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Thermodynamic Properties of Titanium

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This work reviews and discusses the data and information on the thermodynamic properties of titanium available through May 1984. These properties include heat capacity, enthalpy, enthalpy of transition and melting, vapor pressure, and enthalpy of vaporization. The recommended values for heat capacity cover the temperature range from 1 to 3800 K. The recommended values for enthalpy, entropy, Gibbs energy function, and vapor pressure cover the temperature range from 298.15 to 3800 K.

KEY WORDS: critical evaluation; data analysis; enthalpy; enthalpy of transition, enthalpy of melting, enthalpy of vaporization; entropy; Gibbs energy function; heat capcity; recommended values; titanium; vapor pressure.

1. INTRODUCTION

The principal objective of this work is to critically evaluate and analyze available data and information on the heat capacity, enthalpy, and vapor pressure of titanium and to generate the recommended values of these and other thermodynamic properties from 298.15 to 3800 K. The recommended values for the heat capacity are reported from 1 to 3800 K.

The discussion of the thermodynamic properties and the details of data analysis are reported in Section 2.

It is worth noting that the effect of conversion to IPTS-68 on these properties is small and well within the uncertainties of these values. The measurements on the thermodynamic properties which have been carried out on the International Practical Temperature Scale of 1948 or 1958 were not converted to IPTS-68. The value of the gas constant, $R = 8.31441\ J \cdot mol^{-1} \cdot K^{-1}$, is used in all calculations. The details of the data analysis have been discussed elsewhere [1].

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2. THERMODYNAMIC PROPERTIES OF TITANIUM

2.1. Phases and Structures

α-Titanium has an hcp (A3) structure isotypic with Mg; at 1166 ± 7 K [2] (IPTS-68) it transforms to β-Ti with a bcc (A2) structure isotypic with W. Its superconducting transition temperature is around 0.4 K [3]. Its atomic weight is 47.88 and its melting point is 1945 K (IPTS-68) [4]. Other values reported in the literature for the melting point (IPTS-68) are listed in Table I.

It appeared that Bedford et al. [73] selected the value which was based on a set of data which was not corrected to IPTS-68.

2.2. Low-Temperature Heat Capacity

There have been numerous measurements of the electronic specific heat coefficient, γ, and the Debye temperature, θ_D. The recommended values are based on some of the studies listed in Table II. Additionally, Collings and Ho [21] have reported a value of 7.30 $mJ \cdot mol^{-1} \cdot K^{-2}$ for the electronic heat capacity coefficient of β-titanium.

The recommended heat capacity values below 5 K are derived from recommended values for γ and θ_D using the following equation:

$$C_p^0 = \gamma T + [1943.75/\theta_D^3]\, T^3 \quad (1)$$

Agreement of other measurements with the recommended values is as follows: the data of Tomilo [25] are about 10% lower and those of Estermann et al. [26] are as much as 20% higher.

Table I. Melting Point of Titanium

Source	T_{fus} (K)
Cezairliyan and Miiller [2]	1945 ± 5
Deardroff and Hayes [5]	1944 ± 10
Oriani and Jones	1948
Schofield and Bacon [7]	1936 ± 10
Maykuth et al. [8]	1956 ± 10
Adenstedt et al. [9]	1976 ± 10
Hansen et al. [10]	1996 ± 15
Bickerdike and Hughes [11]	1943 ± 8
Rudy and Progulski [12]	1944 ± 8
Berezin et al. [47]	1941 ± 4
Bedford et al. [73]	1943
Recommended value	1945

Table II. Electronic Specific Heat Coefficient and Debye Temperature of Titanium

Source	γ (mJ · mol^{-1} · K^{-2})	θ_D (K)
Agarwal and Betterton [13]	3.11	423
Agarwal and Betterton [14]	3.32 ± 0.02	428 ± 5
Kneip et al. [15]	3.346	427
	3.351	430
Aven et al. [16]	3.38	421
Hake and Cape [17]	3.305	429 ± 7
Heiniger and Muller [18]	3.30	415
Wolcott [19]	3.56	430
Collings and Ho [20]	3.32	410
	3.36	420
	3.36	420
Collings and Ho [21]	3.36	420
Danner and Dummer [22]	3.31	
Dummer [23]	3.31 ± 0.03	
Frye et al. [24]	3.285	
Recommended value	3.332 ± 0.02	425 ± 5

The recommended values from 5 to 298.15 K agree well ($\pm 1.5\%$) with the following measurements: Aven et al. [16], Wolcott [19], Kothen and Johnston [27], Kelley [28], Burk et al. [29], Clusius and Franzosini [30], and Stalinski and Bieganski [31]. Integration of the recommended C_p^0 values yielded $H^0(298.15\text{ K}) - H^0(0\text{ K}) = 4822 \pm 10\text{ J} \cdot \text{mol}^{-1}$ and integration of the C_p^0/T values yielded $S^0(298.15\text{ K}) = 30.686 \pm 0.08\text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$. These values are listed in Table III and C_p^0 values are shown in Fig. 1 along the experimental data.

2.3. High-Temperature Heat Capacity (Solid)

The procedure followed to analyze the data in this temperature range is to convert C_p^0 and enthalpy data to a simple $y(T) = [H^0(T) - H(298.15\text{ K})]/(T - 298.15)$ function, evaluate them simultaneously, and derive the thermodynamic function by the procedure discussed previously [1].

For α-Ti, in the temperature range from 298.15 to 1166 K, there is some disagreement (up to 3.5%) between the adiabatic calorimetric data of Cash and Brooks [32] and the data of earlier investigators. Although Cash and Brooks [32] appear to have taken adequate precautions in their series of experiments and claim an accuracy of $\pm 1\%$, there is a possibility of a systematic error of the order of up to 2% in their C_p^0 values. Therefore, the

Table III. Recommended Low-Temperature Heat Capacity of Titanium

T (K)	C_p^0 ($J \cdot mol^{-1} \cdot K^{-1}$)
1	0.00336
2	0.00687
3	0.0107
4	0.0149
5	0.0198
6	0.0257
7	0.0327
8	0.0412
9	0.0511
10	0.0623
15	0.147
20	0.338
25	0.661
30	1.172
40	2.665
50	4.690
60	6.918
70	9.038
75	10.064
80	11.030
90	12.830
100	14.388
110	15.702
120	16.862
125	17.396
130	17.904
140	18.788
150	19.540
160	20.255
170	20.881
175	21.162
180	21.423
190	21.906
200	22.338
210	22.730
220	23.088
225	23.257
230	23.419
240	23.734
250	24.020
260	24.286
270	24.529
273.15	24.603
280	24.762
290	24.975
298.15	25.142

$C_{(electronic)} = \gamma T, \qquad \gamma = 3.332 \pm 0.02\ mJ \cdot mol^{-1} \cdot K^{-2}$

	Crystal, Ti(s)	Gas, Ti(g)
$H^0(298.15\ K) - H^0(0\ K)$	$4822 \pm 10\ J \cdot mol^{-1}$	$7539 \pm 1\ J \cdot mol^{-1}$
$S^0 298.15\ K)$	$30.686 \pm 0.08\ J \cdot mol^{-1} \cdot K^{-1}$	$180.187 \pm 0.007\ J \cdot mol^{-1} \cdot K^{-1}$

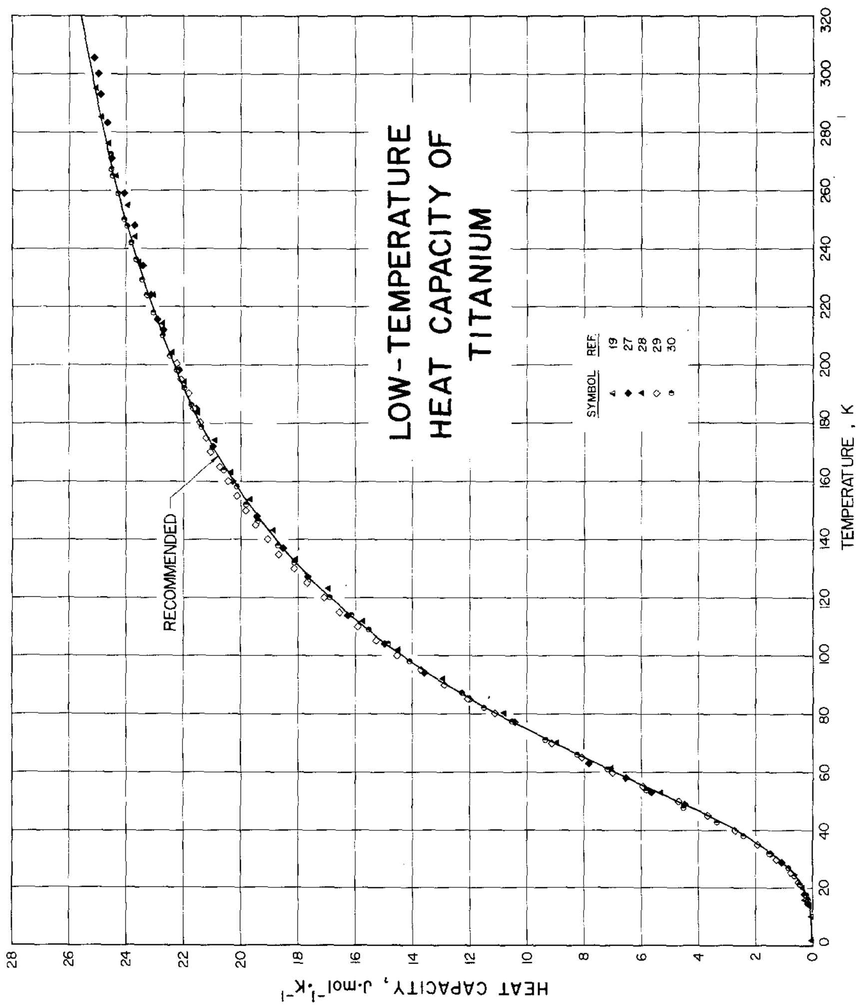

Fig. 1. Low-temperature heat capacity of titanium.

Table IV. Percentage Deviation in Enthalpy of α-Titanium from Recommended Values Given in Table VII

Source	Deviation (%)
Stalinski and Bieganski [31]	−1 (<320 K), 0.6 (>320 K)
Jaeger et al. [34]	Up to −6
Golutvin [38]	Up to 7
Ward et al. [39]	Up to −8
Serebrennikov and Gel'd [41]	Up to −3 (<676 K), up to 3 (>676 K)
Kothen [42]	Up to 4
Berezin et al. [47]	Up to 4

enthalpy values selected by Hultgren et al. [33] were increased by about 2% to accommodate the data of Cash and Brooks [32] and other data, which indicated a higher enthalpy for α-Ti at 1166 K. Comparison between enthalpy data available in the literature and the recommended values is shown in Table IV. α-Ti transforms to β-Ti at 1166 K [2]. The recommended value for $\Delta H_{\alpha-\beta} = 4170 \pm 200\ \mathrm{J \cdot mol^{-1}}$ is based on the pulse-heating measurements of Cezairliyan and Miiller [2]. Comparison of the recommended $\Delta H_{\alpha-\beta}$ values with the literature data is shown in Table V. The

Table V. Enthalpy of Transition from α-Ti to β-Ti

Source	$\Delta H_{\alpha-\beta}$ ($\mathrm{J \cdot mol^{-1}}$)
Cezairliyan and Miiller [2]	4170 ± 200
Hultgren et al. [33]	4255
Scott [35]	4090 ± 100
Parker [36]	3350 ± 200
Golutvin [38]	3430 ± 80
Kohlhaas et al. [40]	4150
Kothen [42]	3946
Martynyuk and Tsapkov [43]	4300
Glushko et al. [44]	3800
Gel'd and Putintsev [45]	4175
Harmelin and Lehr [46]	4213
	3996
Peletskii and Zaretskii [49]	4360 ± 100
Backhurst [52]	3680
Schofield [69]	3400
Cormier and Claisse [0]	3210 ± 400
Recommended value	4170 ± 200

Table VI. Percentage Deviation in Heat Capacity of Titanium from Recommended Values Given in Table VII

Source	Deviation (%)
Cash and Brooks [32]	±2
Scott [35]	±2 (<450 K), up to −10 (>450 K)
Parker [36]	±5 (<828 K), ±15 (>828 K)
Novikov [37]	±1.5
Kohlhaas et al. [40]	−3 (<1156 K), ±1 (1156–1400 K), up to −6 (>1400 K)
Cezairliyan and Miiller [48]	±0.75
Peletskii and Zaretskii [49]	−4 to −8
Arutyunov et al. [50]	1 to 8
Zarichnyak and Lisnenko [51]	−1 to −5
Backhurst [52]	−4.5 (<1100 K), 162 (~1156 K), −4 (1260 K)
Shestopal [53]	2 (1156–1600 K), up to 13 (>1600 K)
Holland [54]	23 to 43

Table VII. Recommended high-temperature thermodynamic properties of titanium[a]

	Condensed phase				Gas phase Ti(g)			
T (K)	C_p^o ($J \cdot mol^{-1} \cdot K^{-1}$)	$H^o - H^o(T_r)$ ($J \cdot mol^{-1}$)	S^o ($J \cdot mol^{-1} \cdot K^{-1}$)	$-[G^o - H^o(T_r)]/T$ ($J \cdot mol^{-1} \cdot K^{-1}$)	C_p^o ($J \cdot mol^{-1} \cdot K^{-1}$)	$H^o - H^o(T_r)$ ($J \cdot mol^{-1}$)	S^o ($J \cdot mol^{-1} \cdot K^{-1}$)	$-[G^o - H^o(T_r)]/T$ ($J \cdot mol^{-1} \cdot K^{-1}$)
298.15	25.142	0	0.000	30.686	24.430	0	0.000	180.187
300	25.182	47	0.156	30.686	24.399	45	0.151	180.188
350	26.091	1330	4.109	30.996	23.661	1245	3.854	180.482
400	26.829	2653	7.642	31.696	23.105	2414	6.975	181.127
450	27.450	4011	10.840	32.613	22.683	3558	9.671	181.951
500	28.016	5397	13.761	33.653	22.360	4684	12.044	182.862
550	28.550	6812	16.457	34.758	22.110	5796	14.163	183.812
600	29.073	8252	18.963	35.896	21.913	6896	16.078	184.771
650	29.585	9719	21.311	37.045	21.757	7988	17.825	185.724
700	30.081	11210	23.521	38.193	21.632	9072	19.433	186.660
750	30.562	12727	25.614	39.331	21.532	10151	20.922	187.574
800	31.025	14266	27.600	40.454	21.454	11226	22.309	188.464
850	31.463	15829	29.495	41.559	21.395	12297	23.608	189.328
900	31.893	17412	31.305	42.644	21.353	13366	24.829	190.166
950	32.330	19018	33.042	43.709	21.329	14433	25.983	190.978
1000	32.850	20646	34.712	44.751	21.326	15499	27.077	191.765
1025	33.168	21471	35.527	45.265	21.334	16032	27.603	192.150
1050	33.523	22306	36.331	45.774	21.334	16565	28.117	192.528
1075	33.968	23148	37.123	46.276	21.346	17099	28.620	192.901
1100	34.655	24006	37.913	46.775	21.362	17633	29.110	193.268
1125	36.050	24887	38.703	47.267	21.383	18167	29.591	193.630
1150	38.905	25823	39.527	47.758	21.409	18702	30.061	193.986
1166(α)	42.000	26470	40.086	48.070	21.428	19044	30.357	194.211
1166(β)	28.656	30640	43.662	48.070	21.428	19044	30.357	194.211
1200	28.895	31618	44.489	48.827	21.473	19774	30.973	194.682
1300	29.750	34549	46.835	50.944	21.657	21930	32.699	196.017
1400	30.782	37574	49.076	52.923	21.910	24107	34.313	197.280
1500	31.893	40708	51.237	54.785	22.228	26314	35.835	198.480
1600	33.064	43955	53.333	56.547	22.604	28555	37.282	199.621
1700	34.276	47321	55.373	58.223	23.029	30836	38.664	200.712
1800	35.660	50816	57.371	59.825	23.497	33162	39.993	201.757
1900	37.376	54466	59.343	61.363	23.999	35537	41.280	202.761
1945(s)	38.280	56168	60.229	62.037	24.234	36622	41.842	203.200
1945(ℓ)	46.290	70718	67.710	62.037	24.234	36622	41.842	203.200
2000	46.290	73264	69.001	63.055	24.529	37963	42.522	203.727
2200	46.290	82522	73.413	66.589	25.648	42979	44.911	205.562
2400	46.290	91780	77.441	69.885	26.819	48225	47.193	207.286
2600	46.290	101038	81.146	72.971	28.019	53709	49.387	208.917
2800	46.290	110296	84.576	75.871	29.235	59434	51.508	210.468
3000	46.290	119554	87.770	78.605	30.456	65403	53.566	211.952
3200	46.290	128812	90.757	81.190	31.671	71616	55.571	213.378
3400	46.290	138070	93.564	83.641	32.870	78071	57.527	214.752
3600	46.290	147328	96.210	85.971	34.041	84762	59.439	216.081
3637	46.290	149041	96.681	86.388	34.250	86025	59.788	216.322
3800	46.290	156586	98.712	88.191	35.173	91685	61.310	217.370

$T_{\alpha-\beta} = 1166$ K $\Delta H_{\alpha-\beta} = 4170 \pm 200\ J \cdot mol^{-1}$ $\Delta S_{\alpha-\beta} = 3.576 \pm 0.172\ J \cdot mol^{-1} \cdot K^{-1}$

$T_{fus} = 1945\ (\pm 5)$ K $\Delta_{fus} H^o = 14550 \pm 500\ J \cdot mol^{-1}$ $\Delta_{fus} S^o = 7.481 \pm 0.250\ J \cdot mol^{-1} \cdot K^{-1}$

[a] Enthalpy reference temperature = T_r = 298.15 K.

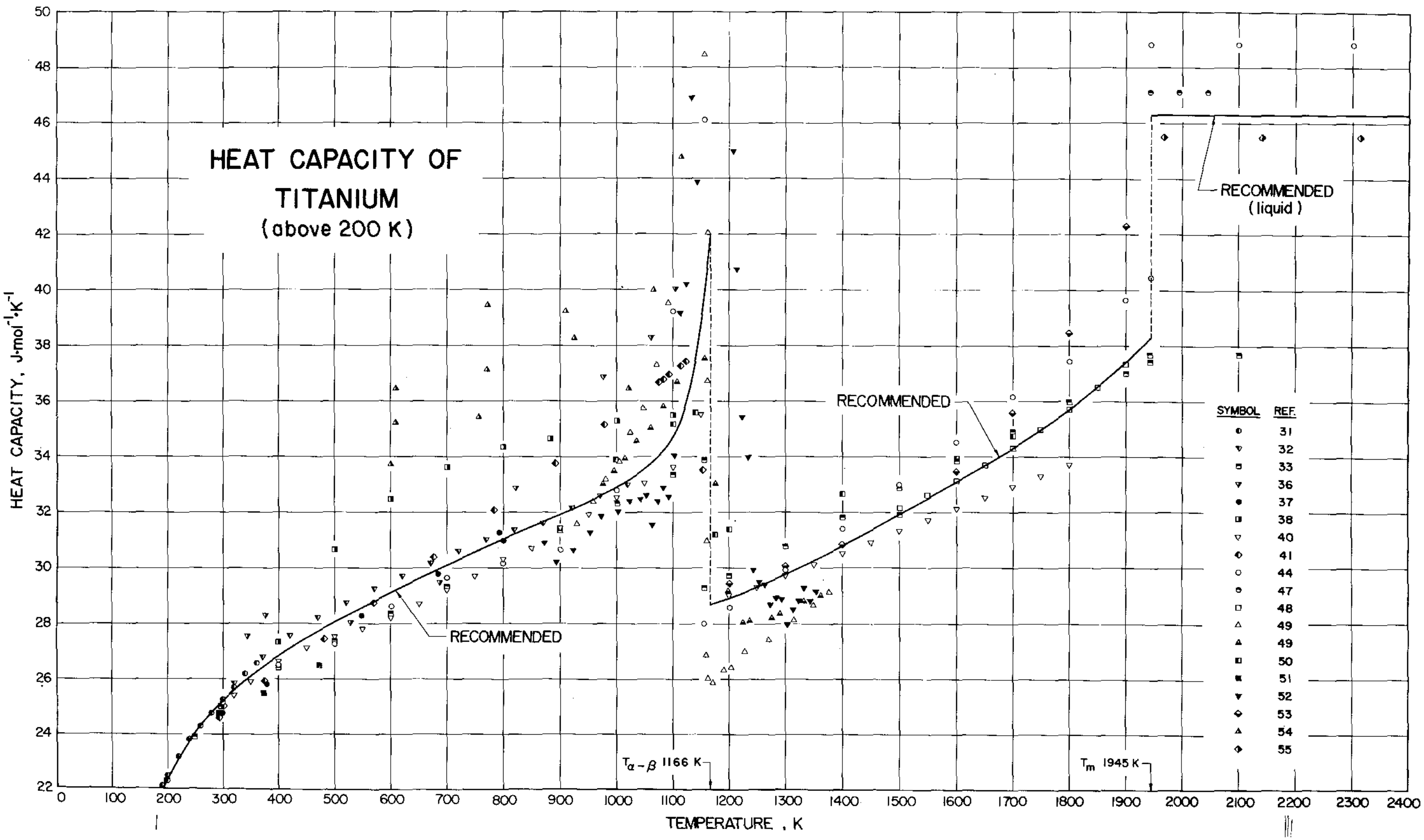

Fig. 2. Heat capacity of titanium (above 200 K).

Table VIII. Enthalpy of Melting of Titanium

Source	$\Delta_{fus}H^0$ (J · mol^{-1})
Martynyuk and Tsapkov [43]	18,000
Berezin et al. [47]	14,146 ± 480
Treverton and Margrave [55]	13,226 ± 500
Elyutin et al. [56]	17,150 ± 420
Maurakh et al. [57]	17,154 ± 460
Bonnel [71]	14,980
Recommended value	14,550 ± 500

recommended enthalpy values for β-Ti from 1166 to 1945 K agree well with the data of Jaeger et al. [4], Golutvin [38], Kothen [42], and Berezin et al. [47].

C_p^0 values derived from the recommended $y(T)$ (enthalpy) values compare with the data reported in the literature as listed in Table VI. The $S^0(T) - S^0(298.15\text{ K})$ values are calculated by integration of C_p^0/T values. Combining the $S^0(T) - S^0(298.15\text{ K})$ and $H^0(T) - H^0(298.15\text{ K})$ values with $S^0(298.15\text{ K})$ from the low-temperature data, the Gibbs energy functions $[G^0(T) - H^0(298.15\text{ K})]/T$ reported in Table VII were generated. The recommended C_p^0 values are listed in Table VII and show in Fig. 2 along experimental data.

2.4. High-Temperature Heat Capacity (Liquid)

The recommended value for the enthalpy of melting, $\Delta_{fus}H^0 = 14{,}550 \pm 500$ J · mol^{-1} was obtained by extrapolating solid and liquid enthalpies to the melting point, $T_{fus} = 1945$ K, and the literature data reported in Table VIII.

Table IX. Heat Capacity of Molten Titanium

Source	C_p^0 (J · mol^{-1} · K^{-1})
Hultgren et al. [33]	37.656
Glushko et al. [44]	46.800
Berezin et al. [47]	47.009
Treverton and Margrave [55]	45.480 ± 1.715
Elyutin et al. [56]	33.472
Recommended value	46.290 ± 1.700

A constant value of 46.290 ± 1.70 recommended for the C_p^0 of molten titanium is based on the values listed in Table IX. Other quantities are calculated by integrating C_p^0 values. The estimated uncertainties in the heat capacity are $\pm 3\%$ below 10 K, $\pm 1.5\%$ from 10 to 298.15 K, $\pm 2\%$ from 298.15 to 1100 K, $\pm 5\%$ near 1156 K (near α–β transition), $\pm 3\%$ from 1300 to 1945 K, and $\pm 3\%$ in the liquid region.

2.5. Ideal-Gas Properties

Thermodynamic quantities for Ti(g) reported in Table VII are calculated from the C_p^0(g) and S^0(298.15 K) values reported by Chase [72].

2.6. Vapor Pressure Data

Various vapor pressure measurements were tested with the aid of the Third Law. The recommended value of $\Delta_{sub}H^0$(298.15 K) is based on the values listed in Table X, giving considerable weight to the data of Edwards

Table X. Enthalpy of Sublimation of Titanium at 298.15 K

Source	$\Delta_{sub}H^0$(298.15 K) (kJ · mol^{-1})
Kuz'min and Palatnik [58], 1635–1820 K, Langmuir method	467.63 ± 0.53
Morrison [59], 1373–1473 K, Langmuir method	469.81 ± 0.83
Edwards et al. [60], 1587–1764 K, Langmuir method	472.89 ± 0.39
Carpenter and Mair [61], 1658–1808 K, Langmuir method	468.43 ± 2.31
Blocher and Campbell [62], 1510–1822 K, Langmuir method	466.82 ± 1.88
Wu and Wahlbeck [63], 1830–1923 K, Knudsen/mass specrometry	473.05 ± 2.15
Koch et al. [64], 1953–2193 K, Langmuir method	466.54 ± 2.56
Koch et al. [65], 1955–2379 K, Langmuir method	469.85 ± 3.71
Sumin et al. [66], 2150–2260 K, Langmuir method	471.47 ± 6.15
Kudryavtsev and Ivanov [67], 1495–1875 K	472.80 ± 3.72
Strassmair and Stark [68], 1554–1772 K, Langmuir method	465.79 ± 1.73
Recommended value	472.55 (± 1.00)

Table XI. Recommended Vapor Pressure of Titanium,[a,b] Ti(s, l) = Ti(g)

T (K)	p (atm)	ΔG^0 ($J \cdot mol^{-1}$)	ΔH^0 ($J \cdot mol^{-1}$)	p (atm)	T (K)
298.15	1.05×10^{-75}	427,976	472,550	10^{-10}	1407
300	3.39×10^{-75}	427,700	472,548	10^{-9}	1495
400	1.25×10^{-54}	412,778	472,311	10^{-8}	1595
500	2.67×10^{-42}	397,946	471,837	10^{-7}	1709
600	4.34×10^{-34}	383,225	471,194	10^{-6}	1842
				10^{-5}	1999
700	3.11×10^{-28}	368,623	470,412	10^{-4}	2191
800	7.53×10^{-24}	354,142	469,510	10^{-3}	2428
900	1.90×10^{-20}	339,780	468,504	10^{-2}	2725
1000	9.90×10^{-18}	325,536	467,403	10^{-1}	3112
1100	1.63×10^{-15}	311,408	466,177	1	3637
1166(α)	2.91×10^{-14}	302,150	465,124	$\Delta_{vap}S^0(3637\ K) = 112.602 \pm$	
1166(β)	2.91×10^{-14}	302,150	460,954		$(0.28)\ J \cdot mol^{-1} \cdot K^{-1}$
1200	1.12×10^{-13}	297,524	460,706		
1300	3.90×10^{-12}	283,955	459,931	$\Delta_{sub}H^0(0\ K) = 469.833 \pm$	
1400	8.12×10^{-11}	270,450	459,083		$(1.00)\ kJ \cdot mol^{-1}$
1500	1.12×10^{-9}	257,008	458,156		
1600	1.11×10^{-8}	243,632	457,150		
1700	8.38×10^{-8}	230,319	456,065		
1800	5.02×10^{-7}	217,072	454,896		
1900	2.48×10^{-6}	203,894	453,621		
1945(s)	4.82×10^{-6}	197,988	453,004		
1945(l)	4.82×10^{-6}	197,988	438.454		
2000	1.01×10^{-5}	191,206	437,249		
2200	1.10×10^{-4}	166,809	433,007		
2400	7.80×10^{-4}	142,788	428,995		
2600	4.05×10^{-3}	119,090	425,221		
2800	1.64×10^{-2}	95,678	421,688		
3000	5.46×10^{-2}	72,509	418,399		
3200	0.155	49,548	415,354		
3400	0.388	26,773	412,551		
3600	0.871	4,136	409,984		
3637	1.000	0	409,534		
3800	1.786	−18,330	407,649		

[a] 1 atm = 101,325 Pa.
[b] ΔG^0 refers to $\Delta_{sub}G^0$ when $T < T_{fus}$ and $\Delta_{vap}G^0$ when $T > T_{fus}$ (and similarly for ΔH^0).

et al. [60], Wu and Wahlbeck [63], Sumin et al. [66], and Kudryavtsev and Ivanov [67]. The values for ΔG^0, p, and ΔH^0 reported in Table XI are calculated using $\Delta_{\text{sub}} H^0$(298.15 K) and the Gibbs values for Ti(s, l) and Ti(g) from Table VII.

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