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Thermodynamics of organoselenium and organotellurium compounds

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Abstract. Experimental values of the enthalpies of formation (ΔH_f°) and of the specific heat (C_p°) of the organic compounds of selenium and tellurium are discussed, including their complexes with dialkylzinc and dialkylcadmium. Different forms of the methods of combustion enthalpy and of reaction calorimetry, used to determine the ΔH_f° values, are examined. The enthalpies of breaking of the chemical bonds formed by selenium and by tellurium are calculated from the ΔH_f° values. Data on the temperature dependence of the specific heat are used to find the absolute entropy of these compounds, their temperature, enthalpy, and entropy of melting, their entropy of formation, and other thermodynamic parameters. Special features of the changes in enthalpy, entropy, and Gibbs free energy of the breaking of the chemical bonds are pointed out. The bibliography includes 62 references.

I. Introduction

The organic compounds of selenium and tellurium are used in the preparation of semiconductor and optoelectronic materials. A thermodynamic analysis of the thermal dissociation, hydrogenation, and oxidation processes in these materials should provide a better understanding of their properties. Data on the thermodynamic characteristics of the reactants (in particular, on their enthalpies of formation and vaporisation, and on their entropy) are needed for the calculation of the parameters of the corresponding reactions. These data are important also in relation to the theory of the chemical bond and the theory of heterogeneous catalysis.

Until recently published data on the thermochemistry of this class of compounds were scarce.[1,2] Thus, a detailed review[1] gave the enthalpies of formation of only two organic compounds of selenium and one of tellurium. A substantial volume of information on these topics is now available, and should allow us to establish general trends in the changes in the thermodynamic characteristics of several compounds of this class. The need to correlate the published data is made even more urgent by the fact that the thermodynamic parameters of some of these compounds are given in the relatively inaccessible symposia and abstracts of specialised conferences.

In the present review we shall discuss the enthalpies of formation (ΔH_f°) and other thermodynamic characteristics of organic compounds of selenium and tellurium published up to the middle of 1994, and we shall tabulate those shown to be the most reliable. In the selection of the ΔH_f° values consideration was given to the method of determination, the purity of the starting preparations, the statistical significance of the results obtained in the analysis of the products given by the reactions under test, and the level of precision of the calorimetric experiment (allowance for all the necessary corrections and measurement and calculation errors).

An analysis of the published information showed that the true precision of the determinations of ΔH_f° for these compounds is not usually better than 3–4 kJ mol^{-1}. The achievement of higher precisions is limited partly by the specific properties of the given calorimetric experiment and partly by the need to use several auxiliary thermochemical quantities in the calculations. Their values are tabulated in the standard handbooks,[3–5] but often their precision is low and they are not mutually consistent. Therefore the experimental values of ΔH_f° are rounded off in the present review.

The vaporisation enthalpies, needed in the calculation of the ΔH_f° value of these substances in the gaseous monomeric state, are quoted (in most cases) in the papers which give the experimental values of their enthalpies of formation in the condensed state. In other cases they are quoted from Refs 6–9.

Experimental values of the enthalpies of formation, the specific heats, and other thermodynamic functions were used in calculations of the average enthalpies, entropies, and Gibbs functions of the breaking of the chemical bonds formed by selenium and tellurium in the various compounds. The error in the thermodynamic quantities corresponds to a 95% confidence level.

II. Auxiliary parameters

To ensure mutual compatibility of the thermochemical parameters discussed in this review the parameters were calculated from a single set of key values, listed in Table 1.

The most important quantities in these calculations were the ΔH_f° parameters for crystalline SeO_2 and TeO_2.

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Table 1. Enthalpies of formation used in the calculation of the thermodynamic parameters of formation of organic compounds of selenium and tellurium.

Substance[a]	ΔH_f° kJ mol^{-1}	Ref.	Substance	ΔH_f° kJ mol^{-1}	Ref.
O (g)	249.2 ± 0.1	4, 5	$CH_2=CH$ (g)	261.5 ± 8.4	4, 5
S (g)	272.8 ± 1.3	4	C_2H_5 (g)	107.5 ± 4.2	4
Se (g)	227.7 ± 4.2	4	C_3H_7 (g)	87.9 ± 8.4	12
Te (g)	191.7 ± 1.0	4	i-C_3H_7 (g)	73.6 ± 4.2	12
CO_2 (g)	−393.51 ± 0.13	4, 5	C_4H_9 (g)	71.1 ± 8.4	12
H_2O (l)	−285.81 ± 0.04	4	C_5H_{11} (g)	38 (estimate)	12
SeO_2 (cr)	−225.5 ± 2.1	10	i-C_5H_{11} (g)	32 (estimate)	12
TeO_2 (cr)	−328.9 ± 1.7	11	C_6H_5 (g)	325 ± 8	12
CH_3 (g)	146.3 ± 0.5	5	$C_6H_5CH_2$ (g)	188 ± 4	12

[a] Here and elsewhere the physical states of the substances for which thermodynamic parameters are denoted by cr (crystal), l (liquid), and g (gas).

The ΔH_f° value for SeO_2(cr) taken from Barnes and Mortimer[10] had been determined from measurements of the enthalpy of combustion of hexagonal selenium by the rotating bomb method (a high-precision measurement). Their result was indistinguishable from those of other workers,[13,14] who used a stationary calorimetric bomb for the combustion of selenium.

On the other hand the ΔH_f° values for TeO_2 obtained in different laboratories differed by ~80 kJ mol^{-1} (Table 2). Therefore the present writers redetermined[11] the enthalpy of formation of TeO_2 by burning very pure crystalline (hexagonal) tellurium in a calorimetric bomb. The value thus obtained for TeO_2(cr) (Table 1) was significantly higher than some reported values,[15,19,20] and differed very markedly from others.[16–18]

Table 2. Enthalpies of formation of crystalline tellurium dioxide (298.15 K).

$-\Delta H_f^\circ$/kJ mol^{-1}	Method of determination	Ref.
321.7 ± 5.0	Combustion calorimetry	15
379.1 ± 1.3	"	16
351.9 ± 12.0	Mass spectrometry	17
301.2 ± 2.1	Measurement of the emf of a reaction involving TeO_2 (cr)	18
321.1 ± 1.3	"	19
320.4 ± 3.0	Reaction calorimetry	20
328.9 ± 1.7	Combustion calorimetry	11

Some of the previous measurements[15,16] had been made by burning tellurium in oxygen in a stationary calorimetric bomb. However, the need to use relatively large samples of tellurium in these experiments led to incomplete oxidation and to the formation of combustion products having a complex composition. The difficulty of determining the appropriate energy corrections is mainly responsible for the inconsistency of the previous results[15,16] and for the difference between those results and ours.[11]

The high value of ΔH_f° for TeO_2(cr) obtained mass-spectroscopically (see Table 2) is probably due to the difficulty of allowing for the excess energy of the products formed from the starting material under the influence of electron collisions.[21]

Cordfunke et al.[20] determined the enthalpy of formation of TeO_2 by two independent methods: by studying the enthalpy of dissolution of solid Te, TeO_2, UO_3, and U_3O_8 in an aqueous solution of H_2SO_4 + $K_2Cr_2O_7$ + $MnSO_4$ and the enthalpy of dissolution of Te, TeO_2, Na_2SO_3, and Na_2SO_4 in an aqueous solution of NaClO + NaOH. By combining the measured effects, enthalpies of dissolution of tellurium dioxide equal respectively to −318.74 ± 7.35 and −320.71 ± 3.22 kJ mol^{-1} were obtained (an averaged value is given in Table 2). Obviously, the reliability of these results[20] depends on the reliability of the auxiliary data. Thus, the use of the parameter ΔH_f° (Na_2SO_3) = −1096.78 ± 0.81 kJ mol^{-1} instead of that used by the writers[20] (−1101.83 ± 0.72 kJ mol^{-1}) makes the value of ΔH_f° for Te_2O(cr) −330.8 ± 3.3 kJ mol^{-1} (see Refs 22 and 23), which differs by more than 10 kJ mol^{-1} from the value given in Table 2 but agrees with our value within experimental error.

III. Enthalpies of formation of organoselenium compounds

The combustion of Se compounds in a calorimetric bomb leads to the formation of solid selenium dioxide, which is easily soluble in the water present in the bomb. The energy corrections associated with the dissolution are applied during the processing of the experimental data.

Because of the rapid dissolution of the SeO_2 in water the combustion of selenium compounds can be carried out successfully in calorimeters with both stationary and rotating bombs. This conclusion is confirmed, in particular, by the good agreement between the enthalpies of combustion (ΔH_f°) of crystalline selenium obtained in a rotating[10] and in a stationary bomb respectively.[13,14]

Because of the relatively small enthalpy of dissolution of selenium dioxide in an excess of water (3.85 ± 0.08 kJ mol^{-1}) possible differences in the concentration of the aqueous solutions in different parts of the stationary calorimeter can be ignored.

The method of combustion in a stationary bomb has been widely used for selenium compounds.[24–29]

In a series of experiments in our laboratory[26–29] the compounds (held in thin-walled glass bulbs) were placed in the bomb in a quartz crucible together with a wafer of the benzoic acid standard. The mass of substance burned was determined from the amount of carbon dioxide formed during the experiment. It was established calorimetrically (from the depression of freezing point) that the total content of organic impurities in samples of dialkyl compounds purified by fractional distillation was not more than 0.05–0.10 mol%, and the content of metals was found (by spectroscopic analysis) to be 1×10^{-3} mol%.

Our value[28] of ΔH_f° for liquid diethyl selenide (−59.8 ± 3.3 kJ mol^{-1}, Table 3) differs markedly from the value reported by Merten and Schlüter[24] (−90.8 ± 3.8 kJ mol^{-1}). The latter was obtained by a low-level calorimetric technique, and it cannot be considered reliable. Thus, though the method of synthesis of the diethyl selenide was stated,[24] the purity of the resulting samples was not characterised, the completeness of the combustion was not established, and only ~20% of the total energy evolved in the experiment was ascribed to the compound under study.

Tsvetkov and Kozyrkin[30] obtained ΔH_f° for liquid $(C_2H_5)_2Se$ by studying the reaction of diethyl selenide with an excess of bromine. It was assumed that $SeBr_4$ was the only product containing selenium formed under these conditions. However, as has been reported,[31] the reaction of $(C_2H_5)_2Se$ with liquid bromine can lead to the formation of $(C_2H_5)_2SeBr_2$: even a trace of this compound among the reaction products could seriously distort the results.[30] Our ΔH_f° value[28] for $(C_2H_5)_2Se$ is given

Table 3. Standard enthalpies of formation (in kJ mol^{-1}) of organoselenium compounds at 298.15 K.

Compound	ΔH_f° (l or cr)	ΔH_f° (g)	Method of determination[a]	Ref.
$(CH_3)_2Se$ (l)	-12 ± 8	18 ± 8	SB	26–28
$(CH_2=CH)_2Se$ (l)	166 ± 8	208 ± 8	SB	26–28
$(C_2H_5)_2Se$ (l)	-60 ± 3	-21 ± 4	SB	28
$(i\text{-}C_3H_7)_2Se$ (l)	-151 ± 3	-108 ± 4	RB	33
$(C_5H_{11})_2Se$ (l)	-225 ± 4	-173 ± 5	RB	33
$(C_6H_5)_2Se$ (l)	226 ± 6	290 ± 6	RB	10
$(C_6H_5CH_2)_2Se$ (cr)	2 ± 20	–	SB	24
$C_8H_7N_2Se$ (cr)	358 ± 8	452 ± 8	SB	25
$(CH_3)_2Se_2$ (l)	9 ± 8	54 ± 8	SB	28
$(C_2H_5)_2Se_2$ (l)	-63 ± 12	-16 ± 12	SB	29
$(C_4H_9)_2Se_2$ (l)	-144 ± 21	-88 ± 21	SB	29
$(C_6H_5)_2Se_2$ (cr)	121 ± 8	237 ± 11	RB	32
$(C_6H_5CH_2)_2Se_2$ (cr)	171 ± 3	301 ± 3	SB	25
C_6H_5SeBr (cr)	34 ± 5	112 ± 6	R	34
$C_6H_5SeBr_3$ (cr)	8 ± 5	79 ± 6	R	34

[a] Here and elsewhere the following symbols are used: SB for combustion in a stationary bomb; RB for combustion in a rotating bomb; R for reaction method.

as the recommended value in Table 3. The combustion of organoselenium compounds in a rotating bomb was first used by Mortimer and coworkers [10,32] to determine the enthalpy of combustion of diphenyl selenide and diphenyl diselenide. The diphenyl selenide (in a polyester bulb) was burned in a thin-walled quartz crucible. By determining the mass of carbon dioxide in the resulting products it was shown that the extent of combustion in the compound under study was not less than 99.94%. 50 cm^3 of distilled water was previously placed in the bomb to dissolve the selenium dioxide produced by the combustion. In order to allow for various side effects (for example, the dissolution of carbon dioxide in the aqueous solution of SeO_2) the authors [10,32] carried out a set of 'comparison experiments'. In these experiments they burned benzoic acid, choosing its mass and the concentration of the aqueous solution of SeO_2 added to the bomb so as to ensure that the final states of the reacting systems in the comparison experiments and in the experiments on the combustion of selenium compounds were as nearly as possible identical.

The rotating bomb method was used also in a study [33] of a series of organic compounds of sulfur, selenium, and tellurium (see Tables 3 and 4).

Table 4. Standard enthalpies of formation (in kJ mol^{-1}) of organotellurium compounds at 298.15 K.

Compound	$-\Delta H_f^\circ$ (l or cr)	ΔH_f° (g)	Method of determination	Ref.
$(CH_3)_2Te$ (l)	-9 ± 5	-44 ± 5	SB	27, 28, 42
$(CH_2=CH)_2Te$ (l)	-216 ± 8	-261 ± 9	SB	27, 28, 42
$(C_2H_5)_2Te$ (l)	46 ± 5	4 ± 5	SB	28
$(C_3H_7)_2Te$ (l)	89 ± 3	44 ± 3	SB	28
$(i\text{-}C_3H_7)_2Te$ (l)	87 ± 3	46 ± 3	SB	28
$(C_4H_9)_2Te$ (l)	107 ± 4	56 ± 4	SB	33
$(C_5H_{11})_2Te$ (l)	196 ± 6	137 ± 6	SB	43
$(i\text{-}C_5H_{11})_2Te$ (l)	200 ± 7	148 ± 7	SB	43
$(C_6H_5)_2Te$ (l)	-240 ± 5	-307 ± 10	SB	44, 45
$(C_3H_7)_2Te_2$ (l)	24 ± 4	-29 ± 4	RB	33
$(C_4H_9)_2Te_2$ (l)	70 ± 5	13 ± 5	RB	33
$(C_6H_5)_2Te_2$ (cr)	-250 ± 5	–	SB	44
$CH_3(C_2H_5)_2TeBr$ (cr)	156 ± 8	–	R	30

A calorimetric determination of the enthalpy of interaction of $(C_6H_5)_2Se_2$ with one and with three moles of bromine, dissolved respectively in carbon tetrachloride and in trichlorobenzene, has been reported. [34] In the first case C_6H_5SeBr was formed quantitatively, in the second $C_6H_5SeBr_3$. The enthalpies of formation of crystalline and of gaseous C_6H_5SeBr and $C_6H_5SeBr_3$ were calculated from the results thus obtained and from the ΔH_f° value for crystalline $(C_6H_5)_2Se_2$ previously obtained. [32] Recommended values of the enthalpies of formation of these organoselenium compounds are shown in Table 3.

There are several reports [35–40] of the enthalpy of reaction (ΔH_r°) of the selenides SeR_2 (R = CH_3, C_2H_5) with the compounds MR_2 (M = Zn, Cd). In the liquid phase this interaction led to the formation of the corresponding equimolecular complexes of the donor-acceptor type. In some cases the ΔH_r° values were obtained directly (by studying a mixture of the compounds in a 1 : 1 ratio) [35,36] in other cases they were obtained by studying the liquid–vapour equilibrium of the corresponding equimolecular mixtures. [37–40]

The enthalpies of vapour formation of the $R_2Se \cdot MR_2$ complexes and of the starting substances were determined [38–40] at 298.15 K in an isothermal differential micro-calorimeter. It had previously been established that the compounds under study were fully dissociated in the gas phase. This allowed the ΔH_r° values to be calculated as the difference between the vaporisation enthalpies of the equimolecular solution and the corresponding individual substances.

The vaporisation enthalpies (ΔH_v°) of the complexes, the reaction enthalpies of the starting components in the liquid phase calculated from them, and the enthalpies of formation of the liquid complexes (in kJ mol^{-1}), obtained experimentally, [38–40] are listed below:

Complexes	ΔH_v°	$-\Delta H_f^\circ$	ΔH_f°
$Zn(CH_3)_2 \cdot Se(CH_3)_2$	66.3 ± 1.9	6.2 ± 2.0	6 ± 8
$Zn(C_2H_5)_2 \cdot Se(C_2H_5)_2$	79.9 ± 0.8	4.2 ± 1.1	-48 ± 4
$Cd(CH_3)_2 \cdot Se(CH_3)_2$	74.6 ± 1.4	6.0 ± 1.4	49 ± 9

In the calculation of the ΔH_f° values allowance was made for the enthalpies of formation of the selenides (see Table 3) and for published data [1] on the enthalpies of formation of liquid $Zn(CH_3)_2$ (23.8 ± 2.1), $Zn(C_2H_5)_2$ (16.3 ± 2.1), and $Cd(CH_3)_2$ (66.9 ± 4.2) kJ mol^{-1}. ΔH_r° values close to those in the above tabulation have also been obtained in a calorimetric study [35,36] of the mixing of the initial components.

IV. Enthalpies of formation of organotellurium compounds

In spite of the large number of organotellurium compounds whose synthesis has been reported [41] and of their great practical interest a systematic study of the thermochemistry of these materials was only recently started: in 1988, when the present writers' laboratory reported a determination [42] of the enthalpies of combustion of dimethyl and divinyl tellurides (see Table 4). The combustion enthalpies of these substances were determined in a calorimeter fitted with a stationary calorimetric bomb. The weight of sample consumed was determined from the quantity of carbon dioxide formed by its combustion to within ~0.1%.

According to the X-ray phase analysis results the solid combustion product was a mixture of tetragonal tellurium dioxide and a small amount (not more than 5%) of the orthorhombic modification. The amount of tellurium in the washings of the bomb after the combustion of the starting compounds was determined by atomic absorption spectroscopy, thus allowing the energy corrections associated with the dissolution of the tellurium products in the water produced by the reaction to be calculated.

A similar method was used[27,28,43-45] to find the enthalpies of formation of several alkyl and phenyl tellurides (see Table 4).

Several tellurium compounds were studied by the rotating bomb method.[33] The sample in a Terylene bulb was placed on an iridium grid below which a platinum crucible containing a wafer of benzoic acid was located. The experimental compounds were located in the maximum temperature region of the burning wafer, and therefore were oxidised almost completely.

An aqueous solution of HNO_3 has been used[33] as the bomb liquid. According to the authors this procedure led to the formation of amorphous hydrated TeO_2, whose enthalpy of formation had been determined in separate experiments. However, the report[33] omits many essential experimental details needed to substantiate the correctness of the proposed method. In particular, combustion equations for the experimental substances are not given, and therefore the chemical mechanism of the processes taking place in the calorimetric bomb cannot be established. The formation of stable hydrates of TeO_2 among the combustion products is arguable, because of the very low solubility of this dioxide in water (1 g TeO_2 dissolves in 15×10^4 g of H_2O).[46] Furthermore the use of a platinum crucible may cause alloying of the platinum with the combustion products containing tellurium.[46] Nevertheless some of the results from Ref. 33 are included in Tables 3 and 4, and have been used to calculate the enthalpies of the breaking of the corresponding bonds.

The only reported use of reaction calorimetry[30] is in an investigation of the enthalpy of interaction of diethyl telluride with an excess of liquid bromine. It was assumed[30] that the products of this interaction are solid $TeBr_4$ and ethyl bromide dissolved in bromine. However, as was pointed out,[31] the products of this reaction can include diethyl dibromotelluride, which requires an allowance for the appropriate energy corrections.

Pavlovskii and coworkers[39,40] determined the enthalpies of vaporisation of the complexes of dimethyl telluride with the methyl compounds of zinc and cadmium. By combining their results with the ΔH_v° values previously obtained for the starting components they calculated the enthalpies of their interaction in the liquid phase, as was done for the selenide complexes discussed above.

The enthalpies of vaporisation of the tellurium complexes, the reaction enthalpies of the starting components in the liquid phase, and the enthalpies of formation of the liquid complexes (in kJ mol^{-1}, the latter two calculated from the former) are listed below:

Complex	ΔH_v°	$-\Delta H_r^\circ$	ΔH_f°
$Zn(CH_3)_2 \cdot Te(CH_3)_2$	70.4 ± 1.1	4.8 ± 1.3	10 ± 6
$Cd(CH_3)_2 \cdot Te(CH_3)_2$	80.4 ± 1.2	6.4 ± 1.3	52 ± 7

The enthalpy of formation of dimethyl telluride (shown in Table 4) and the enthalpies of formation of the dimethyl compounds of zinc and cadmium recommended in Ref. 1 were used to calculate the ΔH_f° values.

We may conclude from these results that the ΔH_f° values for $(CH_3)_2Te$ and those of the same parameter for dimethyl selenide are indistinguishable within the uncertainties of the determination. the enthalpy of the reaction

$$(NH_4)_2PdCl_4(cr) + 2\,Te(C_2H_5)_2(l) \longrightarrow$$

$$\longrightarrow PdCl_2 \cdot 2\,Te(C_2H_5)_2(cr) + 2\,NH_4Cl(cr),$$

was determined calorimetrically[47] as -175.7 ± 4.8 kJ mol^{-1}.

ΔH_f° for $PdCl_2 \cdot 2Te(C_2H_5)_2(cr)$ was calculated from the enthalpies of formation of liquid $(C_2H_5)_2Te$ (see Table 4) and of crystalline $(NH_4)_2PdCl_4$ (-841.0 ± 1.7) and NH_4Cl (-314.4 ± 0.1 kJ mol^{-1}).[47] The result was -480 ± 10 kJ mol^{-1}, which is close to the previously reported value $\Delta H_f^\circ = -456 \pm 10$ kJ mol^{-1} for $PdCl_2 \cdot 2Se(C_2H_5)_2(cr)$, recalculated by the present writers[48] by using a new value of the enthalpy of formation of $(C_2H_5)_2Se$ (see Table 3).

By using the calculated[47] enthalpies of sublimation of the tellurium (192 kJ mol^{-1}) and the selenium complex (160 kJ mol^{-1}) the following ΔH_f° values were obtained: -288 for $PdCl_2 \cdot 2Te(C_2H_5)_2(g)$ and -296 kJ mol^{-1} for $PdCl_2 \cdot 2Se(C_2H_5)_2(g)$.

In this calculation[47] the enthalpy of mixing of liquid diethyl telluride with liquid bromine (-188 ± 4 kJ mol^{-1}) was erroneously taken from Ref. 30 instead of its enthalpy of formation (see Table 4), and this led to an erroneous determination of the ΔH_f° value for crystalline $PdCl_2 \cdot 2Te(C_2H_5)_2$ (-763.8 ± 14.6 kJ mol^{-1}).

V. Specific heats, entropies, and Gibbs free energies of formation of organoselenium and organotellurium compounds

The temperature dependence of the specific heat (C_p°) for a series of alkyl and vinyl compounds of selenium and of tellurium has been determined[49-56] experimentally at 5-310 K. The measurements were made in a vacuum adiabatic calorimeter whose design and methods of calibration, measurement, and calculation offered results with an uncertainty of ~0.2% at 30-310 K, 0.5% at 12-30 K, and 1.5% at even lower temperatures. The experimental materials were specially purified, and according to chromatographic and mass spectrometric analyses their purity was 99.9 mol%. According to the depression of freezing point, measured during the study of the specific heat for each of the samples, the total content of impurities not forming solid solutions with the main substance was less than 0.1 mol%.

In these studies of the specific heat it was found that when rapidly cooled divinyldipropyl-, and dibutyl telluride are easily supercooled with formation of glasses, whereas the dimethyl and the diethyl compound show polymorphism. The thermodynamic characteristics of these transitions were determined in the course of these studies. The melting point (T_m) and the enthalpy (ΔH_m°) and entropy (ΔS_m°) of melting of the compounds were also determined (Table 5).

A special feature of liquid alkyl compounds of selenium and tellurium is an anomalous change in their specific heat. Immediately after melting the specific heat falls a little with increase in temperature, but after going through a minimum it shows the normal behaviour and begins to rise again. It has been suggested that these liquids are partially associated at temperatures close to T_m. Therefore the observed heat capacity includes both the true heat capacity of the liquid and the heat capacity contributed by the dissociation of the associated species. The decrease in the degree of association with increase of temperature suppresses this contribution to the specific heat, leading to the appearance of a minimum on its temperature dependence.

The entropy $[S^\circ(T)]$, the enthalpy of heating $[H^\circ(T) - H^\circ(0)]$, and the Gibbs function $[G^\circ(T) - H^\circ(0)]$ of these compounds in the condensed state were calculated from experimental data on the temperature dependence of the specific heat. The values thus obtained for 298.15 K are shown in Table 5.

From the absolute entropy values for a group of selenium and tellurium compounds their entropies of formation (ΔS_f°) from the elements in the condensed and the gaseous state were calculated. Published data[6-9] on the vapour pressure and on the enthalpies of vaporisation were used in these calculations. The entropies of the elements (needed in these calculations) were taken from standard tabulations.[4,5]

The Gibbs free energy of formation for these compounds (ΔG_f°) were calculated from the enthalpies of formation (see Tables 3 and 4). The results are shown in Table 6.

Table 5. Thermodynamic functions (298.15 K) and melting parameters of selenium and tellurium compounds

Compound	C_p°	S°	$[H^\circ(T)-H^\circ(0)]$	$-[G^\circ(T)-H^\circ(0)]$	T_m°/K	ΔH_m°	ΔS_m°
$(CH_3)_2Se$	121.1	210.8	31.78	31.08	185.14	8.499	49.90
$(CH_2=CH)_2Se$	165.7	262.0	39.94	38.17	178.08	9.374	52.64
$(C_2H_5)_2Se$	174.0	284.9	44.17	40.77	175.30	12.60	71.85
$(CH_3)_2Se_2$	155.0	261.4	38.78	36.16	190.89	8.545	44.76
$(CH_3)_2Te$	125.1	220.5	33.10	32.64	201.87	7.766	38.47
$(C_2H_3)_2Te$	166.1	268.1	41.26	38.67	182.65	9.593	52.52
$(C_2H_5)_2Te$ [a]	183.4	291.0	42.48	44.27	161.50	7.621	47.20
					153.33	7.525	40.87
$(C_3H_7)_2Te$	233.7	362.2	56.38	51.60	191.80	14.28	74.43
$(C_4H_9)_2Te$	286.4	426.0	65.73	62.08	177.05	14.57	82.30
$(C_5H_{11})_2Te$	345.9	501.0	80.88	69.42	215.41	23.11	107.8
$(C_6H_5)_2Te$	305.7	332.4	57.04	42.05	268.53	15.35	57.16

Notes. The parameters C_p°, S°, ΔS_m° are in J mol^{-1} K^{-1}; the functions $[H^\circ(T)-H^\circ(0)]$ and $-[G^\circ(T)-H^\circ(0)]$, and ΔH_m°, are in kJ mol^{-1}. [a] Crystallises in two modifications.

Table 6. Absolute entropies (S°, J mol^{-1} K^{-1}), entropies ($-\Delta S_f^\circ$, J mol^{-1} K^{-1}) and Gibbs free energies (ΔG_f°, kJ mol^{-1}) for the formation of selenium and tellurium compounds at 298.15 K.

Compound	S° (g)	$-\Delta S_f^\circ$ (l)	$-\Delta S_f^\circ$ (g)	ΔG_f° (l)	ΔG_f° (g)
$(CH_3)_2Se$	302.7	234.8	145.5	58	61
$(CH_2=CH)_2Se$	357.6	195.0	99.4	224	237
$(C_2H_5)_2Se$	386.1	431.8	330.6	69	77
$(CH_3)_2Se_2$	–	226.4	–	76	–
$(CH_3)_2Te$	317.7	231.5	130.9	78	83
$(CH_2=CH)_2Te$	361.7	194.7	101.3	274	291
$(C_2H_5)_2Te$	392.4	432.9	331.5	83	95
$(C_3H_7)_2Te$	496.6	633.7	526.3	100	113
$(C_4H_9)_2Te$	534.9	841.8	732.9	144	162
$(C_5H_{11})_2Te$	617.8	1038.7	921.9	114	138

The specific heat and the entropy of the dimethyl compounds of selenium and tellurium in the ideal gas state were calculated also by statistical thermodynamics from spectroscopic data and from information on the structure of the molecules.[57] The calculations were carried out in the rigid rotator–harmonic oscillator approximation for the 273–1500 K temperature range.

The reliability of the calculated results [57] can be established by comparing them with experimental data. For example, the calculated entropies of $(CH_3)_2Se$ and $(CH_3)_2Te$ at 298.15 K are 300 and 309 J mol^{-1} K^{-1} (see Ref. 57), whereas calorimetric measurements for these compounds gave 302.7 and 317.7 J mol^{-1} K^{-1} (see Table 6).

It can be seen that for $(CH_3)_2Se$ the agreement between calculated and experimental results is good, but for $(CH_3)_2Te$ the calculated entropy differs from the calorimetric value by almost 3%, suggesting that the method of calculation used by Mosin et al. [57] should be reconsidered.

Studies of the specific heat in the 6–10 K range have been reported also for some complexes formed by selenium and tellurium compounds with zinc and cadmium alkyls.[58–60] From these values of the specific heat the absolute entropies were calculated, and by using the entropies of the starting components [61] (see Table 6) and their interaction enthalpies the entropies and Gibbs free energies of the reaction (ΔS_r° and ΔG_f° respectively) were also calculated:[38–40]

$$R_2M\ (l) + R_2M'\ (l) \longrightarrow R_2M \cdot R_2M'\ (l),$$

where R = CH_3, C_2H_5; M = Se, Te; M′ = Zn, Cd.

The results of these calculations are shown in Table 7.

Table 7. Specific heats (J mol^{-1} K^{-1}) and entropies of the complexes, entropies (J mol^{-1} K^{-1}) and Gibbs free energies (kJ mol^{-1}) of the synthesis reactions of the liquid complexes at 298.15 K.

Complex	C_p°	S°	$-\Delta S_r^\circ$	$-\Delta G_r^\circ$
$(CH_3)_2Se \cdot Zn(CH_3)_2$	287.2	401.1	11.3	2.8 ± 2.0
$(CH_3)_2Se \cdot Cd(CH_3)_2$	277.7	413.6	−0.8	6.2 ± 1.4
$(CH_3)_2Te \cdot Zn(CH_3)_2$	284.0	420.7	1.4	4.3 ± 1.3
$(CH_3)_2Te \cdot Cd(CH_3)_2$	275.2	413.1	9.5	3.5 ± 1.3
$(C_2H_5)_2Te \cdot Zn(C_2H_5)_2$	399.0	556.9	10.6	–

The uncertainties in the determination of the ΔG_r°(l) values shown in Table 7 are determined mainly by the errors in the enthalpies of interaction of the corresponding components.[38–40] As can be seen from Table 7 the ΔG_r°(l) values for all the complexes have small and not very different negative values.

VI. Average enthalpies, entropies, and Gibbs free energies of the breaking of chemical bonds in the organic compounds of selenium and tellurium

It is interesting to consider the dependence of the strength of chemical bonds on the nature of the atoms and radicals from which the bonds are formed. The determination of the enthalpy of breaking of individual bonds in various compounds is usually a difficult experimental problem, and therefore the average enthalpies of bond breaking ($\bar{D}$) are often calculated.

The $\bar{D}$ values shown in Table 8 for the M–R bonds in the compounds MR_2 (M = Se or Te, R is a radical) are the enthalpy of the reaction $MR_2(g) \rightarrow M(g) + 2R(g)$ divided by the number of bonds. This quantity is calculated by using the formula

$$\bar{D}(M-R) = \tfrac{1}{2}[\Delta H_f^\circ(M, g) + 2\Delta H_f^\circ(R, g) - \Delta H_f^\circ(MR_2, g)],$$

and employing data for the enthalpies of formation of the gaseous reactants in the appropriate reaction.

The $\bar{D}$(M–M) values in the compounds (MR_2) were calculated by means of the equation

$$\bar{D}(M-M) = 2\Delta H_f^\circ(M, g) + 2\Delta H_f^\circ(R, g) - \Delta H_f^\circ[(MR)_2, g] - 2\bar{D}(M-R).$$

It is assumed that the enthalpies of breaking of the M–R bonds are identical in the corresponding MR_2 and $(MR)_2$ compounds.

Table 8. Average enthalpies of bond breaking (298.15 K).

Compound	Bond	$\overline{D}$/kJ mol^{-1}	Compound	Bond	$\overline{D}$/kJ mol^{-1}
$(CH_3)_2O$	$O-CH_3$	360 ± 4	$(C_4H_9)_2Se_2$	$Se-Se$	211 ± 22
$(C_2H_5)_2O$	$O-C_2H_5$	356 ± 4	$(C_6H_5)_2Se_2$	$Se-Se$	280 ± 13
$(C_6H_5)_2O$	$O-C_6H_5$	427 ± 8	C_6H_5SeBr	$Se-Br$	258 ± 12
$(CH_3)_2S$	$S-CH_3$	297 ± 4	$C_6H_5SeBr_3$	$Se-Br$	172 ± 4
$(C_2H_5)_2S$	$S-C_2H_5$	285 ± 4	$(CH_3)_2Te$	$Te-CH_3$	220 ± 3
$(C_6H_5)_2S$	$S-C_6H_5$	347 ± 8	$(CH_2=CH)_2Te$	$Te-C_2H_3$	227 ± 9
$(CH_3)_2Se$	$Se-CH_3$	251 ± 4	$(C_2H_5)_2Te$	$Te-C_2H_5$	206 ± 5
$(CH_2=CH)_2Se$	$Se-C_2H_3$	271 ± 8	$(C_3H_7)_2Te$	$Te-C_3H_7$	206 ± 8
$(C_2H_5)_2Se$	$Se-C_2H_5$	232 ± 5	$(i\text{-}C_3H_7)_2Te$	$Te-i\text{-}C_3H_7$	192 ± 4
$(i\text{-}C_3H_7)_2Se$	$Se-i\text{-}C_3H_7$	241 ± 5	$(C_4H_9)_2Te$	$Te-C_4H_9$	195 ± 8
$(C_5H_{11})_2Se$	$Se-C_5H_{11}$	238	$(C_5H_{11})_2Te$	$Te-C_5H_{11}$	202
$(C_6H_5)_2Se$	$Se-C_6H_5$	294 ± 8	$(i\text{-}C_5H_{11})_2Te$	$Te-i\text{-}C_5H_{11}$	202
$(CH_3)_2Se_2$	$Se-Se$	192 ± 12	$(C_6H_5)_2Te$	$Te-C_6H_5$	267 ± 9
$(C_2H_5)_2Se_2$	$Se-Se$	222 ± 13	$(C_3H_7)_2Te_2$	$Te-Te$	119 ± 5
			$(C_4H_9)_2Te_2$	$Te-Te$	149 ± 6

Table 9. Average values of the entropy (J mol^{-1} K^{-1}) and the Gibbs free energy (kJ mol^{-1}) for the breaking of bonds at 298.15 K.

Compound[a]	Bond	$\Delta\overline{S}$	$\Delta\overline{G}$
$(CH_3)_2O$	$O-CH_3$	141	318
$(C_2H_5)_2O$	$O-C_2H_5$	161	308
$(CH_3)_2S$	$S-CH_3$	135	257
$(C_2H_5)_2S$	$S-C_2H_5$	152	240
$(CH_3)_2Se$	$Se-CH_3$	131	208
$(CH_2=CH)_2Se$	$Se-C_2H_3$	143	229
$(C_2H_5)_2Se$	$Se-C_2H_5$	147	188
$(CH_3)_2Te$	$Te-CH_3$	126	182
$(CH_2=CH)_2Te$	$Te-C_2H_3$	143	184
$(C_2H_5)_2Te$	$Te-C_2H_5$	147	162

[a] Because of the lack of the appropriate auxiliary data the quantities $\Delta\overline{S}$ and $\Delta\overline{G}$ cannot be calculated for all the compounds listed in Tables 3 and 4.

For comparison we show in Table 8 the $\overline{D}$ values for various bonds which include oxygen or sulfur. These calculations relied on data given in Tables 1, 3, and 4 and in published tabulations.[3-5,12,62]

In Table 9 we list the average entropies ($\Delta\overline{S}$) of bond breaking, obtained by the expression

$$\Delta\overline{S}(M-R) = \tfrac{1}{2}[S^\circ(M,\ g) + 2\,S^\circ(R,\ g) - S^\circ(MR_2,\ g)],$$

where S° are the standard entropies of the reactants in the dissociation of the compound MR_2 (see Table 6) into the fragments M and 2R (see Refs 3-5).

The $\Delta\overline{S}(M-R)$ and $\overline{D}(M-R)$ values were used to calculate the average values of the Gibbs free energy ($\Delta\overline{G}$) for the breaking of the M-R bonds, which we used as a measure of their thermodynamic stability (Table 9). The calculations for a temperature of 298.15 K were carried out using the equation

$$\Delta\overline{G}(M-R) = \overline{D}(M-R) - 298.15\,\Delta\overline{S}(M-R).$$

* * *

An analysis of the calculated and the experimental data reported above or previously published has established the following features of the thermodynamic characteristics of the bonds formed by selenium and by tellurium.

1. In the compounds R_2M (where M = O, S, Se, Te) of the same radical R the average enthalpy, entropy, and Gibbs free energy of the breaking of the M-R bond decrease as the atomic number of the element M increases.

2. For a given element M the average enthalpies of bond breaking vary in the following sequence:

$$M-C_6H_5 > M-C_2H_3 > M-CH_3 > M-C_2H_5$$

$$\approx M-C_3H_7 \approx M-C_4H_9 \approx M-C_5H_{11}.$$

3. The enthalpy of breaking of the $Te-C_3H_7$ bond in $Te(n\text{-}C_3H_7)_2$ is higher by 14 kJ mol^{-1} than the same parameter in $Te(i\text{-}C_3H_7)_2$, as is also found in the propyl compounds of mercury, boron, and tin.[1]

4. The parameters $\overline{D}(M-M)$ in the compounds $(RM)_2$ (except diphenyl diselenide) are not markedly dependent on the nature of the R radical; they are much smaller than the $\overline{D}(M-R)$ values in the R_2M compounds with the same radicals (see Table 8) and $\overline{D}(M-M)$ in the M_2 (g) molecules,[11] for which $D(Se-Se)$ = 305 and $D(Te-Te)$ = 259 kJ mol^{-1}.

In spite of the experimental ΔH_f° values available for the crystalline dibenzyl selenide and diselenide (see Table 3) a precise calculation of the enthalpy of breaking of the Se-Se bond in $(C_6H_5CH_2)_2Se_2$ is impossible because of the lack of data on the enthalpy of sublimation of $(C_6H_5CH_2)_2Se$, needed to calculate ΔH_f° for this compound in the gas phase. However, an approximate estimate of $\overline{D}(Se-Se)$ in dibenzyl diselenide can be made by assuming that $\overline{D}(Se-CH_2C_6H_5)$ in dibenzyl selenide is $\sim$63 kJ mol^{-1} lower than $\overline{D}(Se-C_2H_5)$ in diethyl selenide (see Table 8), i.e. as is observed in tetraethyl- and tetrabenzylgermanium,[1] for which $\overline{D}(Ge-C_2H_5) = 243 \pm 4$ and $\overline{D}(Ge-CH_2C_6H_5) = 180 \pm 4$ kJ mol^{-1}. In this case the calculation of $\overline{D}(Se-Se)$ in dibenzyl diselenide by the equation given above gives a value of 192 kJ mol^{-1}, identical to $\overline{D}(Se-Se)$ for $(CH_3)_2Se_2$ (see Table 8).

The large difference between the $\overline{D}(Se-Se)$ values for the diphenyl and the dialkyl compounds can be ascribed to lack of precision of the available experimental data or to specific properties of the chemical bonds formed by selenium in these compounds.

5. By using the given values of ΔH_f° for gaseous $PdCl_2 \cdot 2\,M(C_2H_5)_2$ and $M(C_2H_5)_2$ (M = Se or Te) and the ΔH_f° ($PdCl_2$, g) value 128.4 $\pm$ 10.5 kJ mol^{-1} (see Ref. 4) the $\overline{D}(Pd-M)$ values for these complexes were calculated by the equation

$$\overline{D}(Pd-M) = \tfrac{1}{2}\{\Delta H_f^\circ\,(PdCl_2,\ g) + 2\,\Delta H_f^\circ\,[M(C_2H_5)_2,\ g]$$

$$-\Delta H_f^\circ[PdCl2.2M(C2H5)2, g].$$

This calculation gave the very similar values $\overline{D}(Pd-Se) = 191 \pm 10$ and $\overline{D}(Pd-Te) = 204 \pm 10$ kJ mol^{-1}.

It is interesting to note that $\overline{D}(Pd-Se)$ is close to $\overline{D}(Se-Se)$ in dialkyl diselenides, and $\overline{D}(Pd-Te)$ coincides within the error of the determination with $\overline{D}(Te-R)$ in dialkyl tellurides and is significantly higher than $\overline{D}(Te-Te)$ in the alkyl compounds R_2Te_2 (see Table 8).

6. The main contribution to the parameter $\Delta\overline{G}(M-R)$ comes from the enthalpy factor $\overline{D}$, whereas only 15%–20% of the $\overline{D}$ value contributes to the entropy component ($298.15\Delta\overline{S}$). It follows that the relative thermodynamic stability of these compounds can be established from the $\overline{D}(M-R)$, values, which are experimentally much better characterised than the $\Delta\overline{G}(M-R)$ values.

Further developments in the experimental thermochemical studies of selenides and tellurides should offer a more detailed understanding of the special features found in the thermodynamic characteristics of compounds of this type.

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References

1. V I Tel'noi, I B Rabinovich *Usp. Khim.* **49** 1137 (1980) [*Russ. Chem. Rev.* **49** 603 (1980)]
2. L Batt *The Chemistry of Organic Selenium and Tellurium Compounds* (Eds S Patai, Z Rappoport) (New York: Wiley, 1986) p. 157
3. D D Wagman, W H Evans, V B Parker, J Halow, S M Baidley, R H Schumm *Selected Values of Chemical Thermodynamic Properties* (Washington, DC: National Bureau of Standards) Technical Note 270-1 (1965); 270-2 (1967); 270-4 (1969); 270-5 (1971)
4. V P Glushko (Ed.) *Termicheskie Konstanty Veshchestv. Spravochnik* (Thermal Constants of Substances. Handbook) Vol. 1–10 (Moscow: Nauka, 1965–1981)
5. V P Glushko (Ed.) *Termodinamicheskie Svoistva Individual'nykh Veshchestv Spravochnik* (Thermodynamic Properties of Individial Substances. Handbook) Vols 1, 2 (Moscow: Nauka, 1978, 1979)
6. A K Baev, Yu P Gubar', B I Kozyrkin, in *Trudy po Khimii i Khimicheskoi Tekhnologii* (Proceedings on Chemistry and Chemical Technology) (Gor'ky: Gor'ky State University, 1975) Vol. 4, p. 83
7. A K Baev, Yu P Gubar', I L Gaidym, B I Kozyrkin, in *Tez. Dokl. II Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Second Conference on the Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University, 1976) p. 22
8. B I Kozyrkin, E S Burdina, B I Salamatin, L L Ivanov, in *Tez. Dokl. II Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Second Conference on the Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University, 1976) p. 26
9. A I Podkovyrov, A K Baev, B I Kozyrkin, in *Tez. Dokl. VI Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Sixth Conference on the Thermodynamics of Organic Compounds) (Minsk: Belorussian State University, 1990) p. 73
10. D S Barnes, C T Mortimer *J. Chem. Thermodyn.* **5** 371 (1973)
11. V I Tel'noi, K V Kir'yanov, V N Larina, E N Karataev *Vysokochis. Veshchestva* (4) 80 (1992)
12. L V Gurvich, G V Karachevtsev, V N Kondrat'ev, Yu A Lebedev, V A Medvedev, V K Potapov, Yu S Khodeev, in *Energii Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu* (Energies of Rupture of Chemical Bonds. Ionisation Potentials and Electron Affinity) (Ed. V N Kondrat'ev) (Moscow: Nauka, 1974) p. 351
13. G Gattow *Z. Anorg. Allg. Chem.* **317** 245 (1962)
14. C N Gadzhiev *Zh. Fiz. Khim.* **40** 241 (1966)
15. A Schneider, G Zintl *Z. Anorg. Allg. Chem.* **308** 290 (1961)
16. S N Gadzhiev, K A Sharifov *Izv. Akad. Nauk Azerb. SSR, Ser. Fiz.-Tekh. Khim. Nauk* (1) 47 (1962)
17. D W Muenow, J W Hastie, R Hauge, R Bautista, J L Margrave *Trans. Faraday Soc.* **65** 3210 (1969)
18. D Chatterji, J V Smith *J. Electrochem. Soc.* **120** 889 (1973)
19. C Mallika, O M Sreedharan *J. Chem. Thermodyn.* **18** 727 (1986)
20. E H P Cordfunke, W Ouwelties, G Prins *J. Chem. Thermodyn.* **19** 369 (1987)
21. B I Zhuk, A M Ob'edkov, G A Domrachev *Dokl. Akad. Nauk SSSR* **257** 923 (1981)
22. P A G O'Hare, K T Jensen, G K Johnson *J. Chem. Thermodyn.* **18** 765 (1986)
23. C Vanderzee, L A Noll *J. Chem. Thermodyn.* **19** 417 (1987)
24. H Merten, H Schlüter *Chem. Ber.* **69** 1364 (1936)
25. M R Arshadi, M Shabrand *J. Chem. Soc., Perkin Trans. 2* 1732 (1973)
26. V I Tel'noi, V N Larina, E N Karataev, V K Stankevich *Metalloorg. Khim.* **1** 1102 (1988)
27. V I Tel'noi, V N Larina, E N Karataev, S V Amosova *Zh. Obshch. Khim.* **59** 2012 (1989)
28. V I Tel'noi, I B Rabinovich, V N Larina, E N Karataev, in *Termodinamika Organicheskikh Soedinenii* (Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University, 1989) p. 3
29. V N Larina, E N Karataev, N A Korchevin, V I Tel'noi, in *Tez. Dokl. VI Vsesoyuz. Soveshch. "Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov", Nizhnii Novgorod, 1991* (Abstracts of Reports at the Sixth All-Union Meeting "Application of Organometallic Compounds for the Preparation of Inorganic Coatings and Materials" (Nizhny Novgorod: Nizhny Novgorod State University, 1991) Part I, p. 32
30. V G Tsvetkov, B I Kozyrkin, in *Termodinamika Organicheskikh Soedinenii* (Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University,1978) Vol. 7, p. 73
31. G C Hayward, P J Hendra *J. Chem. Soc., A* 1760 (1969)
32. C T Mortimer, I Waterhouse *J. Chem. Thermodyn.* **12** 961 (1980)
33. M G Voronkov, V A Klyuchnikov, S N Kolabin, G N Shvets, P I Varushin, E N Deryagina, N A Korchevin, S I Tsvetnitskaya *Dokl. Akad. Nauk SSSR* **307** 1139 (1989)
34. C T Mortimer, I Waterhouse *Thermochim. Acta* **131** 91 (1988)
35. V G Tsvetkov, B I Kozyrkin, K K Fukin, R F Galliulina *Zh. Obshch. Khim.* **47** 2155 (1977)
36. V G Tsvetkov, B I Kozyrkin, K K Fukin, Z F Galliulina, V E Bychkov, in *Tez. Dokl. II Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Second Conference on the Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University, 1976) p. 9
37. G E Coates *J. Chem. Soc.* 2003 (1951)
38. S I Gerasimchuk, I A Feshchenko, E N Karataev, M Yu Gatilov, L V Stepanova, in *Tez. Dokl. Vserossiiskogo Seminara po Khimicheskoi Termodinamike i Kalorimetrii, Nizhnii Novgorod, 1994* (Abstracts of Reports at the All-Russian Seminar on Chemical Thermodynamics and Calorimetry) (Nizhny Novgorod: Nizhny Novgorod State University, 1994) p. 38
39. Yu P Pavlovskii, N S Kachurina, Yu Ya Van-Chin-Syan, E N Dregich', in *Tez. Dokl. Vsesoyuz. Konf. "Poluchenie, Svoistva, Analiz i Primenenie Soedinenii s Molekulyarnoi Kristallicheskoi Reshetkoi dlya Novoi Tekhniki", Nizhnii Novgorod, 1991* (Abstracts of Reports at the All-Union Conference "Production, Properties, Analysis, and Application of Compounds with a Molecular Crystal Lattice in Modern Technology") (Nizhny Novgorod: Nizhny Novgorod State University, 1991) p. 27
40. Yu P Pavlovskii, V V Kochubei, E N Karataev, I A Feshchenko, A D Zorin, in *Tez. Dokl. VI Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Sixth Conference on the Thermodynamics of Organic Compounds) (Minsk: Belorussian State University, 1990) p. 71
41. A I Gal', O V Kuz'min, K A Chernyshev, R A Rostunova, E N Lebedev, O S Sheveleva, in *Elementoorganicheskie Soedineniya i Ikh Primenenie* (Organoelement Compounds and Their Application (Moscow: NIITEKhIM, 1981) p. 30
42. V I Tel'noi, V N Larina, E N Karataev, E N Deryagina *Zh. Fiz. Khim.* **62** 3108 (1988)

43. V I Tel'noi, V N Larina, E N Karataev, K V Kir'yanov, in *Tez. Dokl. V Vsesoyuz. Konf. po Metalloorganicheskoi Khimii, Riga, 1991* (Abstracts of Reports at the Fifth All-Union Conference on Organometallic Chemistry) (Riga: Institute of Organic Synthesis, Academy of Sciences Latv. SSR, 1991) p. 61
44. I B Rabinovich, V N Larina, G P Kamelova, N A Korchevin, V I Tel'noi, M S Sheiman, in *Tez. Dokl. Vsesoyuz. Konf. "Poluchenie, Svoistva, Analiz i Primenenie Soedinenii s Molekulyarnoi Kristallicheskoi Reshetkoi dlya Novoi Tekhniki", Nizhnii Novgorod, 1991* (Abstracts of Reports at the All-Union Conference "Production, Properties, Analysis, and Application of Compounds with a Molecular Crystal Lattice in Modern Technology") (Nizhny Novgorod: Nizhny Novgorod State University, 1991) p. 26
45. V I Tel'noy, V N Larina, V T Demarin, in *The 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 1994 (Book of Abstracts)* (Grado: University of Trieste, 1994) p. 300
46. A A Kudryavtsev *Khimiya i Tekhnologiya Selena i Tellura* (Chemistry and Technology of Selenium and Tellurium) (Moscow: Metallurgiya, 1968) p. 339
47. A Evans, C T Mortimer *Thermochim. Acta* **131** 103 (1988)
48. A Evans, C T Mortimer *J. Chem. Thermodyn.* **7** 363 (1975)
49. I B Rabinovich, A D Zorin, V I Tel'noi, M S Sheiman, in *Termodinamika Organicheskikh Soedinenii* (Thermodynamics of Organic Compounds) (Gor'ky: Gor'ky State University, 1988) p. 27
50. I B Rabinovich, M S Sheiman, V P Nistratov, E N Karataev, I A Feshchenko, L V Stepanova, M G Voronkov, E N Deryagina, N A Korchevin, in *Tez. Dokl. II Vsesoyuz. Konf. po Metalloorganicheskoi Khimii, Ufa, 1985* (Abstracts of Reports at the Second All-Union Conference on Organometallic Chemistry) (Ufa: Bashkir. Division at the Academy of Sciences of the USSR, 1985) Part 1, p. 80
51. M S Sheiman, V P Nistratov, G P Kamelova, E N Karataev, I A Feshchenko, V B Fedoseev, in *Tez. Dokl. XI Vsesoyuzn. Konf. po Kalorimetrii i Khimicheskoi Termodinamike, Novosibirsk, 1986* (Abstracts of Reports at the XIth All-Union Conference on Calorimetry and Chemical Thermodynamics) (Novosibirsk: Institute of Inorganic Chemistry, Siberian Division of the Academy of Sciences of the USSR, 1986) p. 159
52. I B Rabinovich, V P Nistratov, M S Sheiman, G P Kamelova, K G Shvetsova, E N Karataev, in *Tez. Dokl. IV Vsesoyuz. Konf. po Metalloorganicheskoi Khimii, Kazan', 1988* (Abstracts of Reports at the Fourth All-Union Conference on Organometallic Chemistry) (Kazan': Kazan' State University, 1988) p. 353
53. I B Rabinovich, M S Sheiman, G P Kamelova, V P Nistratov, E N Karataev *Zh. Fiz. Khim.* **65** 2071 (1991)
54. G P Kamelova, B I Kozyrkin, K G Shvetsova, Yu A Manin, I A Zelyaev, in *Tez. Dokl. VI Vsesoyuz. Konf. po Termodinamike Organicheskikh Soedinenii* (Abstracts of Reports at the Sixth Conference on the Thermodynamics of Organic Compounds) (Minsk: Belorussian State University, 1990) p. 68
55. M S Sheiman, G P Kamelova, V I Tel'noy, V N Larina, in *Abstracts of the 11th IUPAC Conference on Chemical Thermodynamics, Como, Italy, 1990* (Como: A Volta, 1990) p. 285
56. M S Sheiman, G P Kamelova, V P Nistratov, in *The 6th European Symposium on Thermal Analysis and Calorimetry, Grado, Italy, 1994 (Book of Abstracts)* (Grado: University of Trieste, 1994) p. 282
57. A M Mosin, Yu Kh Shaulov, N I Andreeva *Zh. Fiz. Khim.* **48** 2356 (1974)
58. B V Lebedev, T G Kulagina *J. Chem. Thermodyn.* **22** 21 (1990)
59. B V Lebedev, T G Kulagina *J. Chem. Thermodyn.* **23** 1 (1991)
60. B V Lebedev, T G Kulagina, M S Sheiman, V P Nistratov *J. Chem. Thermodyn.* **24** 673 (1992)
61. V P Nistratov, I B Rabinovich, in *Primenenie Metalloorganicheskikh Soedinenii dlya Polucheniya Neorganicheskikh Pokrytii i Materialov* (Application of Organometallic Compounds for the Preparation of Inorganic Coatings and Materials) (Moscow: Nauka, 1986) p. 34
62. D R Stull, E F Westrum Jr, G C Sinke, in *The Chemical Thermodynamics of Organic Compounds* (Translated into Russian; Moscow: Mir, 1971) p. 807