Drop calorimetry of the compounds $NbCl_5$, $TaCl_5$, $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$, and $CsTaCl_6$

E. E. SHAWKI,[1] S. N. FLENGAS, AND D. R. SADOWAY[2]

Department of Metallurgy and Materials Science, University of Toronto, Toronto, Ont., Canada M5S 1A4

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Enthalpy contents for $NbCl_5$, $TaCl_5$, $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$, and $CsTaCl_6$ were measured as functions of temperature using a high temperature aluminum block drop calorimeter. It was found that the solid compounds $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$, and $CsTaCl_6$ undergo allotropic solid–solid transformations and the enthalpies and entropies associated with these phase changes, as well as from fusion, have been evaluated.

Molar heat capacities for the systems investigated are reported as linear functions of temperature.

The molar heat capacities for solid and molten $NbCl_5$ or $TaCl_5$ were used together with available vapour pressure data to express enthalpies and free energies of vaporization for these compounds as functions of temperature through the third law calculation method.

Key words: calorimetry, heat capacities, transition enthalpies, niobium compounds, tantalum compounds.

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Utilisant un calorimètre adiabatique en aluminium opérant à haute température, on a mesuré les enthalpies du $NbCl_5$, du $TaCl_5$, du $RbNbCl_6$, du $CsNbCl_6$, du $RbTaCl_6$ et du $CsTaCl_6$ en fonction de la température. On a trouvé que les composés solides $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$ et $CsTaCl_6$ subissent des transformations allotropiques solide–solide et on a évalué les enthalpies et les entropies associées avec ces changements de phase ainsi qu'avec la fusion.

On rapporte les capacités calorifiques molaires des systèmes étudiés sous la forme de fonctions linéaires de la température.

Faisant appel à la méthode de calcul de la troisième loi de la thermodynamique et utilisant les capacités calorifiques molaires des $NbCl_5$ et $TaCl_5$ solides et fondus de concert avec les données disponibles relatives aux pressions de vapeur, on a pu obtenir une expression permettant de relier les enthalpies et les énergies libres de vaporisation de ces composés en fonction de la température.

Mots clés: calorimétrée, capacités calorifiques, enthalpies de transition, composés de niobium, composés de tantalum.

[Traduit par la revue]

Introduction

The complex compounds $NaNbCl_6$, $NaTaCl_6$, $KNbCl_6$, $KTaCl_6$, $RbNbCl_6$, $RbTaCl_6$, $CsNbCl_6$, and $CsTaCl_6$ have been synthesized in this laboratory by the reaction of $NbCl_5$ or $TaCl_5$ vapours with the respective alkali metal chlorides, in closed reactors, under specific temperature and vapour pressure conditions. The preparation method has been given elsewhere (1). X-ray diffraction patterns were also determined and temperatures for phase transformations were measured by the cooling curve technique.

These compounds represent thermodynamically stable forms of the volatile covalently bonded pentachlorides of Nb and Ta (2, 3) and, as such, they are of interest for the separation of Nb from Ta (4), and as potential electrolytes for the recovery of these metals by used salt electrolysis.

Crystal structures of the $AMCl_6$ type compounds, where A is an alkali metal like Na, K, Rb, and Cs, and M is either Nb or Ta, and parts of the phase diagrams of the ACl–MCl_5 type binary systems have also been reported by several investigators (1, 5–9).

In the present investigation the thermal properties of the compounds $NbCl_5$, $TaCl_5$, $RbNbCl_6$, $CsNbCl_6$, $RbTaCl_6$, and $CsTaCl_6$ were measured by drop calorimetry from various high temperatures. From these measurements molar heat capacities have been calculated as functions of temperature, and enthalpy changes representing solid–solid allotropic transformations and melting have been obtained.

Thermal data for these compounds, with the exception of $NbCl_5$ and $TaCl_5$, are not available in the literature.

Experimental

The preparation of anhydrous $NbCl_5$ and $TaCl_5$ having a purity better than 99.99% by weight and the synthesis of the stoichiometric $AMCl_6$-type compounds having a purity better than 99.8% by weight, have been described elsewhere (1, 2). The stoichiometry of each complex compound was determined from the weight gain of the alkali chloride when it is reacted with either $NbCl_5$ or $TaCl_5$ vapours. In all cases the mole ratio MCl_5/ACl was better than 0.995.

The twin Al-block drop calorimeter used for these measurements was the same instrument previously designed and built in this laboratory (10, 11).

The calorimeter proper was calibrated with synthetic sapphire certified by the U.S. Bureau of Standards. Its enthalpy content is known to be the following function of temperature (12),

$$[1] \quad H_T - H_0 = 82.1461 + 1.7106 \times 10^{-6}T^2 - 46.9949 \times \log_{10} T + 0.1485704\,T \text{ (in kJ mol}^{-1}\text{)}$$

where T is in Kelvin.

A typical calorimetric trace is given in Fig. 1.

The measured thermopile signals were all referred to a common reference temperature of 298 K, using the linear correction method of Goodkin *et al.* (13).

Since evacuated silica glass capsules lined with Pt-foil 0.5 mm thick were used as containers for the sapphire and for the salt samples, experiments were performed to determine the thermopile output per gram of silica and per gram of Pt, for temperatures up to 650°C. The least squares fit to 27 experimental points for SiO_2 corresponds to the linear equation,

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[1] Present address: Ubichem Limited, Chandlers Ford Industrial Estate, Eastleigh, Hampshire 5O5 3AR, U.K.

[2] Present address: Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139, U.S.A.

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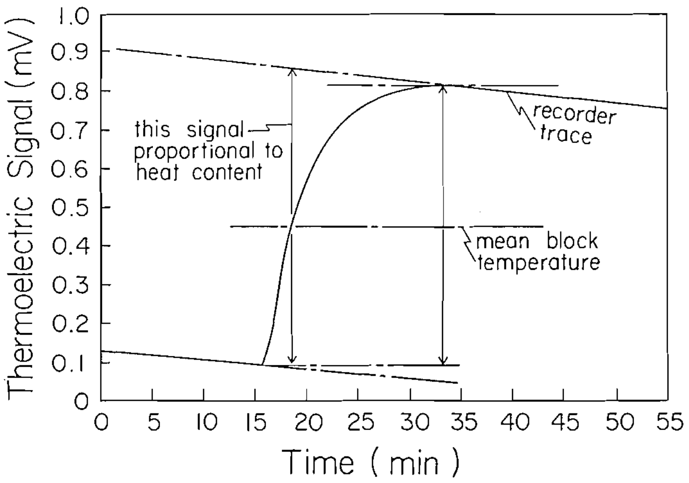

FIG. 1. Typical calorimetric trace of the thermopile signal.

$$[2] \quad V_{SiO_2} = -2.3943 \times 10^{-2} + 6.4691 \times 10^{-5} T + 1.83271 \times 10^{-8} T^2 + 849.5 \times 10^{-3} T^{-1} \text{ (in mV/g SiO}_2\text{)}$$

where T is given in Kelvin. The correlation coefficient is 0.9997 and the standard error of estimate is 3.129×10^{-3} mV/g SiO_2.

The latter is a measure of the scatter about the linear regression curve and is calculated from the well known expression

$$S_{y,x} = \sqrt{\frac{\Sigma d^2}{n}}$$

where d's are the differences between the experimental and the estimated values of a dependent variable y, where $y = f(x)$.

The corresponding thermoelectric signal for platinum, based on eleven determinations, was

$$[3] \quad V_{Pt} = 4.692 \times 10^{-3} + 4.498 \times 10^{-6} T + 3.205 \times 10^{-9} T^2 + 177.194 \times 10^{-6} T^{1/2} \text{ (in mV/g Pt)}$$

The correlation coefficient is 0.9996 and the standard error is 6.5×10^{-6} mV/g Pt, for temperatures up to 650°C.

Eleven drops were made with capsules containing the NBS sapphire to cover the temperature range from 150 to 650°C.

In a typical calibration experiment, the weight of the silica capsule was 7.0 g, the weight of Pt liner was 1.0 g, and that of the synthetic sapphire was 7 g.

The calorimetric constant of the instrument, or the number of joules corresponding to one millivolt of thermopile emf, was calculated from eqs. [1], [2], and [3]. The mean of eleven determinations, from 160 to 663°C, gave a value of 11 853 ± 259 J per mV.

There was no detectable temperature dependence.

With this value, and eqs. [1] and [2], the enthalpy contents of silica and platinum, at 600°C, were calculated and compared well with literature values (14). Thus, $H_{600} - H_{298}$ for platinum, which is given as 8 066 J mol^{-1}, compares well with the present value of 8 100 J mol^{-1} calculated from the present results. Similarly, for silica, the literature value of 16 556 J mol^{-1} compares well with the present 16 300 J mol^{-1}.

From such comparisons and from calculations of the standard errors, it is estimated that the calorimeter used for the present measurements was capable of measuring enthalpy contents with confidence to better than 2%.

Enthalpy contents for the various compounds were measured on at least two samples for each compound. Sample weights were between 10 and 15 g. The vapour space in the capsules was small enough that vaporization had a negligible effect on enthalpies.

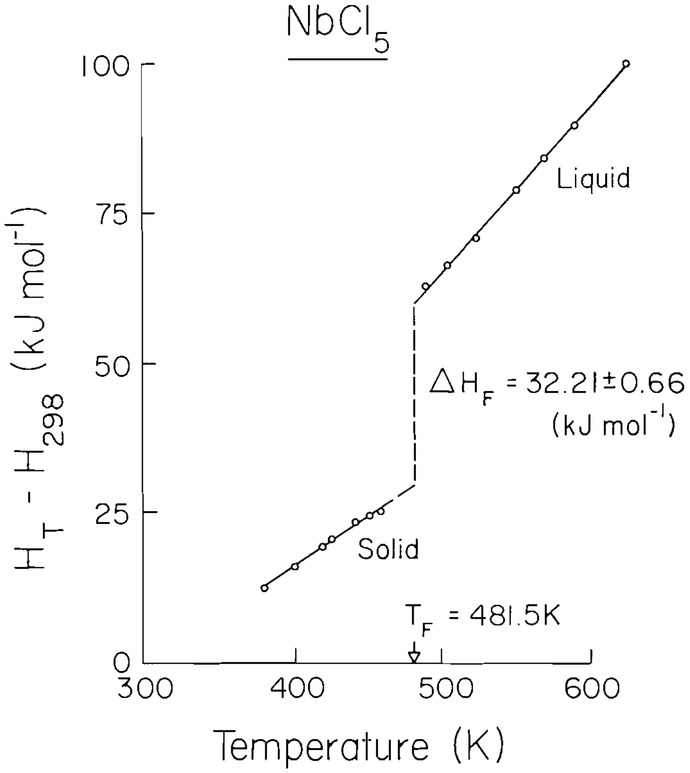

FIG. 2. Enthalpy content of $NbCl_5$ as a function of temperature. Points are experimental. Curves drawn through points represent the least squares fit from Table 1.

Results

Plots of $H_T - H_{298}$ for the various compounds investigated are presented in Figs. 2 to 7. The data have been fitted by least squares to second order polynomials of the form,

$$[4] \quad H_T - H_{298} = a + bT + cT^2 \text{ (kJ mol}^{-1}\text{)}$$

Values of the coefficients a, b, and c are given in Table 1 together with the corresponding standard errors and the temperature ranges of measurements.

Molar heat capacities are readily calculated from eq. [4] from the expression $(\partial H / \partial T)_p = C_p$, as

$$[5] \quad C_p = A + BT \text{ (J K}^{-1}\text{ mol}^{-1}\text{)}$$

The coefficients A and B for the molar heat capacities, transition enthalpies, and transition temperatures, are given in Table 2.

Enthalpy changes corresponding to solid–solid transformations, or to melting, have been obtained by extrapolating the enthalpy contents for any two different phases to the corresponding transition temperatures.

Prior to a drop, solid samples of a compound in either the α or the β configuration were kept at the desired constant high temperature for time periods differing by over 6 h with no detectable effect on their enthalpy contents. It appears, therefore, that complete conversion to the higher temperature configuration was achieved in all cases.

Discussion

A survey of the literature shows only one other calorimetric study of the enthalpy content of $NbCl_5$. Keneshea *et al.* (15) measured the enthalpy increments above 298 K for solid and

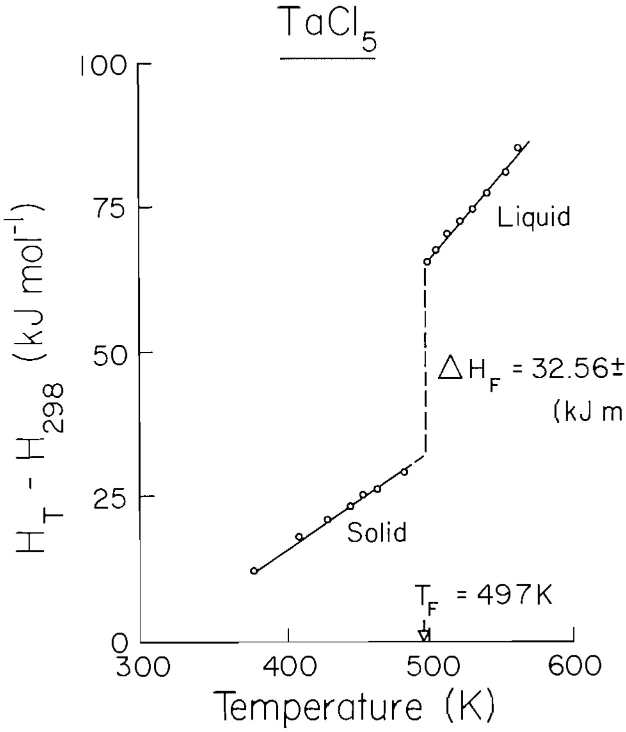

FIG. 3. Enthalpy content of $TaCl_5$ as a function of temperature. Points are experimental. Curves drawn through points represent the least squares fit from Table 1.

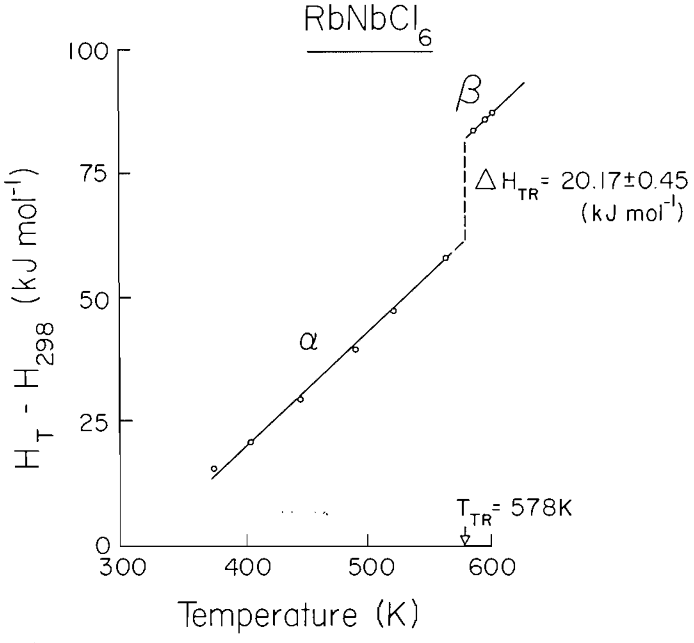

FIG. 4. Enthalpy content of $RbNbCl_6$ as a function of temperature. Curves drawn through the experimental points represent the least squares fit from Table 1.

liquid $NbCl_5$. Their results are given respectively as,

[6] $(H_T^0 - H_{298}^0)_s = -44.06 + 14.79 \times 10^{-2} T$, $\pm$ 0.29 kJ mol^{-1} for solid $NbCl_5$

and

[7] $(H_T^0 - H_{298}^0)_l = -50.71 + 23.96 \times 10^{-2} T - 30.71 \times 10^{-9} T^3$, $\pm$ 0.92 kJ mol^{-1} for liquid $NbCl_5$

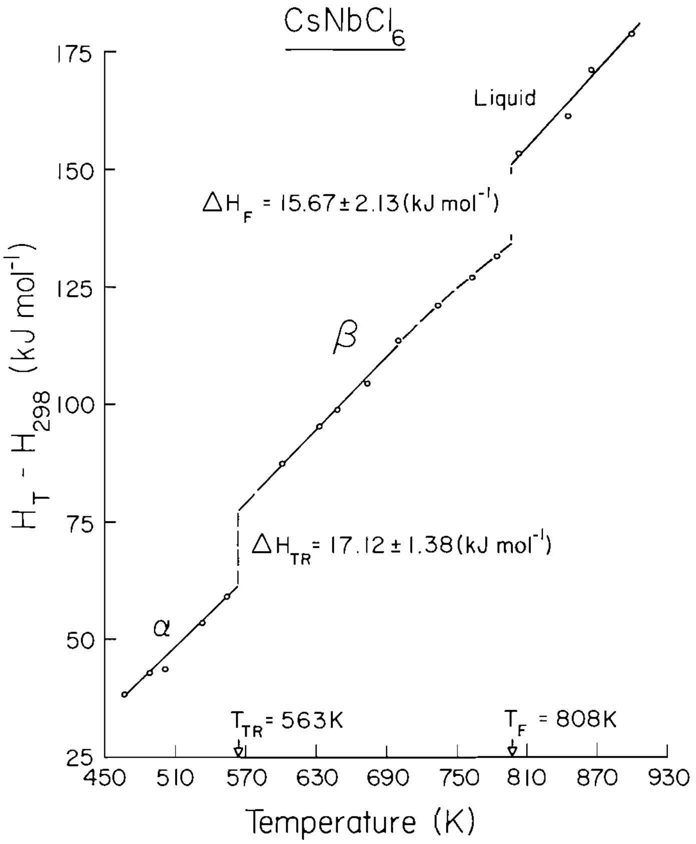

FIG. 5. Enthalpy content of $CsNbCl_6$ as a function of temperature. Curves drawn through the experimental points represent the least squares fit from Table 1.

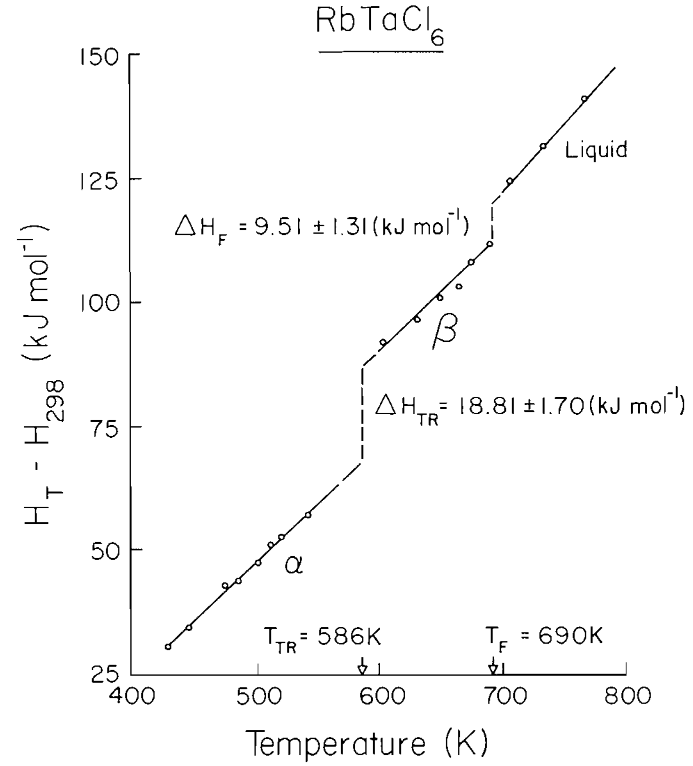

FIG. 6. Enthalpy content of $RbTaCl_6$ as a function of temperature. Curves drawn through the experimental points represent the least squares fit from Table 1.

TABLE 1. Calorimetric enthalpy data fitted by least squares to the equation $H_T - H_{298} = a + bT + cT^2$ (kJ mol^{-1})

Compound	a	$b \times 10^2$	$c \times 10^6$	Standard error of estimate (±)	Temperature range of measurements (K)	Sample characteristics
$NbCl_5$ (s)	−46.67	15.673	—	0.364	380–481	Yellow powder
$NbCl_5$ (ℓ)	−68.032	26.819	—	0.552	481–626	
$TaCl_5$ (s)	−45.062	14.820	21.757	0.318	379–497	White powder
$TaCl_5$ (ℓ)	−87.885	30.694	—	0.585	497–563	
α-$RbNbCl_6$ (s)	−37.664	7.795	162.76	0.443	376–578	Green powder (3)
β-$RbNbCl_6$ (s)	−51.149	23.012	—	0.088	578–602	
α-$CsNbCl_6$ (s)	−59.844	18.560	51.463	0.410	467–563	Green powder (3)
β-$CsNbCl_6$ (s)	−38.752	18.263	43.93	1.314	563–808	
$CsNbCl_6$ (ℓ)	−74.425	28.192	—	1.682	808–898	
α-$RbTaCl_6$ (s)	−69.350	23.259	—	1.301	429–586	White powder (3)
β-$RbTaCl_6$ (s)	−58.844	24.673	—	1.096	586–690	
$RbTaCl_6$ (ℓ)	−51.170	24.941	—	0.720	690–812	
α-$CsTaCl_6$ (s)	−77.722	25.983	—	0.749	480–569	White powder (3)
β-$CsTaCl_6$ (s)	−81.245	28.966	—	1.623	569–821	
$CsTaCl_6$ (ℓ)	−83.755	30.652	—	0.744	821–877	

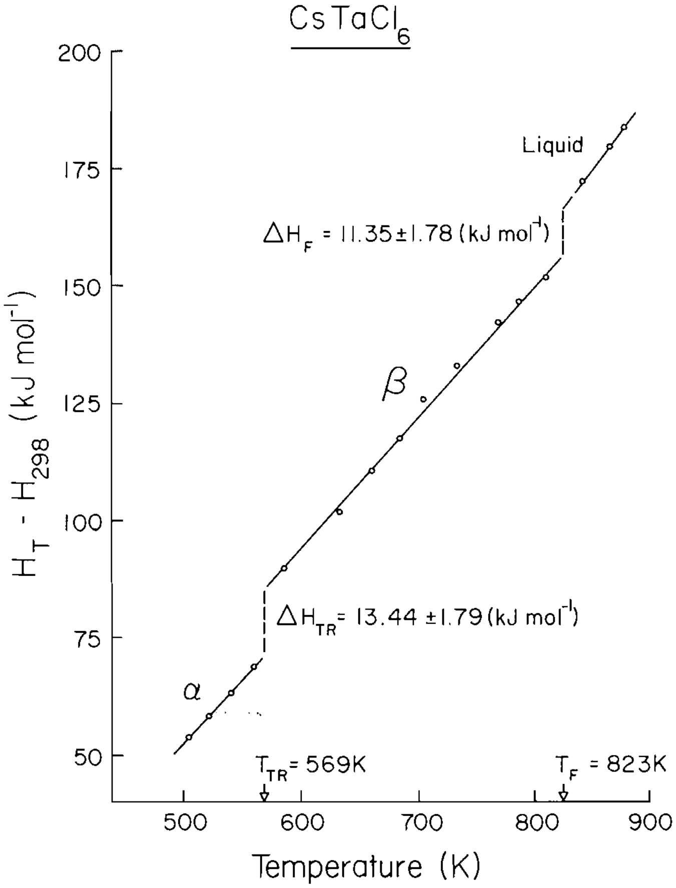

FIG. 7. Enthalpy contents of $CsTaCl_6$ as a function of temperature. Curves drawn through the experimental points represent the least squares fit from Table 1.

Experimental measurements of the heat capacities of solid and liquid $TaCl_5$ could not be found in the literature. However, Schaefer and Kahlenberg (16) estimated the heat capacity of $TaCl_5$ by comparison with the heat capacities of $ZrCl_4$ and $HfCl_4$. According to their estimates

$$[8] \quad C_{p(s)TaCl_5} = 159.0 - 12.55 \times 10^5 T^{-2} \text{ (J K}^{-1}\text{ mol}^{-1})$$

Heat capacities for solid $TaCl_5$ calculated from eq. [8] are about 8% lower than the present results.

A comparison between enthalpies of fusion for $NbCl_5$, reported by several investigators, is given in Table 3.

The standard enthalpy and entropy increments for $TaCl_5$ up to 550 K calculated from the present results are tabulated in Table 1.

Interpolation of the solid and liquid enthalpy lines to the melting points at 497 K gives the heat of fusion of $TaCl_5$ as

$$\Delta H_{f(TaCl_5)} = 32.56 \pm 0.66 \text{ (kJ mol}^{-1})$$

This value is compared with the literature values in Table 3. It appears from the above comparison that the measured enthalpy of fusion is in excellent agreement with values by Shchukarev *et al.* (19) and by Saeki *et al.* (20) calculated from vapour pressure measurements. The present value is about 10% lower than that obtained by Dobrotin *et al.* (17) from calorimetric measurements for which no error limits were given.

Uncertainties in transition enthalpies are obtained by taking the square root of the sum of the squares of the standard errors of estimates for each of the enthalpy curves before and after a transition temperature, respectively.

As the equilibrium vapour pressures for the pure solid and pure liquid $NbCl_5$ (1, 21–26) and $TaCl_5$ (27), respectively, are available, the temperature dependence of the thermodynamic functions for each system may be calculated using the well known Σ-function method (28).

Molar heat capacities for gaseous $NbCl_5$ and $TaCl_5$ are also known and have been included in Table 2. If the heat capacities of either the gaseous or condensed state materials are represented by eq. [5]. The Σ-function for either the vaporization or sublimation reactions of $NbCl_5$ and $NbCl_5$ is given as

$$[9] \quad \Sigma = \frac{\Delta H_0}{T} + \mathrm{I} = -R \ln P + \Delta A \ln T + \frac{\Delta B}{2} T$$

where ΔA and ΔB are the differences between the heat capacity constants of the gaseous and the corresponding condensed phases.

The enthalpy of vaporization, ΔH_v, or sublimation, ΔH_s, can then be expressed in the form

TABLE 2. Molar heat capacities and transition thermodynamic properties calculated from data in Table 1*

Compound	$C_p = A + BT$* (J K^{-1} mol^{-1})		Temperature range (K)	T_{Tr} Transition temperature $\alpha \rightarrow \beta$ (K)	ΔH_T* at T_{Tr} (kJ mol^{-1})	ΔS_{T} (J K^{-1} mol^{-1})	T_{F} fusion temperature (K)	ΔH_{F}* at mp (kJ mol^{-1})	ΔS_{F} (J K^{-1} mol^{-1})	C_p† at 298 K (J K^{-1} mol^{-1})	Crystal structure
	A	$B \times 10^3$									
$NbCl_5$ (s)	156.73	—	380–481	—	—	—	481 (3)	32.21±0.66	67.15±1.77	156.73	Monoclinic (31)
$NbCl_5$ (ℓ)	268.20	—	481–626	—	—	—	—	—	—	268.20	—
$TaCl_5$ (s)	144.43	43.51	379–497	—	—	—	497	32.56±0.66	65.52±1.33	157.40	Monoclinic (31)
$TaCl_5$ (ℓ)	306.94	—	497–563	—	—	—	—	—	—	306.94	—
α-$RbNbCl_6$ (s)	77.95	325.52	376–568	578 (3)	20.17±0.45	34.90±0.78	—	—	—	174.83	Incongruently melting compound, tetragonal (8)
β-$RbNbCl_6$ (s)	230.12	—	578–602	—	—	—	653 (3)	—	—	230.12	—
α-$CsNbCl_6$ (s)	185.60	102.93	467–563	563 (3)	17.12±1.38	30.41±2.45	—	—	—	218.36	Tetragonal (8)
β-$CsNbCl_6$ (s)	182.63	87.86	563–808	—	—	—	808 (3)	15.67±2.13	19.39±2.64	208.94	—
$CsNbCl_6$ (ℓ)	281.92	—	801–898	—	—	—	—	—	—	281.92	—
α-$RbTaCl_6$ (s)	232.60	—	429–586	586 (3)	18.81±1.70	32.10±2.90	—	—	—	232.60	—
β-$RbTaCl_6$ (s)	246.73	—	586–690	—	—	—	690 (3)	9.51±1.31	13.77±1.90	246.73	Hexagonal (3)
$RbTaCl_6$ (ℓ)	249.41	—	690–812	—	—	—	—	—	—	249.41	—
α-$CsTaCl_6$ (s)	259.83	—	480–569	569 (3)	13.44±1.79	23.64±3.14	—	—	—	259.83	Hexagonal (3)
β-$CsTaCl_6$	289.66	—	569–821	—	—	—	813 (3)	11.35±1.78	13.81±2.19	289.53	—
$CsTaCl_6$ (ℓ)	306.52	—	823–877	—	—	—	—	—	—	306.69	—

*Data rounded up to the second decimal. For $NbCl_{5\,(\mathrm{vap})}$ (29): $C_p = 132.76 - 11.205 \times 10^5 T^{-2}$ in J K^{-1} mol^{-1}.

†Extrapolated values. For $TaCl_{5(\mathrm{vap})}$: $C_p = 132.2 - 15.48 \times 10^5 T^{-2}$ in J K^{-1} mol^{-1} (estimated (16)).

TABLE 3. Comparison of enthalpy of fusion values for $NbCl_5$ and $TaCl_5$

Compound	ΔH_T* at mp (kJ mol^{-1})	Method	Reference
$NbCl_5$	32.21 ± 0.66	Drop calorimetry	This work
$NbCl_5$	33.85 ± 0.96	Drop calorimetry	15
$NbCl_5$	34.72 ± 1.67	Phase equilibria	18
$NbCl_5$	28.66 ± 2.30	Vapour pressures	2
$TaCl_5$	32.56 ± 0.66	Drop calorimetry	This work
$TaCl_5$	35.98	Calorimetry	17
$TaCl_5$	26.15 ± 3.56	Vapour pressure	2
$TaCl_5$	32.63	Vapour pressure	19
$TaCl_5$	33.05	Vapour pressure	20
$TaCl_5$	25.52	Vapour pressure	21

*The melting points are those reported in the respective investigations.

$$[10] \quad \Delta H_{\mathrm{v\ or\ s}} = \Delta H_0 + \Delta A T + \frac{\Delta B}{2} T^2$$

and similarly, the free energies of vapourization or sublimation are given as

$$[11] \quad \Delta G_{\mathrm{v\ or\ s}} = IT + \Delta H_0 - \Delta A T \ln T - \frac{\Delta B}{2} T^2$$

the unknowns in the above equations, i.e., ΔH_0 and I, are integration constants that can be determined from a plot of Σ versus $1/T$, as the slope and the intercept, respectively.

For the vaporization reaction,

$$[12] \quad NbCl_{5(\mathrm{liquid})} \rightarrow NbCl_{5(\mathrm{vapour})}$$

for temperatures up to 600 K, the corresponding Σ-plot was linear and least squares regression analysis yielded the enthalpy and free energy functions as

$$[13] \quad \Delta H_{\mathrm{v}} = 126.54 - 0.1354\,T + 11.20 \times 10^5\,T^{-1} \quad (\pm\ 0.79\ \mathrm{kJ\ mol^{-1}})$$

and as

$$[14] \quad \Delta G_{\mathrm{v}} = 126.53 + 1.0924\,T + 0.1354\,T \ln T + 5.6 \times 10^{-3}\,T^{-1} \ (\pm\ 0.79\ \mathrm{kJ\ mol^{-1}})$$

The enthalpy of vaporization calculated from eq. [13] at the boiling temperature of 502.3 K is 60.67 ± 0.79 kJ mol^{-1}. Literature values vary from 46.86 to 62.76 ± 6.3 kJ mol^{-1}, while the vapour pressures calculated from the free energy function in eq. [14] compare very well with the vapour pressures measured in our laboratory (2).

For the sublimation reaction,

$$[15] \quad NbCl_{5(s)} \rightarrow NbCl_{5(\mathrm{vap})}$$

$$[16] \quad \Delta H_{\mathrm{s}} = 95.621 + 1.548 \times 10^3\,T^{-2}\ (\pm\ 3.0\ \mathrm{kJ\ mol^{-1}})$$

For $TaCl_5$, the upper temperature limit for vapourization was 511 K, where the vapour pressure of $TaCl_5$ reaches 1 atm pressure. Σ-function plots for vapourization were linear, and the enthalpy and free energy functions by the least squares method are given, respectively, as:

$$[17] \quad \Delta H_{\mathrm{v(TaCl_5)}} = 141.038 - 0.1747\,T + 1.548 \times 10^3\,T^{-1} \quad (\pm\ 0.21\ \mathrm{kJ\ mol^{-1}})$$

and as

$$[18] \quad \Delta H_{\mathrm{v(TaCl_5)}} = 141.038 - 1.3694\,T + 0.1747\,T \ln T + 7.74 \times 10^2\,T^{-1}\ (\pm\ 0.21\ \mathrm{kJ\ mol^{-1}})$$

ΔH_{v} at the boiling temperature of 502.7 K, is 56.27 ± 0.21 kJ mol^{-1}. Literature values vary between 62.34 and 48.95 (±4 kJ mol^{-1}).

Again, vapour pressures for $TaCl_5$ calculated from eq. [18] compare well with experimental measures (2).

For the sublimation reaction

$$[19] \quad TaCl_{5(s)} \rightarrow TaCl_{5(\mathrm{vap})}$$

the Σ-function method yielded the equation,

$$[20] \quad \Delta H_{\mathrm{s}} = 93.960 + 1.548 \times 10^3\,T^{-2}\ (\pm\ 3.94\ \mathrm{kJ\ mol^{-1}})$$

The larger errors shown in eqs. [16] and [20] reflect differences between the available experimental vapour pressure data and possible uncertainty in the molar heat capacity data from which the Σ-function values were evaluated.

The linearity of the Σ-plots is usually taken as an indication of the accuracy and of compatibility between the calorimetric molar heat capacities and the corresponding vapour pressure data representing the equilibria between the condensed and the vapour phases. Thus, the Σ-function method is also a test of the accuracy of the experimental data used for the calculations, because, if either the calorimetric or the vapour pressure measurements are in error then the Σ versus $1/T$ plots cannot be linear (28).

Regarding the four complex compounds, $CsNbCl_6$, $RbNbCl_6$, $CsTaCl_6$, and $RbTaCl_6$, the large enthalpy and entropy effects associated with their allotropic changes suggest that their solid structures undergo dramatic changes before melting. Such large enthalpy and entropy effects may indicate fast-ion conduction in the high-temperature phases and to the possible use of these compounds in solid state chemical sensors (30).

1. D. R. SADOWAY and S. N. FLENGAS. Can. J. Chem. **56**, 2013 (1978).
2. D. R. SADOWAY and S N. FLENGAS. Can. J. Chem. **54**, 1692 (1976).
3. D. R. SADOWAY and S. N. FLENGAS. Can. J. Chem. **56**, 2538 (1978).
4. D. R. SADOWAY and S. N. FLENGAS. Metall. Trans. B, **11B**, 57 (1980).
5. K. HUBER, E. JOST, E. NEUENSCHWANDER, M. STUDER, and B. ROTH. Helv. Chim. Acta, **41**, 2411 (1958).
6. I. S. MOROZOV and A. T. SIMONICH. Russ. J. Inorg. Chem. **2**(8), 311 (1957).
7. E. K. SMIRNOVA, I. V. VASIL'KOVA, and N. F. KUDRYASHOVA. Russ. J. Inorg. Chem. **9**, 268 (1964).
8. E. K. SMIRNOVA and V. M. TSINTSIUS. Russ. J. Inorg. Chem. **16**, 303 (1971).
9. K. W. BAGNALL and D. BROWN. J. Chem. Soc. 581 (1964).
10. W. T. THOMPSON and S. N. FLENGAS. Can. J. Chem. **49**, 1550 (1971).
11. A. S. KUCHARSKI and S. N. FLENGAS. Can. J. Chem. **52**, 946 (1974).
12. G. T. FURUKAWA, T. B. DOUGLAS, R. E. MCCOSKEY, and D. C. GINNINGS. J. Res. Natl. Bur. Stand. **57**, 67 (1956).
13. J. GOODKIN, C. SOLOMONS, and G. T. JANZ. Rev. Sci. Instr. **29**, 105 (1958).
14. O. KUBASCHEWSKI and C. B. ALCOCK. Metallurgical thermochemistry. 5th ed. Pergamon Press, Oxford. 1979.

15. F. J. Keneshea, D. Cubicciotti, G. Whithers, and H. Eding. J. Phys. Chem. **72**, 1272 (1968).
16. H. Schaefer and F. Kahlenberg. Z. Anorg. Allgem. Chem. **305**, 178 (1960).
17. R. B. Dobrotin, A. V. Suvorov, and Yu. V. Kondratiev. Vestn. Leningr. Univ. Ser. Fiz. Khim. **4**, 95 (1964).
18. G. Meyer, J. F. Oosterom, and W. J. Van Oeveren. Rec. Trav. Chim. Pays-Bas, **80**, 502 (1961).
19. S. A. Shchukarev and A. R. Kurbanov. Vestn. Leningr. Univ. Ser. Fiz. Khim. **10**, 144 (1962).
20. Y. Saeki, R. Matsuzaki, M. Yanai, and K. Funaki. Kogyo Kagaku Zasshi, **71**, 350 (1968).
21. L. I. Staffansson and P. Enghag. Scand. J. Metall. **2**, 305 (1973).
22. M. A. Opykhtina and N. A. Fleisher. Zh. Obshch. Khim. **7**, 2016 (1937).
23. D. N. Tarasenkov and A. V. Komandin. Zh. Obshch. Khim. **10**, 1319 (1940).
24. K. M. Alexander and F. Fairbrother. J. Chem. Soc. **52**, S223 (1949).
25. J. W. Johnson, W. J. Silva, and D. Cubicciotti. High Temp. Sci. **2**, 20 (1970).
26. W. Hart and G. Meyer. Rec. Trav. Chim. **83**, 1233 (1964).
27. J. M. Brink and F. D. Stevenson. J. Chem. Eng. Data, **17**, 143 (1972).
28. L. S. Darken and R. W. Gurry. *Physical chemistry of metals*. McGraw-Hill Co., New York. 1953. p. 225.
29. R. D. Werder, R. A. Frey, and H. Guenthard. J. Chem. Phys. **47**, 4159 (1967).
30. F. W. Poulsen, N. H. Andersen, K. Clausen, D. R. Sadoway, and L. H. Ogendal. Super ionic conduction in alkali metal hexachloro niobates and tantalates. *In* Solid State Ionics. In press.
31. A. Zalkin and D. E. Sands. Acta Crystallogr. **11**, 615 (1958).

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