Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1991, **1(3)**, 86–87

Mendeleev Communications

Mass Spectrometric Study of the Gaseous Caesium Tellurides. The Enthalpies of Formation of CsTe(g), Cs_2Te(g), $CsTe_2$(g) and Cs_2Te_2(g)

Lev N. Gorokhov, Michail Yu. Ryzhov, Yuri S. Khodeev, Adolph M. Emel'yanov and Aleksei A. Nasretdinov
Thermocenter, Institute for High Temperatures, Academy of Sciences of the USSR, Moscow, USSR

Using a Knudsen cell effusion technique with mass spectrometric detection the vapour composition over the Cs–Te system has been investigated; molecules CsTe, Cs_2Te, $CsTe_2$ and Cs_2Te_2 were detected and their enthalpies of formation and atomization energies determined.

Caesium tellurides are of interest because caesium and tellurium are fission products. In the case of an accident at a nuclear reactor they are able to react and may be transported from the active zone not only as Cs and Te, but also in the form of Cs–Te compounds. In order to predict the behaviour of both Cs and Te reliable thermodynamic properties of gaseous substances in the Cs–Te system are required. The available thermodynamic data concerning Cs_2Te(cr) and its evaporation[1–3] are incomplete and seem to be contradictory. Cordfunke *et al.*[1] have measured the vapour pressure over Cs_2Te using a transpiration technique, assuming that only Cs_2Te molecules are present in the gas phase. More recently[2,3] the ions Cs^+, Te^+, Te_2^+, Te_3^+, $CsTe^+$, Cs_2Te^+, $CsTe_2^+$ and $Cs_2Te_2^+$ were detected in mass spectra obtained over Cs_2Te, thus indicating the complex of the composition vapour. An identification of the molecular precursors of the ions was not made, however, so the presence in the gas phase of the neutral molecules Cs_mTe_n corresponding to $Cs_mTe_n^+$ ions was not proven (except for the $Cs_2Te_2^+$ ion, which is evidently formed from the Cs_2Te_2 molecule).

In this connection the present study of the vapour composition in the Cs–Te system and a determination of the enthalpies of formation of the vapour components was undertaken.

Two samples were investigated: (1) with excess of tellurium over the stoichiometric composition of Cs_2Te (the investigation was performed using an MS 7301 quadrupole mass spectrometer), (2) with excess of caesium (the investigation was performed using an MS 1301 magnetic mass spectrometer). The effusion cells containing the samples (cell material: molybdenum) were kept in sealed glass tubes. To avoid hydrolysis of the samples during mounting of the cells into the molecular beam source the effusion orifices were closed by plates or needles, which were removed immediately before placing the source into the mass spectrometer. Before starting the measurements the samples were degassed for several hours at 50–100 °C, after which the temperature was raised slowly. The following ions were detected in the mass spectra at 1000 °C: for the sample with excess of Te: Cs^+, Te^+, Te_2^+, $CsTe^+$, $CsTe_2^+$; for the sample with excess of Cs: Cs^+, Te^+, Te_2^+, $CsTe^+$, Cs_2Te^+, $Cs_2Te_2^+$; Te_3^+ ions were not detected. The molecular precursors of the ions were determined by measuring the appearance potentials from the ionization efficiency curves, *i.e.*, the relationship between the ion current and the ionization voltage. The molecule Te_2, with a well-known ionization potential 8.29($\pm$0.03) eV,[4] was chosen as a standard. Low appearance potentials were obtained for all the $Cs_mTe_n^+$ ions. These data indicate direct formation of these ions from molecules of the same composition. Thus the results obtained are the ionization potentials of the Cs_mTe_n molecules: CsTe 6.1, Cs_2Te 4.5, $CsTe_2$ 5.9, Cs_2Te_2 5.0 eV. The uncertainty in the ionization potential values was evaluated as $\pm$0.3 eV. No significant breaks were found in the ionization efficiency curves, indicating a low degree of dissociative ionization for the molecules studied. The intensities of the molecular ion peaks were taken

Table 1 Mass spectra of vapour over the Cs–Te system[a]

Ion	Cs^+	Te^+	Te_2^+	$CsTe^+$	Cs_2Te^+	$CsTe_2^+$	$Cs_2Te_2^+$
Sample 1	0.38	3.2	100	0.29	–	0.48	–
Sample 2	100	0.1	0.02	1	0.4	–	0.6

[a] (1) Sample with excess of tellurium; quadrupole mass spectrometer, T = 980 K. (2) Sample with excess of caesium; magnetic mass spectrometer, T = 1036 K.

Mendeleev Commun., 1991, 1(3), 86–87

Table 2 Reactions investigated in Cs–Te system

No.	Reaction	Instrument	T/K	Number of points	$\Delta_r H°(0)$/kJ mol^{-1}
1	$Cs + Te_2 \rightarrow CsTe + Te$	Quadr.	923–1151	29	64.5(± 7)
1a	$Cs + Te_2 \rightarrow CsTe + Te$	Magn.	1023–1129	8	59.1(± 7)
2	$2Te_2 + Cs \rightarrow 2Te + CsTe_2$	Quadr.	980–1090	11	73.7(± 12)
3	$Cs_2Te \rightarrow 2Cs + Te$	Magn.	1023–1129	8	403.0(± 12)
4	$CsTe \rightarrow Cs + Te$	Magn.	1023–1129	8	196.4(± 7)
5	$Cs_2Te_2 \rightarrow 2CsTe$	Magn.	1023–1129	8	293.6(± 16)

as a measure of the vapour pressures. In order to determine the enthalpies of formation and the atomization energies of the caesium tellurides the gas phase reactions between Cs, Te, Te_2 and the Cs_mTe_n molecules were investigated. For the calculation of the equilibrium constants all the ion currents were measured with the same excess (3 eV) of electron energy over the threshold value. Table 1 shows the typical mass spectra thus obtained. The evolution of the samples was observed during the experiments. Sample 1 lost mainly Te and sample 2 lost mainly Cs. The equilibrium constants for the AB + C→AC + B type reactions were calculated using eqn. (1), where I = ion current,

$$K_p = \frac{I_{AC} I_B \sigma_{AB} \sigma_C}{I_{AB} I_C \sigma_{AC} \sigma_B} \quad (1)$$

σ = ionization cross-section (the additivity rule was used for molecules).

The enthalpies of reaction were calculated by the so-called equation of the third law of thermodynamics [eqn. (2)], where

$$\Delta_r H°(0) = T[\Delta\phi°(T) - R\ln K_p] \quad (2)$$

$\Delta_r H°(0)$ = enthalpy of the reaction at 0 K, $\Delta\phi°(T)$ = free energy function and R = gas constant. Thermodynamic functions from the data bank IVTANTHERMO[5] were used.

The reactions investigated and their enthalpies, together with an evaluation of the total uncertainty in the determined values are given in Table 2. The enthalpies of formation and atomization energies of the caesium tellurides were calculated from the enthalpies of reaction obtained using the values $\Delta_f H°$ (Cs, g, 0) = 78.014[6] and $\Delta_f H°$ (Te, g, 0) = 209.362 and $\Delta_f H°$ (Te_2, g, 0) = 165.426[5] kJ mol^{-1}. These values are given in Table 3.

The present work has shown that the vapour over the Cs–Te system contains Cs and Te atoms and Te_2, CsTe, $CsTe_2$, Cs_2Te and Cs_2Te_2 molecules. The stability of the caesium telluride molecules has been determined. The enthalpies of formation determined in the present study were obtained from gas-phase reactions and are independent of the state of the condensed phase.

Table 3 Enthalpies of formation and atomization energies of the caesium tellurides

No.	Molecule	$\Delta_f H°(0)$ /kJ mol^{-1}	D_0/kJ mol^{-1} [reaction][a]
1	CsTe	98.6(± 7)	188.8(± 7) [1]
		93.2(± 7)	194.2(± 7) [1a]
		91.0(± 7)	196.4(± 7) [4]
		av. 94.2(± 7)	av. 193.1(± 7)
2	Cs_2Te	− 37.6(± 12)	403.0(± 12) [3]
3	$CsTe_2$	63.9(± 12)	432.9(± 12) [2]
4	Cs_2Te_2	− 105.1(± 16)	679.9(± 16) [5]

[a] See Table 2.

The authors are grateful to Prof L. V. Gurvich (Institute for High Temperatures) for encouragement and suppoprt. We also thank Prof V. I. Tsirel'nikov and Dr. M. I. Nikitin for the samples.

Received in USSR, 12th December 1990
Received in UK, 14th March 1991; Com. 0/05641C

References

1 E. H. P. Cordfunke, F. Kleverlaan and W. Ouweltjes, *Thermochim. Acta*, 1986, **102**, 387.
2 D. J. Wren, F. Garisto, N. H. Sagert and F. C. Igleas, *High Temp. Sci.*, 1987, **24**, 103.
3 R. Portman, M. J. Quinn, N. H. Sagert, P. P. S. Saluja and D. R. Wren, *Thermochim. Acta*, 1989, **144**, 21.
4 H. M. Rosenstock, K. Draxl, B. W. Steiner and J. T. Herron, *J. Phys. Chem. Ref. Data*, 1977, **6**, Suppl. No. 1.
5 L. V. Gurvich, *Vestn. Akad. Nauk SSSR*, 1983, **3**, 54.
6 *Termodinamicheskie svoistba individual'nyx beshchestb* (Thermodynamic Properties of Individual Substances) ed. V. P. Glushko, vols. 1–4, Nauka, Moscow, 1978–1982.