > 5; and (2) the increment in atomization enthalpy shows a maximum for tellurium at *i* = 5, while for selenium and sulfur, it is nearly uniform around a mean value of $281 \pm 7 \text{ kJ mol}^{-1}$ for sulfur (Rosinger et al. [24]) and $236 \pm 11 \text{ kJ mol}^{-1}$ for selenium (this work). In this context, although the concluding statement by

Berkowitz and Chupka [18] that the abundance of a vapor species is not just a consequence of greater energy per bond, but also its accidental volatility might appear to be of some relevance, the validity of this statement is arguable since the volatility in equilibrium (in Knudsen, if not in Langmuir conditions) is known to be determined by thermochemical characteristics of condensed and gaseous components, resulting from bond energy. Caution was also advocated by Rosinger et al. [24] against the use of bond energy data in thermodynamic cycles for assuming ring structure to the sulfur gaseous species.

4. Conclusions

Knudsen effusion mass spectrometric studies on elemental tellurium and selenium were conducted in the temperature range of 590–690 K and 380–480 K, respectively. The neutral species observed were: $\text{Te}_i(g)$ (*i* = 2–7) and $\text{Se}_i(g)$ (*i* = 2–9). The major species

over elemental tellurium was confirmed to be $\text{Te}_2(\text{g})$ (1.0 Pa at $T = 640 \text{ K}$; $\sim 95\%$) and that over elemental selenium was found to be $\text{Se}_6(\text{g})$ ($2.64 \times 10^{-3} \text{ Pa}$ at $T = 430 \text{ K}$; $\sim 47\%$), closely followed by $\text{Se}_5(\text{g})$ ($1.06 \times 10^{-3} \text{ Pa}$ at $T = 430 \text{ K}$; $\sim 25\%$). From the partial pressures, the thermodynamic data for the sublimation reactions $i \text{ Te(s)} = \text{Te}_i(\text{g})$ and $i \text{ Se(s)} = \text{Se}_i(\text{g})$ were deduced by second- and third-law methods. The recommended enthalpy of sublimation at $T = 298 \text{ K}$ for tellurium clusters varied from the lowest of (158.6 ± 6.6) kJ mol^{-1} for $\text{Te}_2(\text{g})$ to the highest of (236.5 ± 15.9) kJ mol^{-1} for $\text{Te}_7(\text{g})$. The recommended enthalpy of sublimation at $T = 298 \text{ K}$ for selenium clusters varied from the lowest of (140.1 ± 3.2) kJ mol^{-1} for $\text{Se}_6(\text{g})$ to the highest of (160.1 ± 13.5) kJ mol^{-1} for $\text{Se}_9(\text{g})$. The atomization enthalpies of tellurium and selenium clusters were also deduced by using the recommended enthalpies of formation of monomeric species. Comparison of our results with those from previous studies reveal that while there is a general agreement amongst different studies about the near total dominance of $\text{Te}_2(\text{g})$ in tellurium vapor and the highest abundance of Se_6 in selenium vapor, somewhat glaring discrepancies still exist with regard to minor species. Perhaps, a new Knudsen effusion mass spectrometric study by another group having modern equipment might help resolving these discrepancies.

References

- [1] B. Saha, R. Viswanathan, M. Sai Baba, C.K. Mathews, *High Temp.-High Press.* 20 (1988) 47–58.
- [2] M. Sai Baba, R. Viswanathan, C.K. Mathews, *Rapid Commun. Mass Spectrosc.* 10 (1996) 691–698.
- [3] T.S. Lakshmi Narasimhan, R. Viswanathan, *Open Thermodynam. J.* 7 (Suppl 1:M3) (2013) 10–20.
- [4] T.S. Lakshmi Narasimhan, R. Viswanathan, *ECS Trans.* 46 (1) (2013) 229–249.
- [5] R. Viswanathan, *J. Nucl. Mater.* 444 (2014) 101–111.
- [6] B. Saha, R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, D. Karunasagar, C.K. Mathews, *J. Nucl. Mater.* 130 (1985) 316–325.
- [7] F.J. Mompean, J. Perrone (Eds.), *Chemical Thermodynamics of Selenium*, Chemical Thermodynamics 7, Elsevier, Amsterdam, 2005.
- [8] R. Viswanathan, *Studies on Binary Systems of Tellurium with Chromium and Molybdenum by Using Knudsen Effusion Mass Spectrometry*, Ph D thesis, University of Madras, 1991.
- [9] R. Viswanathan, M. Sai Baba, D. Darwin Albert Raj, R. Balasubramanian, C.K. Mathews, A high temperature mass spectrometric study of tellurium and selenium clusters, in: J.F.J. Todd (Ed.), *Advances in Mass Spectrometry*, vol. 10, John Wiley & Sons., 1985, pp. 1087–1088.
- [10] N. Jacobson, T. Markus, (Eds.), in: *Proceedings of the Workshop on Knudsen Effusion Mass Spectrometry*, April 23–25, 2012, Juelich. ECS Transactions vol. 46, No. 1., 2013.
- [11] K.C. Mills, *Thermodynamic Data for Inorganic Sulphides Selenides and Tellurides*, Butterworths, London, 1974.
- [12] F. Grönvold, J. Drowart, E.F. Westrum Jr., *The Chemical Thermodynamics of Actinide Elements and Compounds. Part 4. The Actinide Chalcogenides (Excluding Oxides)*, IAEA, Vienna, 1989.
- [13] K. Niwa, Z. Sibata, *J. Chem. Soc. Japan* 61 (1940) 770–774.
- [14] K. Niwa, Z. Sibata, *J. Fac. Sci. Hakkaido Univ. Ser. 3* 3 (1940) 53–73 (The reference as quoted in Refs. [7] and [11]; and vapor pressure equation, as quoted in Ref. [11]).
- [15] A. Neubert, *J. Chem. Thermodyn.* 10 (1978) 261–267.
- [16] P. Goldfinger, M. Jeunehomme, in: J.D. Waldronin (Ed.), *Advances in Mass Spectrometry*, The Pergamon Press Ltd., 1959.
- [17] H. Fujisaki, J.B. Westmore, A.W. Tickner, *Can. J. Chem.* 44 (1966) 3063–3071.
- [18] J. Berkowitz, W.A. Chupka, *J. Chem. Phys.* 45 (1966) 4289–4302.
- [19] R.T. Grimley, Q.G. Grindstaff, T.A. DeMercurio, J.A. Forsman, *J. Phys. Chem.* 86 (1982) 976–982.
- [20] J.Y.-K. Huang, P.W. Gilles, J.E. Bennett, *High Temp. Sci.* 17 (1984) 109–133.
- [21] R. Yamdagni, R.F. Porter, *J. Electrochem. Soc.* 115 (1968) 601–604.
- [22] T.S. Lakshmi Narasimhan, R. Balasubramanian, P. Manikandan, R. Viswanathan, *J. Alloys Comp.* 581 (2013) 435–445.
- [23] C.E. Moore, NSRDS-NBS 34 (Nat. Stand. Ref. Data Ser., Nat. Bur. Standard., U.S., 34), 1970.
- [24] W. Rosinger, M. Grade, W. Hirshwald, *Ber. Bunsenges. Phys. Chem.* 87 (1983) 536–542.
- [25] J. Drowart, in: J. Marsel (Ed.), *Mass Spectrometry, Proceedings International School of Mass Spectrometry*, Stefan Institute, Lubljana, 1969, pp. 187–242 (1971).
- [26] J. Drowart, in: E. Rutner, P. Goldfinger, J.P. Hirth (Eds.), *Condensation and Evaporation of Solids*, Gordon and Breach, New York, 1964, pp. 255–310.
- [27] I.V. Korneeva, A.S. Pashinkin, A.V. Novoselova, Yu.A. Priselkov, *Zhur. Neorg. Khim.* 2 (1957) 1720–1724 (English Translation: *Journal of Inorganic Chemistry, USSR*, p. 14–21).
- [28] H. Keller, H. Rickert, D. Detry, J. Drowart, P. Goldfinger, *Z. Phys. Chem. N.F.* 75 (1971) 273–286.