Electrochemical and Specific Heat Measurements on Tellurium-Halogen Systems

J. Haag, U. v. Alpen, E. Gmelin and A. Rabenau

Max-Planck-Institut für Festkörperforschung, Stuttgart

Z. Naturforsch. **34a**, 969–975 (1979); received June 8, 1979

Gibbs free energies of reaction in the systems Te-TeX_4 (X = Cl, Br, I) were determined from e.m.f. measurements of solid state galvanic cells using silver halides as auxiliary electrolytes. From the temperature dependence of the e.m.f. the standard entropies and enthalpies of formation S^0 (298.15 K) and ΔH_f^0 (298.15 K) have been calculated for α-TeI, TeI_4, Te_2Br, $TeBr_4$, Te_3Cl_2 and $TeCl_4$. The specific heats of α-TeI and Te_2Br were determined from 1.5 K to 300 K by adiabatic and differential scanning calorimetry.

1. Introduction

In the peritectic systems Te-TeI_4 [1–3], Te-$TeBr_4$ [4, 5] and Te-$TeCl_4$ [4, 6] the compounds α-TeI [3], Te_2Br [4, 5] and Te_3Cl_2 [4] are the only thermodynamically stable intermediate phases. As to the formally low oxidation state of tellurium in these compounds (Te: $X \geqq 1$; X = Cl, Br, I), they are called tellurium subhalides and pose interesting problems of chemical bonding.

The structure of the subhalides is related to that of elemental tellurium with its threefold screw axis, as shown schematically in Figure 1 [7]. The halogen atoms exhibit covalent bonds to tellurium and there exist at least two different coordinations for tellurium in each compound. In Te_3Cl_2 every third tellurium atom binds two chlorine atoms axially showing a trigonal-bipyramidal coordination, if the nonbinding electron pair is included. In Te_2Br zig-zag chains of alternating trigonal-bipyramidal and square planar tellurium atoms are crosslinked in a way that results in a ribbon of sixmembered tellurium rings with boat configuration. In α-TeI the building principle is degenerated to a Te_4-ring (the Te_4I_4 molecule), the molecules forming chains parallel to the *c*-axis. These structural features have been confirmed by tellurium-125 Mössbauer spectroscopy [8, 9]. The structures of the isostructural $TeCl_4$ and $TeBr_4$ [10] and TeI_4 [11] are formed of tetramer Te_4X_{16} units.

Physical properties like optical absorption [12, 13] and electrical conductivities [14] of the subhalides have been measured and compared with elemental tellurium.

The present paper reports thermodynamic data of the subhalides as well as those of the respective tetrahalides. These data are obtained with two different methods, i.e., measurements of the e.m.f. of galvanic cells with silver halides as auxiliary electrolytes and the determination of the specific heats of α-TeI and Te_2Br.

2. Materials and Methods

Single crystals of the subhalides have been obtained by the Bridgman technique. As starting materials served the elements in the case of α-TeI and Te_2Br, and Te and $TeCl_4$ in the case of Te_3Cl_2. Whereas α-TeI grows from a stoichiometric melt, an excess halogen content and a modified Bridgman technique have been applied for the preparation of Te_2Br and Te_3Cl_2 [15, 16]. $TeCl_4$ and $TeBr_4$ have been prepared as described in the literature [17] and have been purified by sublimation. TeI_4 has been formed with a slight excess of iodine which was removed afterwards by extraction with CCl_4.

Silver bromide was obtained by precipitation from a KBr-solution by dropwise addition of a 1 n-silver nitrate solution. The precipitate was rinsed and dried in a dark room.

Silver iodide was used as delivered by CERAC (−40 mesh, 99.999% purity). It should be noted here that the silver iodide used in the galvanic cells was in the metastable γ-form which is formed by rapid cooling of the melt and shows pure ionic conductivity [18, 19]. As could be shown by x-ray diffraction after the e.m.f. experiments have been performed, the metastable form still prevailed after

Reprint requests to Herrn Prof. Dr. A. Rabenau, Max-Planck-Institut für Festkörperforschung, Heisenbergstr. 1, D-7000 Stuttgart 80.

0340-4811 / 79 / 0800-0969 $ 01.00/0

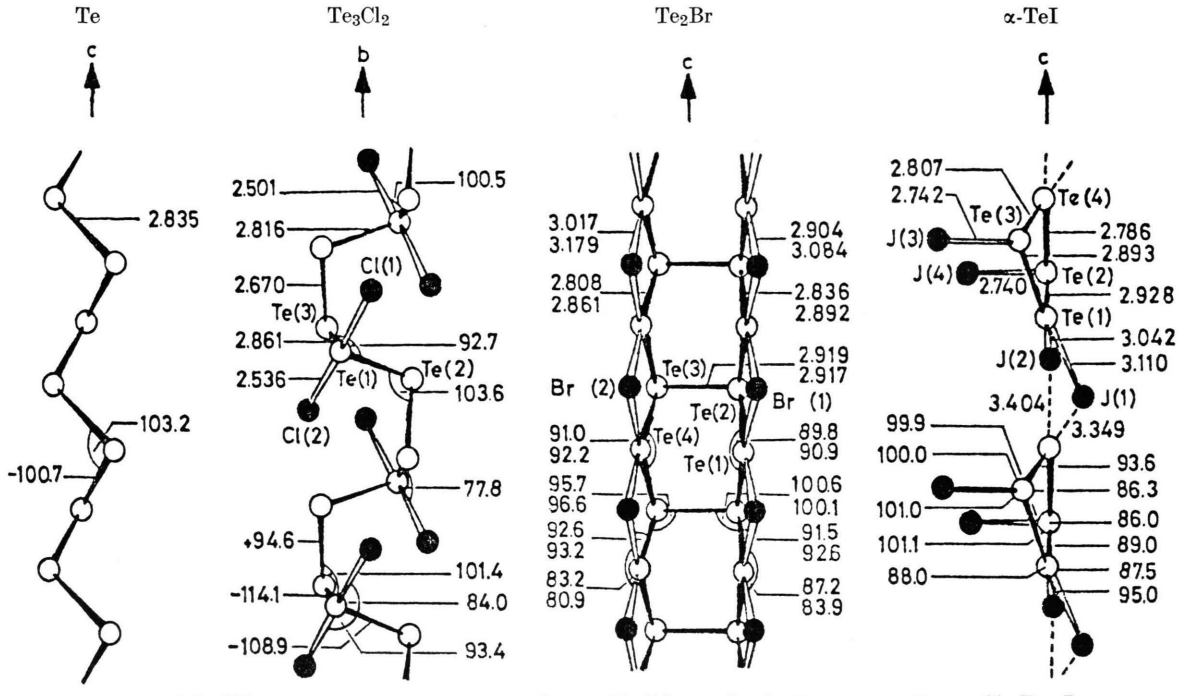

Fig. 1. Structural building units of the stable tellurium subhalides and of tellurium. ○ Te; ● Cl, Br, I.

more than one hundred hours at temperatures close to the transformation point to the α-phase (420 K), whereas other authors propose a rapid transformation to the stable low-temperature β-phase at temperatures around 400 K [20].

Electromotive Force Measurements

The use of solid state galvanic cells involving α-TeI has been described previously [21]. The technique is improved in the present work, and a simple and highly reproducible method is obtained for the determination of thermodynamic data of tellurium halides. The cell arrangement is presented in Figure 2. The silver halide electrolyte has been melted into the glass tube in order to prevent a gas leakage between the silver anode and the cathode. In addition, the cathode was separated gas tight from the outer atmosphere to prevent evaporation of the respective halogen species. The free space over the cathode was kept small to obtain steady state conditions within reasonable time. The steady state e.m.f. of the cell is measured with a digital electrometer of extremely high input impedance ($R_I > 2 \cdot 10^{14}\,\Omega$ Keithley 616), the cell voltage being partially compensated by a highly constant voltage source (Knick S 15). The temperature stability of the electronically controlled furnace between 300 K and 450 K was better than ± 0.4 K. The standard deviation of the measured e.m.f. values was calculated to be less than 0.6 mV, corresponding to an error of ± 70 J val^{-1}. This precision is rather high compared to other methods.

The thermodynamic data ΔG_f^0, ΔH_f^0 and S^0 of the interesting tellurium halides can be calculated from the e.m.f. of the galvanic cell and its temperature dependence, taking into account the data for the other compounds which are involved in the

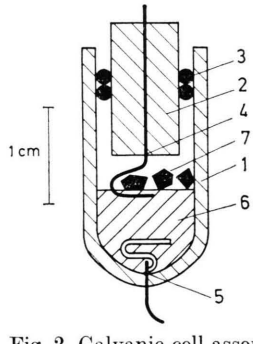

Fig. 2. Galvanic cell assembly. 1, outer glass tube; 2, glass piston with 0.5 mm capillary; 3, rubber rings; 4, 0.3 mm platinum wire, melted into the capillary; 5, silver wire, discharge welded to platinum wire; 6, melted-in solid electrolyte; 7, cathode mixtures.

total cell reaction [22]. Literature data of the standard enthalpies of formation and standard entropies of silver [23], silver iodide [24], silver chloride [23], silver bromide [25] and tellurium [24] have been used for the calculations in the present investigation. The thermodynamic values of α-tellurium iodide and tellurium tetraiodide have been obtained from the e.m.f.'s of the cell arrangements (I) and (II), with the corresponding total cell reactions (1) and (2), respectively:

$$\alpha\text{-TeI} + \text{Ag} = \text{AgI} + \text{Te}, \quad (1)$$

$$\text{TeI}_4 + 3\,\text{Ag} = 3\,\text{AgI} + \alpha\text{-TeI}, \quad (2)$$

$$\text{Pt, Ag} \mid \text{AgI} \mid \text{C, Te, } \alpha\text{-TeI, Pt}, \quad (\text{I})$$

$$\text{Pt, Ag} \mid \text{AgI} \mid \alpha\text{-TeI, TeI}_4\text{, Pt}. \quad (\text{II})$$

For the tellurium bromides the cell reactions are shown in (3) and (4) when the cell arrangements shown in (III) and (IV) are used, respectively:

$$\text{Te}_2\text{Br} + \text{Ag} = \text{AgBr} + 2\,\text{Te}, \quad (3)$$

$$2\,\text{TeBr}_4 + 7\,\text{Ag} = 7\,\text{AgBr} + \text{Te}_2\text{Br}, \quad (4)$$

$$\text{Pt, Ag} \mid \text{AgBr} \mid \text{Te}_2\text{Br, Te, Pt}, \quad (\text{III})$$

$$\text{Pt, Ag} \mid \text{AgBr} \mid \text{C, TeBr}_4\text{, Te}_2\text{Br, Pt}. \quad (\text{IV})$$

For the tellurium chlorides the cell reactions are listed in (5) and (6), when the cell arrangements (V) and (VI) are used:

$$\text{Te}_3\text{Cl}_2 + 2\,\text{Ag} = 2\,\text{AgCl} + 3\,\text{Te}, \quad (5)$$

$$3\,\text{TeCl}_4 + 10\,\text{Ag} = 10\,\text{AgCl} + \text{Te}_3\text{Cl}_2, \quad (6)$$

$$\text{Pt, Ag} \mid \text{AgI} \mid \text{AgCl, Te}_3\text{Cl}_2\text{, Te, Pt}, \quad (\text{V})$$

$$\text{Pt, Ag} \mid \text{AgI} \mid \text{AgCl, TeCl}_4\text{, Te}_3\text{Cl}_2\text{, Pt}. \quad (\text{VI})$$

Silver iodide was used in this case as auxiliary electrolyte because silver chloride always showed visible cracks when it was molten into the glass tube, thus causing chlorine gas passing through the electrolyte to the silver electrode and decreasing the e.m.f. in an undefined manner. Since the equilibrium partial pressure of chlorine in the cathode compartment is rather low (about 10^{-15} Pa, as calculated from measured e.m.f. data) no reaction of the halogen with silver iodide occurs to form silver chloride and iodine.

Four to six individual cells of any cell type, (I) to (VI), were mounted and used for the measurements.

A stable e.m.f. was obtained with cells (I) and (II) within 2 to 5 hours even at temperatures slightly higher than room temperature where equilibrium is established slowly (26). Heating and cooling cycles did not show noticeable differences, the e.m.f.'s being stable to ± 0.5 mV up to 90 hours. In contrast to that, experiments with cell arrangements (III) to (VI) were much more difficult and time-consuming. Equilibrium at temperatures higher than 400 K could not be reached within at least 10 hours. Cooling cycles did not give stable e.m.f. values even after allowing more than one day for equilibration.

Calorimetric Measurements

The specific heat of α-TeI and Te_2Br has been measured in the temperature range from 1.5 K to 100 K with an adiabatic calorimeter [27] and in the temperature range from 100 K to 350 K using a commercial differential scanning calorimeter [28] (Perkin Elmer, DSC-2).

The adiabatic calorimetric measurements using the well known Nernst-method were carried out by means of a fully automatic process control, data acquisition and data analysis system in conjunction with an on-line-computer [29]. The same sample holder was used for both specimen, having masses of $m(\text{TeI}) = 10.143$ g and $m(\text{Te}_2\text{Br}) = 5.774$ g. The heat capacity of the sample holder was determined in a separate run and amounted to less than 10 per cent of the total heat capacity throughout the applied temperature range. The sample temperatures have been registered using a commercial, calibrated semiconductor thermometer [30], the calibration of which was checked against the He^4-vapour pressure scale (T^{68}-scale and the IPTS 68-scale). Systematic errors have been ruled out by measuring a standard copper sample (T 4.2) [31]. We therefore estimate that our experimental results have a higher accuracy than 1 per cent ($\Delta T/T < 2 \cdot 10^{-3}$).

The differential scanning calorimeter (DSC) used in our experiments is a twin cell heat flow instrument. The samples with masses of about 10 mg have been encapsuled into standard aluminium pans. The sample chamber of the DSC was continuously flushed with a gentle stream of pure dry helium gas and the heater block cooled by a liquid nitrogen bath.

The investigation of the heat capacities was performed by comparison with standard samples of either benzoic-acid or synthetic sapphire. The temperature and calorimetric calibration was adjusted using melting points, crystallo-

graphic transition temperatures and the corresponding transition enthalpies of known materials (indium, benzoic acid, octadecane, dodecane, n-nonane, cyclohexane, cyclopentane). The temperature error did not exceed ± 0.25 °C; the absolute caloric resolution was better than $\pm 25\ \mu$J s^{-1}. Thus the total error of the measured molar specific heat is 1.5 per cent or less.

3. Results and Discussion

E.m.f. data as function of temperature T may be linearized in the given temperature range by the formula [26]:

$$E = A + B \cdot T . \tag{1}$$

The coefficients A and B which result from the experimental data are listed in Table 1.

Even in those cases when a constant e.m.f. was observed, this does not necessarily reflect the real cell reaction but may be influenced by several other factors, e.g. partial electronic conductivity or microcracks, causing a constant halogen loss and thus a lower e.m.f. Whereas the latter influence was apparently negligible in the cases of cell arrangements (I) and (II) with higher halogen activities, it played an important role in cells (III) to (VI), where the results of different individual cells lead to a standard deviation of more than 5 mV. The linear fits for cell reactions (3) to (6) presented in Table 1 are based on 5 to 7 data points for two cells of each type. The points were selected following two principles:

i) the highest stable e.m.f. is likely to be the best, because all considered deviations (halogen loss, partial electronic conductivities) tend to lower the cell voltage.

ii) If three or more measured e.m.f.'s as a function of temperature of an individual cell result in a straight line, the results seem more reliable since a possible halogen loss is not likely to be linearly dependent on temperature.

Table 2. Thermodynamic data of the cell reactions (1) to (6).

	Cathode	ΔG_r(298.15 K) (kJ mol^{-1})	ΔS_r(298.15 K) (J mol^{-1} K^{-1})	ΔH_r(298.15 K) (kJ mol^{-1})
1	α-TeI, Te	-54.16 ± 0.06	20.3 ± 1	-48.1 ± 0.4
2	TeI_4, α-TeI	-167.67 ± 0.12	52.7 ± 2.5	-152.0 ± 1.0
3	Te_2Br, Te	-55.72 ± 0.06	16.0 ± 2.0	-51.0 ± 0.6
4	$TeBr_4$, Te_2Br	-388.5 ± 0.5	83.75 ± 13.5	-363.5 ± 4.5
5	Te_3Cl_2, Te	-109.0 ± 0.1	30.3 ± 1.9	-100.0 ± 0.65
6	$TeCl_4$, Te_3Cl_2	-508.5 ± 0.1	154.85 ± 3.5	-462.3 ± 1.1

The thermodynamic data for the cell reactions (1) to (6) and the derived data for the formation reaction of the interesting compounds, as calculated from the e.m.f. data, are listed in Tables 2 and 3. Reported literature data obtained with other methods are cited in Table 3.

The temperature dependence of the experimental molar heat capacity C_p of α-TeI and Te_2Br are represented in Figure 3. The data refer to molar weights of 254.5 (α-TeI) and 335.11 (Te_2Br). For sake of clarity only representative points of a smoothed curve $C_p(T)$ obtained from the best fit to the about 250 individual experimental points below 100 K are plotted. Above 100 K the C_p-data are directly computed from the DSC-recorder output at selected temperatures (5 K steps). The coefficients of the best fit for the adiabatic data points between 4 K and 120 K are given in Table 4. The fits were carried out using the general formula (Eq. (2)):

$$C_p = \sum_{i=1}^{n} p_i\, T^{i-1} . \tag{2}$$

Table 1. E.m.f. values for the cell reactions (1) to (6) in terms of A and B of Equation (1). Electrochemical valency, n, as well as temperature range and number of points used for the linear fit are indicated.

	Cathode	n	A (mV)	$10^4\ B$ (V K^{-1})	Temp. range (°C)	No. of points
1	α-TeI, Te	1	498.6 ± 0.6	2.11 ± 0.1	85—150	25
2	TeI_4, α-TeI	3	525.0 ± 0.4	1.82 ± 0.1	40—150	28
3	Te_2Br, Te	1	528.0 ± 0.6	1.66 ± 0.2	135—170	7
4	$TeBr_4$, Te_2Br	7	538.0 ± 0.7	1.24 ± 0.2	120—170	5
5	Te_3Cl_2, Te	2	518.0 ± 0.45	1.57 ± 0.2	60—150	6
6	$TeCl_4$, Te_3Cl_2	10	497.0 ± 0.1	1.6 ± 0.05	110—150	7

Table 3. Standard heats of formation and standard entropies of tellurium halides.

Compound	H_f^0(298.15 K) (kJ mol^{-1})	S^0(298.15 K) (J mol^{-1} K^{-1})	Method	Ref.
α-TeI	− 7.91 ± 0.4	101.6 ± 1	e.m.f.	this work
	− 7.95	118.6	vapor press.	[32]
		108.7 ± 1	spec. heat	this work
TeI_4	− 42.16 ± 1	264.0 ± 2.5	e.m.f.	this work
	− 45.18	272.4	vapor press.	[32]
	− 69. ± 12.5	226 ± 16.7	vapor press.	[33]
	− 35.9 ± 8.4		heat of solut.	[34]
Te_2Br	− 48.22 ± 0.6	147.53 ± 2	e.m.f.	this work
		147.8 ± 1.5	spec. heat	this work
$TeBr_4$	−189.4 ± 4.5	257.85 ± 13.5	e.m.f.	this work
	−184.48 ± 8.4		heat of solut.	[34]
	−177.8 ± 1.7		heat of react.	[35]
	−208.4		—	[25]
Te_3Cl_2	−154.14 ± 0.65	225.55 ± 1.9	e.m.f.	this work
$TeCl_4$	−320.8 ± 1.1	202.5 ± 1.9	e.m.f.	this work
	−312.84 ± 8.4		heat of solut.	[34]
	−326.35		—	[24,36]
	−323.0		—	[25]

The DSC-data were fitted to a straight line as a function of temperature according to the formula [Eq. (3)]:

$$C_p = C + D \cdot 10^{-3}\, T\,. \tag{3}$$

The respective parameters p_i of Eq. (2) and the values C and D of Eq. (3) are listed in Table 4 for α-TeI and Te_2Br.

Integration of the $C_p(T)$ curves yields the standard values of the entropy $S^0(T)$, enthalpy difference $H^0(T) - H^0(0)$ and the so-called Gibbs-function $-[G^0(T) - H^0(0)]/T$. The integral values, calculated for 298.15 K are included in Table 4. The entropies are also listed in Table 3 in comparison with the e.m.f. data.

The insert of Fig. 3 illustrates the low temperature behaviour of $C_p(T)$ in terms of a C_p/T versus T^2 plot in the temperature range from 1.5 K to 5 K, from which the Debye-temperatures at 0 K, θ_0 are deduced. θ_0 and θ_∞, the extrapolated Debye-temperature at high temperatures, are listed in Table 4.

The experimental e.m.f. data and the independently achieved calorimetric values are in good agreement with respect to the calculation of S^0(298.15 K) for α-TeI and Te_2Br. This shows that the determination of e.m.f. values are well suited to calculate thermodynamic functions.

The comparatively low Debye-temperatures θ_0 for α-TeI and Te_2Br demonstrate the rather small binding forces in these covalent compounds,

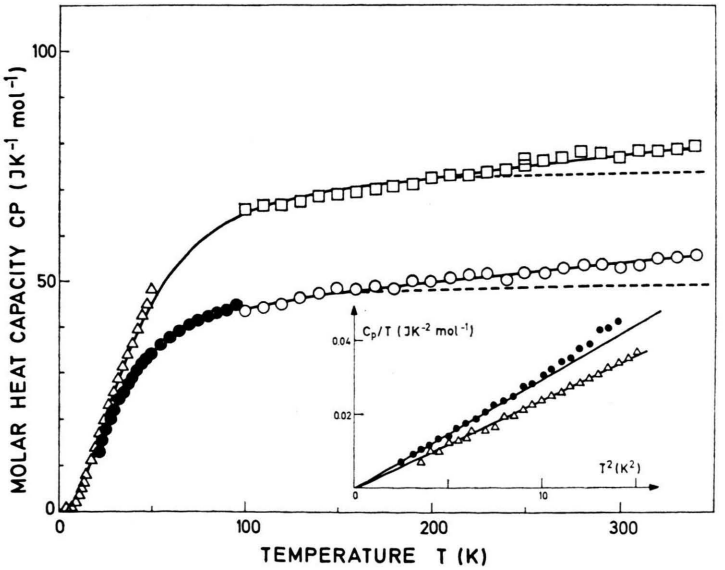

Fig. 3. Molar heat capacities of α-TeI (●, ○) and Te_2Br (△, □) measured by adiabatic calorimetry (●, △) and by differential scanning calorimetry (○, □).

Table 4. Debye-Temperatures θ_0 and θ_∞, thermodynamic quantities $S^0(298.15\ \mathrm{K})$, $H^0(298.15) - H^0(0)$, $-[G^0(298.15) - H^0(0)]/T$ and coefficients P_i $(1 < i < 8)$, C and D according to Eqs. (2) and (3), representing the temperature dependence of $C_p(T)$ in J mol^{-1} K^{-1}.

	θ_0 (K)	θ_∞ (K)	$S^0(298.15\ \mathrm{K})$ (J mol^{-1} K^{-1})	$H^0(298.15) - H^0(0)$ (kJ mol^{-1})	$-[G^0(298.15) - H^0(0)]/T$ (J mol^{-1} K^{-1})
α-TeI	111 ± 0.5	147	108.7 ± 1.1	12.5	66.9
Te_2Br	135 ± 0.5	176	147.8 ± 1.5	18.05	87.7

	p_i [Eq. (2)]			C and D [Eq. (3)]
	3 K < T < 12 K	10 K < T < 45 K	35 K < T < 120 K	T > 120 K
α-TeI	− 6.807	8.507	−10.863	C = 42.4 ± 0.5
	7.918	− 3.131	1.444	D = 38.4
	− 3.786	0.437	− 0.013	
	0.967	− 0.0247	0.00004	
	− 0.142	0.000828		
	0.0122	− 0.0000168		
	− 0.000564	0.000000189		
Te_2Br	0.454	125.83	−24.431	C = 62.1 ± 0.6
	− 0.644	−43.938	2.175	D = 50.9
	0.358	6.143	− 0.0185	
	− 0.0987	− 0.440	0.0000566	
	0.0153	0.0179		
	− 0.00122	− 0.000417		
	0.0000467	0.00000516		
	− 0.000000646	− 0.0000000263		

composed of heavy elements. The bonds are stronger in Te_2Br with double-chain structure compared to the molecular like α-TeI (with the Te_4I_4 ring-like elements). A detailed inspection of the $\theta(T)$-curve of both compounds in the temperature range between 10 K and 50 K did not reveal a deviation from the known, normal $\theta(T)$ behaviour. This is in contrast to the findings in elemental tellurium ($\theta_0 = 141$ K), where the C_p data show a constant molar heat capacity slope in the range 15 K to 30 K, reflecting the typical one-dimensional character of the Te-chain [37, 38]. The measurements of the subhalides suggest a less anisotropic behaviour.

It should be noted that a detailed comparison between subhalides and tellurium is quite difficult from the point of view of a lattice dynamical approach, because of the differences in the crystalline structures. The unharmonic term (at $T \approx \theta_0/2$) being in first order approximation proportional to T is rather large because of the low θ_0-values.

Neumann-Kopp's rule is satisfied within the limits of error, showing again the "normal" behaviour of the subhalides.

An interesting result with regard to the thermodynamic properties of tellurium halides is indicated in Tables 5a and b. In Table 5a the standard entropies are expressed per atom. The values are

Table 5. Standard entropies $S^0(298.15)$ and standard heats of formation $\Delta H_f^0(298.15)$ of tellurium halides per g · atom and per halogen atom, respectively.

Table 5a

	$S^0(298.15)$ in (J g atom^{-1} K^{-1})			
	Subhalides		Tetrahalides	
Chlorides	45.11	(Te_3Cl_2)	40.5	($TeCl_4$)
Bromides	49.2	(Te_2Br)	51.6	($TeBr_4$)
Iodides	50.6	(α-TeI)	52.8	(TeI_4)

Table 5b

	$\Delta H_f^0(298.15)$ in (kJ mol^{-1}) per halogen atom			
	Subhalides		Tetrahalides	
Chlorides	77.0	(Te_3Cl_2)	80.2	($TeCl_4$)
Bromides	48.2	(Te_2Br)	47.4	($TeBr_4$)
Iodides	7.9	(α-TeI)	10.5	(TeI_4)

almost the same, not only within the group of subhalides and tetrahalides and tetrahalides, respectively, but for all of the compounds and correspond to that of elemental tellurium with 49.5 J atom^{-1} K^{-1} [24]. This reflects the covalent character which is common to these groups, but does not show any details of coordination, bond strengths and bond lengths as they may be deduced for example from x-ray and Mössbauer measurements [7, 8, 9].

Table 5b on the other hand shows the standard heat of formation, expressed in kJ per halogen atom, that is per halogen-tellurium bond. It is indeed this value which determines the heat of formation regardless whether we look at subhalides or tetrahalides.

Thermodynamics, as a macroscopic and statistic entity, seems therefore to be less suited to reflect details of structure and bonding compared to spectroscopy and x-ray methods.

Acknowledgement

We are indebted to Dr. W. Weppner for valuable suggestions and discussions.

[1] A. Rabenau, H. Rau, Proc. 6th Int. Symp. on the Reactivity of Solids ,Schenectady, U.S.A., Aug. 25—30, 1968, John Wiley Intersci., New York, p. 763.
[2] S. A. Ivashin, E. S. Petrov, and T. I. Samsonova, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim Nauk **1969**, 51 (6).
[3] R. Kniep, A. Rabenau, and H. Rau, J. Less-Common Metals **35**, 325 (1974).
[4] A. Rabenau and H. Rau, Z. anorg. allg. Chem. **395**, 273 (1973).
[5] S. A. Ivashin and E. S. Petrov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim Nauk **1970**, 149 (1).
[6] S. A. Ivashin and E. S. Petrov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk **1970**, 48 (5).
[7] R. Kniep, D. Mootz, and A. Rabenau, Z. anorg. allg. Chem. **422**, 17 (1976).
[8] M. Takeda and N. N. Greenwood, J. Chem. Soc. Dalton Trans. **1976**, 631.
[9] C. H. W. Jones and M. Mauguin, J. Chem. Phys. **68**, 3067 (1978).
[10] B. Buss and B. Krebs, Inorg. Chem. **10**, 2795 (1971).
[11] B. Krebs and V. Paulat, Acta Cryst. B **32**, 1470 (1976).
[12] W. Bauhofer and R. Kniep, Mat. Res. Bull. **8**, 989 (1973).
[13] A. Rabenau, in: Reactivity of Solids, J. Wood et al. (Eds.), Plenum Press, New York 1977, p. 731.
[14] U. v. Alpen and R. Kniep, Solid State Commun. **14**, 1033 (1974).
U. v. Alpen and R. Kniep, in: Physics of Semiconductors, M. H. Pilkuhn (Ed.), Verlag Teubner, Stuttgart 1974, p. 308.
[15] W. Stetter and E. Schönherr, Abstr. Dreiländerjahrestagung über Kristallwachstum und Kristallzüchtung, September 17—19, 1975, Jülich, Germany.
[16] J. Haag, Thesis, University of Stuttgart, 1978.
[17] Handbuch der präparativen anorganischen Chemie, G. Brauer (Ed.), 3rd Ed., Vol. I, Enke-Verlag, Stuttgart 1975.
[18] T. Takahashi, K. Kuwabara, and O. Yamamoto, J. Electrochem. Soc. **116**, 357 (1969).
[19] J. Haag, U. v. Alpen, and A. Rabenau, in preparation.
[20] J. N. Mrgudich, J. Electrochem. Soc. **107**, 475 (1960).
[21] U. v. Alpen, J. Haag, and A. Rabenau, Mat. Res. Bull. **11**, 793 (1976).
[22] H. Rickert, Elektrochemie fester Stoffe, Springer-Verlag, Berlin 1973.
[23] CODATA Task Group: Recommended Key Values for Thermodynamics 1973, in: J. Chem. Thermodyn. **7**, 1 (1975).
[24] B. I. Barin and O. Knacke, Thermodynamic Properties of Inorganic Substances, Springer-Verlag, Berlin 1973; Supplement, Springer-Verlag, Berlin 1977.
[25] Handbook of Physics and Chemistry, 57th Ed., Chemical Rubber Co., Cleveland 1976.
[26] L. E. Topol, Inorg. Chem. **7**, 451 (1968).
[27] E. Gmelin, Thermochimica Acta **29**, 1 (1979).
[28] M. J. O'Neill, Anal. Chem. **38**, 1331 (1966).
[29] E. Gmelin and P. Roedhammer, submitted to J. Phys. E.
[30] Resistor CR 1000, No. 4789 from CRYOCAL Inc. Riviera Beach, Florida.
[31] D. W. Osborne, H. E. Flotow, and F. Schreiner, Rev. Sci. Instrum. **38**, 159 (1967). Sample T 4.2, 20th Ann. Cal. Conf., 1965, Ames, Iowa.
[32] H. Rau, private communication, as calc. from data reported in [1].
[33] H. Oppermann, G. Stöver, and E. Wolf, Z. anorg. allg. Chem. **419**, 200 (1976).
[34] H. Oppermann, G. Kunze, and E. Wolf, Z. anorg. allg. Chem. **432**, 182 (1977).
[35] V. G. Tsvetkov, Zh. Neorg. Khim. **23**, 1976 (1978); Russ. J. Inorg. Chem. **23** (7), 1086 (1978).
[36] O. Kubaschewski, E. LL. Evans, and C. B. Alcock, Metallurgical Thermochemistry, 4th Ed., Pergamon Press, Oxford 1967.
[37] L. K. Walford, G. J. Carron, and J. A. Schoeffel, Mat. Res. Bull. **3**, 911 (1968).
[38] W. De Sorbo, J. Chem. Phys. **21**, 764 (1953).