CHEMICAL THERMODYNAMICS AND THERMOCHEMISTRY

The Heat Capacity of Titanium Di- and Tetrachloride over the Temperature Range 7–314 K

G. A. Berezovskii^a and E. M. Snigireva^b

^a Institute of Inorganic Chemistry, Siberian Division, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia

e-mail: berez@che.nsk.su

^b Moscow Physicotechnical Institute, Institutskii proezd 9, Dolgoprudnyi, Moscow oblast, 141700 Russia

e-mail: snigireva-helen@mail.ru

Received October 31, 2005

Abstract—The temperature dependences of the heat capacities of titanium di- and tetrachloride were studied by vacuum adiabatic calorimetry. The parameters of fusion (T_{tr} , $\Delta_{tr}H$, and $\Delta_{tr}S$) were determined for TiCl₄. The thermodynamic functions of the substances were calculated over the temperature range 10–300 K. The results obtained were compared with literature data.

DOI: 10.1134/S0036024406100189

The thermodynamic characteristics of titanium chlorides, which have been widely used in technological processes, are contained in data banks and handbooks [1, 2]. However, no experimental data on lowtemperature heat capacities had been reported for the Ti–Cl system up to 1990. In this system, three stable chlorides, namely, TiCl₂, TiCl₃, and TiCl₄, exist. The heat capacity of TiCl₃ was measured from 53 to 296 K only [3], and the thermodynamic characteristics of titanium chlorides at 298.15 K are given in [1, 2] with a reference to a private communication. Numerous references to works in which the temperature and enthalpy of fusion of $TiCl_4$ were measured are given in [1]. In database [2], the heat capacities of titanium chlorides at 100 and 200 K and, for TiCl₄, also at the melting point (249.046 K) are given. We, however, know of no original works in which the heat capacity of TiCl₄ in the crystalline state was measured. Note that, in [4], thermodynamic calculations were performed using the titanium chloride parameters from [2]. Work [4] contains abundant bibliography on the thermodynamic properties of the Ti-Cl system. In 1990, we published the results obtained in measurements of the heat capacities of two titanium chlorides, TiCl_{2.07 \pm 0.05} and TiCl_{2.98 \pm 0.02}, from 5 to 315 K [5, 6]. That work was part of complex studies of the Ti-Cl system. Here, we present the experimental data on two more samples, titanium tetrachloride and titanium dichloride with a composition closer to stoichiometry than that of the sample studied in [6]. We found that the $TiCl_{2.07 \pm 0.05}$ sample contained a substantial amount of titanium trichloride as an impurity.

Titanium tetrachloride of os. ch. (special purity) grade was additionally distilled. Titanium dichloride

was synthesized following the procedure described in [7] from titanium metal shavings obtained from titanium refined by the iodine process and titanium tetrachloride. According to the chemical analysis data, the compositions of the samples were $\text{TiCl}_{4.00 \pm 0.02}$ and $\text{TiCl}_{2.00 \pm 0.02}$. Titanium was determined gravimetrically in the form of TiO₂, and chlorine, potentiometrically by titration with a solution of silver nitrate. The diffractogram of the $\text{TiCl}_{2.00}$ sample on the whole corresponded to the literature data on titanium dichloride [8]. The samples were hygroscopic and easily oxidizable and were therefore handled in a dry box in the atmosphere of a dry purified inert gas.

The isobaric heat capacity C_p of titanium chlorides was measured in an adiabatic vacuum calorimeter with pulsed heating [5]. A nickel calorimetric ampule was used to work with chemically active compounds. The temperature of the ampule was measured by a TSPN-4 ($R_0 = 50 \Omega$) platinum resistance thermometer and calculated by the SST-68 standard table. Tests with a reference compound (benzoic acid) gave close agreement with the standard values. The TiCl₄ and TiCl₂ sample weights were 5.385 and 4.302 g, respectively.

The heat capacity of titanium tetrachloride was measured over the temperature range 6.93–314 K (Table 1). Below the melting point T_m , the $C_p(T)$ dependence was a smooth curve without anomalies (figure). The mean deviation of the experimental heat capacity values from the smoothed $C_p(T)$ curve was 1.5% below 20 K and 0.1% from 30 K to T_m . The heat capacity of the liquid phase from 249 to 300 K was constant to within 0.2%. The actually measured value C_s (heat

<i>Т</i> , К	C_p	<i>T</i> , K	C_p	<i>T</i> , K	C_p	Т, К	C_p
Series 1		Series 3		Series 4		13.14	8.032
301.91	148.9	79.93	77.24	241.12	149.5	14.14	9.826
305.74	149.2	83.43	78.97	242.92	148.8	15.36	12.00
309.88	149.2	87.57	80.75	245.52	149.2	16.83	14.53
313.99	149.2	91.51	82.37	249.05	148.4	18.32	17.12
Seri	es 2	95.74	83.97	253.35	148.9	19.68	19.44
182.33	110.2	100.26	85.82	258.02	258.02 149.6		21.97
187.44	111.6	104.61	87.40	278.26	149.1	23.29	25.42
192.48	112.7	108.81	88.84	285.80	149.6	25.86	29.46
197.46	114.1	112.99	90.12	Seri	Series 5		33.22
202.38	115.2	117.22	91.36	259.42	148.9	31.17	36.96
207.25	116.6	121.43	92.87	264.25	148.5	34.03	40.78
212.08	117.8	125.53	93.99	268.86	148.4	36.94	44.44
216.86	119.0	129.79	95.39	273.83	148.5	43.43	51.71
221.59	120.2	134.20	96.73	278.76	148.5	47.47	56.02
226.27	121.4	139.22	98.15	Series 6		52.23	60.37
231.15	122.8	144.83	99.65	6.93	1.374	56.96	64.60
236.22	124.1	150.32	101.22	7.41	1.602	62.45	68.54
240.83	128.3	155.70	102.9	8.29	2.194	68.08	71.37
244.94	135.4	160.97	104.4	9.26	3.131	73.47	74.23
		166.52	106.0	10.16	3.989	78.98	76.96
		172.59	107.6	11.10	5.057		
		178.56	109.1	12.14	6.473		

Table 1. Experimental heat capacities (C_p , J/(mol K)) of titanium tetrachloride, M = 189.712 g/mol

capacity at saturated vapor pressure) was assumed to equal C_p , because the difference between these values close to the melting point was less than 0.1% and could therefore be ignored. Note that the first three points in series 4 (Table 1, points from 241.1 to 245.5 K) corresponded to the heat capacity of the supercooled liquid phase. Three experiments were performed to determine the enthalpy of fusion $\Delta_{fus}H$. The second and third experiments were conducted with interrupting heating in certain time intervals following the procedure described in [9]. This procedure allows the melting points of absolutely pure compounds (T_m°) and samples under study (T_m) and the amount of impurities in the samples to be determined. The results of the second and third experiments were $T_{\rm m} = 248.85$ and 248.88 K and $T_{\rm m}^{\circ}$ = 248.88 and 248.93 K, respectively. The amount of impurities N in the sample calculated by the equation

$$N = [\Delta_{\rm m} H (T_{\rm m}^{\circ} - T_{\rm m}) / R (T_{\rm m}^{\circ})^2] \times 100\%,$$

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY Vol. 80 No. 10

was 0.085 mol %. The entropy of fusion was determined as $\Delta_{fus}H/T_m$. The characteristics of fusion of TiCl₄ are summarized in Table 2.



Heat capacities of (1) TiCl₄ and (2) TiCl₂ over the temperature range 7–314 K.

2006

Table 2. Characteristics of phase transitions in $TiCl_4$ and $TiCl_3$ according to our data and [1, 5]

Compound	T _{tr} , K	$\Delta_{\rm tr} H^{\circ},$ J/mol	$\Delta_{tr}S^{\circ},$ J/(mol K)					
Fusion								
TiCl ₄	248.91 ± 0.02	9960 ± 40	40.03 ± 0.16					
TiCl ₄ [1]	249.05 ± 0.01	9970 ± 40	40.00					
Polymorphic transition								
TiCl ₃ [5]	219.5 ± 0.2	1790 ± 10	8.150 ± 0.005					
TiCl ₃ [1]	220.1 ± 0.1	1480 ± 10	6.74					

The heat capacity of titanium dichloride was measured from 8.4 to 313 K (Table 3). The mean deviation of the experimental heat capacities from the smoothed $C_p(T)$ curve was 1.0% below 20 K and ~0.1% from 20 to 270 K. No anomalies were observed over the whole temperature range. No experimental values were obtained between 270 and 300 K. The data on TiCl_{2.07} [6], however, show that the $C_p(T)$ curve is smooth over this temperature interval too. Note that several points deviate from the smoothed $C_p(T)$ curve by no more than 1% close to 220 and 250 K. Clearly, this is explained by the presence of titanium trichloride and tetrachloride impurities. A comparison of the excess enthalpies of these impurity anomalies with the enthalpies of transitions in TiCl₃ and TiCl₄ led us to conclude that these impurities were present in exceedingly small amounts, less than 0.01% each. They could not substantially influence the enthalpies and entropies of TiCl₂ at 298 K. It is, however, of interest that heat capacity measurements are a very sensitive method for detecting small impurities. Of course, if the impurities are substances with phase transitions.

The smoothed $C_p(T)$ dependences obtained for TiCl₄ and TiCl₂ were used to calculate the $\Phi^{\circ}(T)$, $S^{\circ}(T)$, and $H^{\circ}(T)$ – $H^{\circ}(0)$ thermodynamic functions at several selected temperatures (Tables 4 and 5). The extrapolation of the heat capacities to 0 K was performed on the assumption that the $C_p(T)$ dependences below 8 K were proportional to T^3 . The accuracy of the thermodynamic functions was estimated from the spread of experimen-

Table 3. Experimental heat capacities (C_p , J/(mol K)) of titanium dichloride, M = 118.79 g/mol

<i>Т</i> , К	C_p	Т, К	C_p	Т, К	C_p	<i>Т</i> , К	C_p
Series 1		217.06	62.69	Series 5		Series 7	
300.57	70.08	218.25	62.91	111.26	40.79	8.39	0.1361
303.59	69.57	218.97	62.41	115.57	42.42	9.40	0.2913
306.72	70.30	219.68	63.16	119.74	43.82	10.45	0.3182
310.00	71.00	220.40	63.38	124.27	45.40	11.54	0.4270
313.07	70.79	221.22	64.06	128.68	46.62	12.53	0.5570
Seri	Series 2		63.83	133.45	48.21	13.58	0.6952
79.81	27.84	224.31	63.94	139.06	49.58	14.68	0.9416
81.64	28.53	Seri	es 4	147.13 51.41		15.80	1.185
83.41	29.42	227.88	63.98	157.53	53.68	16.87	1.188
85.14	30.29	232.05	64.40	167.56	55.60	17.96	1.389
86.81	31.00	236.20	64.80	177.25	57.43	19.13	1.581
88.45	31.82	240.20	65.16	186.68	59.01	20.60	1.902
90.04	32.38	244.17	65.53	195.86	60.20	22.27	2.267
94.82	34.45	248.26	66.09	Series 6		24.03	2.696
100.21	36.70	252.52	66.71	45.04	10.44	26.40	3.344
102.96	37.68	256.75	66.90	48.62	12.27	29.11	4.154
Series 3		260.74	67.04	52.33	14.03	31.63	5.001
205.80	61.56	264.70	67.34	57.41	16.62	34.06	5.909
210.00	61.96	268.62	67.47	63.26	19.70	36.52	6.889
214.16	62.40			68.79	22.34		

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY Vol. 80 No. 10 2006

Table 4. Main thermodynamic functions of TiCl₄ ($C_p^{\circ}(T)$, $\Phi^{\circ}(T)$, and $S^{\circ}(T)$, J/(mol K); $H^{\circ}(T) - H^{\circ}(0)$, J/mol)

Table 5. Main thermodynamic functions of TiCl ₂ ($C_p^{\circ}(T)$,
$\Phi^{\circ}(T)$, and $S^{\circ}(T)$, J/(mol K); $H^{\circ}(T) - H^{\circ}(0)$, J/mol)

<i>Т</i> , К	$C_p^{\circ}(T)$	$\Phi^{\circ}(T)$	$S^{\circ}(T)$	$H^{\circ}(T) - H^{\circ}(0)$	<i>Т</i> , К	$C_p^{\circ}(T)$	$\Phi^{\circ}(T)$	$S^{\circ}(T)$	$H^{\circ}(T) - H^{\circ}(0)$
10	3.816	0.394	1.443	10.49	10	0.278	0.037	0.128	0.908
15	11.17	1.164	4.270	46.59	15	1.004	0.099	0.353	3.799
20	19.88	2.466	8.680	124.3	20	1.763	0.209	0.735	10.53
25	28.04	4.231	14.01	244.4	25	2.953	0.363	1.251	22.20
30	35.40	6.337	19.78	403.3	30	4.447	0.564	1.917	40.57
35	42.04	8.683	25.75	597.2	35	6 272	0.814	2,735	67.24
40	48.06	11.19	31.76	822.7	40	8 283	1 113	3 703	103.6
45	53.51	13.81	37.74	1077	40	10.47	1.115	1.002	150.4
50	58.41	16.50	43.64	1357	45	10.47	1.401	4.805	150.4
60	66.54	21.98	55.04	1984	50	12.89	1.856	6.030	208.7
70	72.61	27.48	65.78	2681	60	17.97	2.778	8.825	362.8
80	77.47	32.90	75.80	3432	70	22.99	3.864	11.98	567.8
90	81.77	38.19	85.17	4228	80	27.85	5.088	15.36	822.2
100	85.66	43.34	93.99	5066	90	32.41	6.425	18.91	1124
120	92.37	53.16	110.2	6848	100	36.57	7.855	22.55	1469
140	98.36	62.37	124.9	8756	120	43.93	10.92	29.88	2276
160	104.1	71.05	138.4	10780	140	49.80	14.14	37.12	3216
180	109.6	79.24	151.0	12920	160	54.18	17.45	44.06	4258
200	114.7	87.01	162.8	15160	180	57.87	20.78	50.66	5379
220	119.8	94.42	174.0	17510	200	60.77	24.08	56.92	6567
240	125.0	101.5	184.6	19950	200	62.22	27.00	62.92	7909
248.91	127.4	104.5	189.2	21070	220	05.52	27.54	02.05	7000
248.91	148.7	104.5	229.2	31030	240	65.25	30.53	68.42	9094
260	148.7	110.0	235.7	32680	260	67.03	33.65	73.72	10420
280	148.7	119.4	246.7	35650	280	68.32	36.70	78.74	11770
300	148.7	128.2	257.0	38620	300	69.77	39.66	83.50	13150
298.15	148.7 ± 0.3	127.4 ± 0.3	256.0 ± 0.5	38350 ± 80	298.15	69.63 ± 0.15	39.40 ± 0.10	83.07 ± 0.16	13020 ± 20

Table 6. Heat capacity and thermodynamic functions of titanium chlorides at 298.15 K (according to our data and [1, 2, 6])

Compound	$C_p^{\circ}(T), $ J/(mol K)	$S^{\circ}(T)$, J/(mol K)	$H^{\circ}(T) - H^{\circ}(0), \text{kJ/mol}$	$\Phi^{\circ}(T)$, J/(mol K)
TiCl ₄	148.7 ± 0.3	256.0 ± 0.3	38.35 ± 0.04	127.4 ± 0.2
TiCl ₄ [1, 2]	145.2 ± 0.2	252.4 ± 0.4	37.49 ± 0.60	126.6
TiCl ₃ [6]	98.60 ± 0.10	135.0 ± 0.2	20.81 ± 0.03	65.2 ± 0.2
TiCl ₃ [1, 2]	97.15 ± 0.30	139.7 ± 1.2	20.92 ± 0.08	69.5
TiCl ₂	69.63 ± 0.12	83.07 ± 0.16	13.02 ± 0.02	39.4 ± 0.1
TiCl ₂ [1, 2]	69.83 ± 0.40	87.4 ± 4.0	13.30 ± 0.08	42.8
TiCl _{2.07} [6]	71.13 ± 0.11	85.98 ± 0.26	13.42 ± 0.03	40.97 ± 0.15

RUSSIAN JOURNAL OF PHYSICAL CHEMISTRY Vol. 80 No. 10 2006

tal values over the whole temperature range of measurements. All the thermodynamic parameters at 298.15 K known for titanium chlorides are listed in Table 6. The discrepancies between our and the literature data are evidence that experimental heat capacity measurements like those performed in this work are necessary. At the same time, our and literature [1] data on the parameters of fusion of TiCl₄ are in close agreement (Table 2). This can be explained by repeated measurements of the temperature and enthalpy of fusion of titanium tetrachloride. For completeness, Tables 2 and 6 also contain the thermodynamic data on $TiCl_3$ obtained by us in [5, 6]. In the present work, we used pure samples and a verified procedure for measurements. This allows us to claim the absence of substantial systematic errors in the thermodynamic characteristics of titanium chlorides obtained.

The results obtained for titanium chlorides were sent to the IVTANTERMO bank of thermodynamic data.

REFERENCES

- Thermal Constants of Substances: A Handbook, Ed. by V. P. Glushko (VINITI, Moscow, 1974), Vol. 7, Part 1, p. 142 [in Russian].
- 2. JANAF Thermochemical Data, Ed. by M. W. Chase (U.S. GRO, Washington, DC, 1979).
- E. Y. King, W. W. Weller, A. U. Christensensen, and K. K. Kelley, Rept. Investing Bur. Mines, U.S. Dept. Interior, No. 5799 (1961).
- 4. S. P. Kirby, E. M. Marshall, and J. B. Pedley, J. Phys. Chem. Ref. Data **15** (3), 943 (1986).
- E. M. Snigireva, G. A. Berezovskii, and V. I. Tsirel'nikov, Zh. Fiz. Khim. 64 (8), 2250 (1990).
- E. M. Snigireva, G. A. Berezovskii, and V. I. Tsirel'nikov, Zh. Fiz. Khim. 64 (12), 3370 (1990).
- W. Klemm and L. Z. Grimm, Z. Anorg. Allg. Chem. 249, 189 (1942).
- L. V. Biryukova and Yu. G. Saksonov, Zh. Neorg. Khim. 5 (5), 993 (1960).
- S. M. Skuratov, V. P. Kolesov, and A. F. Vorob'ev, *Thermochemistry* (Mosk. Gos. Univ., Moscow, 1966), Part 2, p. 252 [in Russian].