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Thermodynamic Properties of Vanadium[1]

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This work reviews and discusses the data and information on the various thermodynamic properties of vanadium available through March 1985. These include the heat capacity and enthalpy, enthalpy of melting, vapor pressure, and enthalpy of vaporization. The existing data have been critically evaluated and analyzed, and the recommended values for heat capacity, enthalpy, entropy, and Gibbs energy function covering the temperature range from 1 to 3800 K have been generated. These values are referred to temperatures based on IPTS-1968. The units used for various properties are joules per mole ($J \cdot mol^{-1}$). The estimated uncertainties in the heat capacity are ±3% below 15 K, ±10% from 15 to 150 K, ±3% from 150 to 298.15 K, ±2% from 298.15 to 1000 K, ±3% from 1000 to the melting point (2202 K), and ±5% in the liquid region.

KEY WORDS: critical evaluation; data analysis; enthalpy; enthalpy of melting; enthalpy of vaporization; Gibbs energy function; heat capacity; recommended values; vanadium; vapor pressure.

1. INTRODUCTION

The principal objective of this work is to critically evaluate and analyze all the available data and information on the heat capacity, enthalpy, and vapor pressure of vanadium and to generate the recommended values of these and other thermodynamic properties from 1 K to the melting point and above.

The discussion of the thermodynamic properties and the details of data analysis are reported in Section 2. The recommended values cover the temperature range from 1 to 3200 K.

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2. THERMODYNAMIC PROPERTIES

2.1. Phases and Structures

Vanadium has a bcc (A2) structure isotypic with W. Its atomic weight is 50.9415. A careful study of the values for the superconducting transition temperature, T_c, reported in the literature reveals that T_c is based on the data of Leupold et al. [1] and of Keesom and Radebaugh [2]. Its melting point of 2202 K selected previously by Hultgren et al. [31] was adopted after converting to IPTS-68. This compares with those reported by Rudy [3] (2202 K) and Margrave [4] (2194 K). This temperature and other thermodynamic properties reported here are based on the IPTS-1968.

Table I. Electronic Specific Heat Coefficient, Debye Temperature, and Superconducting Transition Temperature of Vanadium

Source	γ (mJ · mol^{-1} · K^{-2})	θ_D (K)	T_c (K)
Leupold et al. [1]	9.67	397.2	5.435
Keesom and Radebaugh [2]	9.92	399	5.37
Radebaugh [6]	9.82	382	5.379
Corak et al. [7]	8.996	298	
Corak et al. [8]	9.26	338	
Sellers et al. [9]		399	
Chernoplekov et al. [10]	9.80	373	
Ishikawa [11]	9.63	423	5.52
Cheng et al. [12]	8.87	315	
Shen [13]	9.64		5.084
	9.64		5.068
Worley et al. [14]	8.996	308	
	8.954	274	
	8.828	273	
Van Reuth [15]	9.079	247	4.69
	9.247	345	
Pan et al. [16]	9.60	314	
Ohlendorf and Wicke [17]	9.47	357	5.35
Takahashi et al. [18]		366	
Kumagai and Ohtsuka [19]	10.4	411	
Corsan and Cook [20]	9.45	377	5.17
Junod et al. [21]	9.9	399	5.30
Martin [22]		391	
Comsa et al. [23]	9.9		5.4
Vergara et al. [24]	8.8	382	5.37
Radebaugh and Keesom [25]	9.82	382	5.379
Recommended value	9.75 ± 0.30	385 ± 5	5.4 ± 0.3

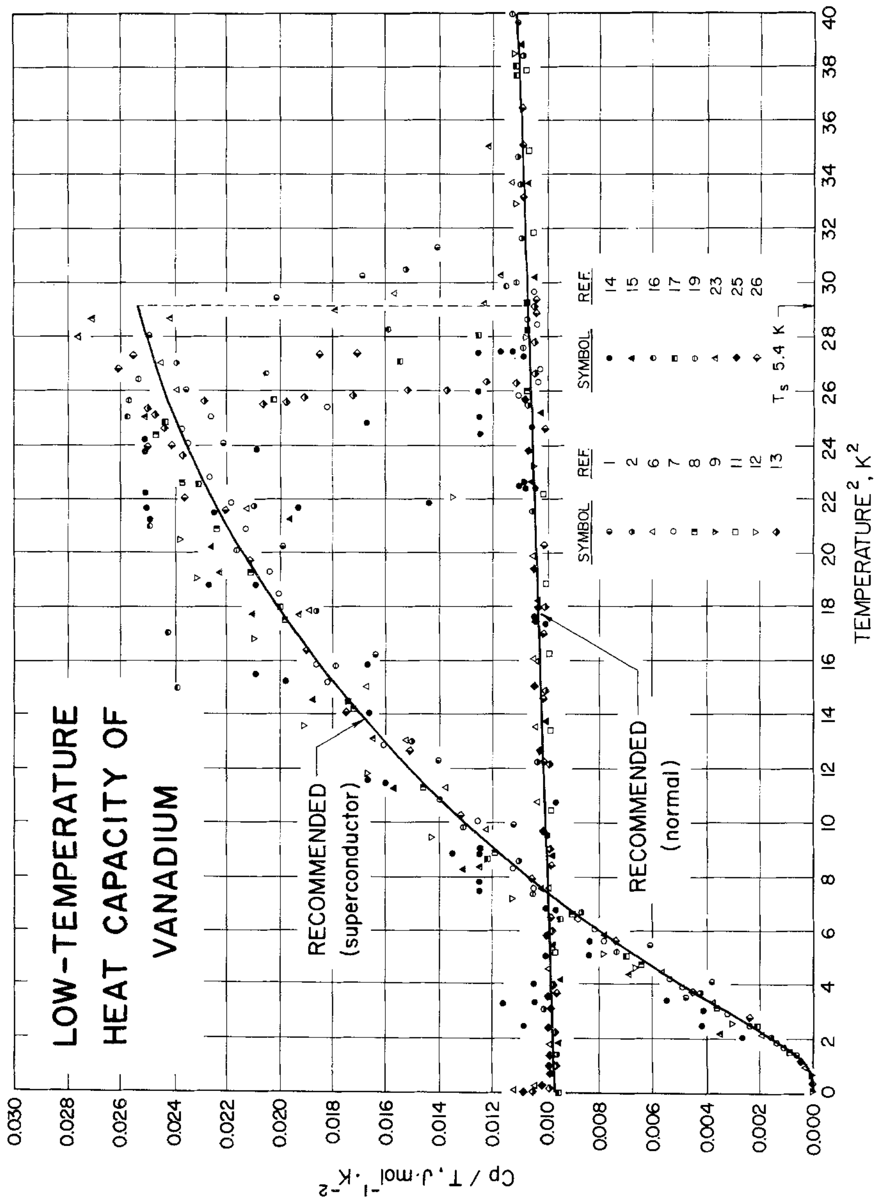

Fig. 1. Very low-temperature (0–40 K) heat capacity of vanadium.

2.2. Low-Temperature Heat Capacity

There have been numerous measurements of the electronic specific heat coefficient, γ, the Debye temperature, θ_D, and the superconducting transition temperature, T_c; some of them from which the recommended values are derived are listed in Table I. Additionally, Comsa et al. [23] and Vergara et al. [24] reported the data for ultrafine particles, indicating that T_c and γ increase with decreasing particle size.

Table II. Recommended Low-Temperature Heat Capacity of Vanadium

T (K)	C_p^0 (J · mol^{-1} · K^{-1})		T (K)	C_p^0 (J · mol^{-1} · K^{-1})
1	0.00024[a]	0.00978[b]	120	16.508
2	0.00992[a]	0.0198[b]	125	17.032
3	0.03573[a]	0.0302[b]	130	17.520
4	0.07448[a]	0.0412[b]	140	18.429
5	0.1196[a]	0.0530[b]	150	19.220
5.4	0.1369[a]	0.0580[b]	160	19.924
6	0.0659		170	20.549
7	0.0791		175	20.837
8	0.0929		180	21.107
9	0.1074		190	21.601
10	0.1220		200	22.041
15	0.213		210	22.438
20	0.360		220	22.793
25	0.675		225	22.961
30	1.113		230	23.121
40	2.348		240	23.411
50	4.021		250	23.663
60	5.968		260	23.882
70	8.105		270	24.089
75	9.177		273.15	24.155
80	10.250		280	24.286
90	12.256		290	24.471
100	13.934		298.15	24.612
110	15.341			

$C_{(\text{electronic})} = \gamma T, \quad \gamma = 9.75 \pm 0.03 \text{ mJ} \cdot \text{mol}^{-1} \cdot \text{K}^{-2}$

	Crystal [$V(s)$]	Gas [$V(g)$]
$H^0(298.15\text{ K}) - H^0(0\text{ K})$	4707 ± 10 J · mol^{-1}	7907 ± 4 J · mol^{-1}
$S^0(298.15\text{ K})$	29.708 ± 0.08 J · mol^{-1} · K^{-1}	182.189 ± 0.007 J · mol^{-1} · K^{-1}

[a] Superconductor.

[b] Nonsuperconductor in magnetic field.

The recommended C_p^0 values for the normal (nonsuperconducting) state below 5.4 K are calculated from the recommended values for γ and θ_D using the following equation:

$$C_p^0 = \gamma T + [1943.73/\theta_D^3]\, T^3$$

The recommended C_p^0 values for the superconducting state are based on the data of Leupold et al. [1], Keesom and Radebaugh [2], Corak et al. [7, 8], Kumagai and Ohtsuka [19], and Ohlendorf and Wicke [17]. A comparison of these and other results with the recommended values is shown in Fig. 1.

The recommended C_p^0 values up to 298.15 K are based on the data of Takahashi et al. [27] (−0.8%) and of Anderson [28] (±2%). The data of Ishikawa [11] are up to 20% and those of Bieganski and Stalinski [29] are ±2% above 70 K and considerably lower below 50 K. The data of Takahashi et al. [18] are −1% above 200 K and up to 10% higher below 200 K. The data of Clusius et al. [30] are up to 10% lower and those of Chernoplekov et al. [10] are considerably higher above 10 K and lower below 10 K than the recommended values. It is worth noting that the data of Chernoplekov et al. [10] and those of Takahashi et al. [18] suggest higher C_p^0 values (from 10 to 140 K) than those previously selected by Hultgren et al. [31]. The present recommendations in this temperature range are slightly higher than those recommended by Hultgren et al. [31]. It is thought that more studies are required to corroborate the higher values, especially those of Takahashi et al. [18]. Takahashi et al. [18] observed an anomaly at 220 to 230 K on the electropolished sample which disappeared after annealing at 1000 K. Pan et al. [16] found an anomaly at 195 K evidently connected with a second-order phase transition which may be produced by the ordering of interstitial impurity of hydrogen atoms. The recommended C_p^0 values (Table II) along with the experimental data are shown in Fig. 2. Integration of the recommended C_p^0 and C_p^0/T values yielded H^0 (298.15 K) − H^0 (0 K) and S^0 (298.15 K) values, listed in Table III along with the values from other sources.

Table III. Room-Temperature Thermodynamic Constants of Vanadium

Source	C_p^0 (298.15 K) ($J \cdot mol^{-1} \cdot K^{-1}$)	H^0 (298.15 K) − H^0 (0 K) ($J \cdot mol^{-1}$)	S^0 (298.15 K) ($J \cdot mol^{-1} \cdot K^{-1}$)
Present	24.612 ± 0.15	4707 ± 10	29.708 ± 0.08
Hultgren et al. [31]	24.895	4640	28.911 ± 0.4
Smith [52]	24.35 ± 0.1	4756 ± 50	30.89 ± 0.34
Glushko et al. [53]	24.48	4580	28.67

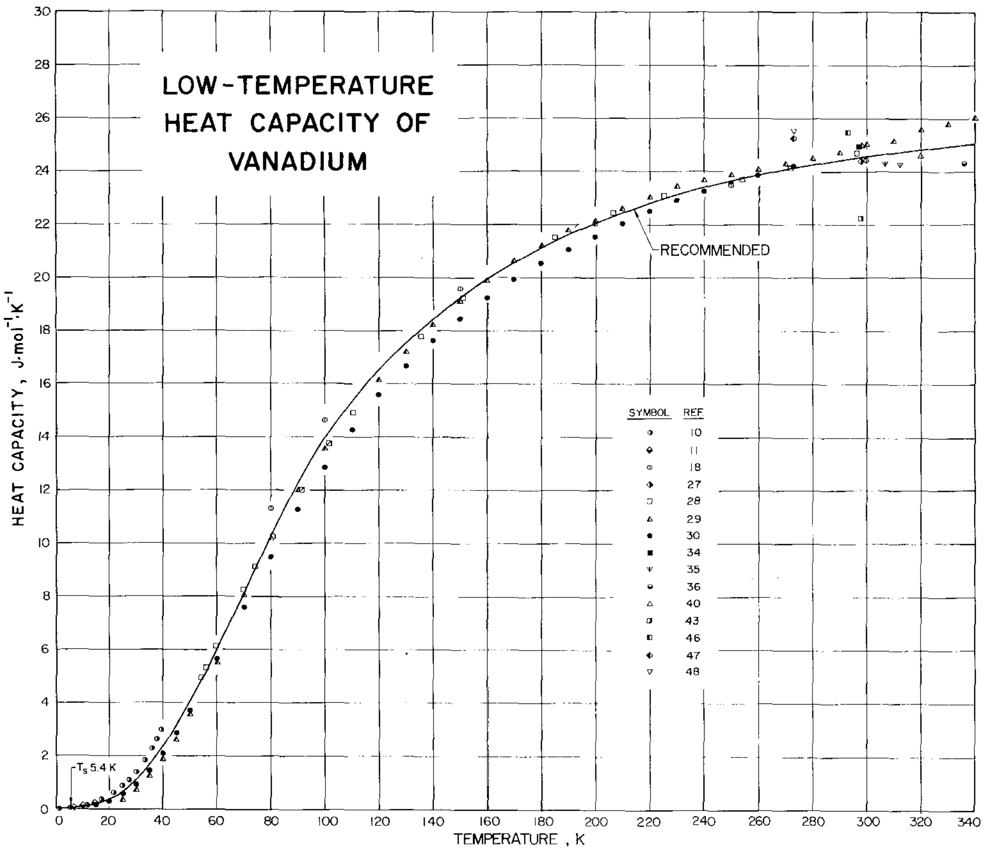

Fig. 2. Low-temperature (0–340 K) heat capacity of vanadium.

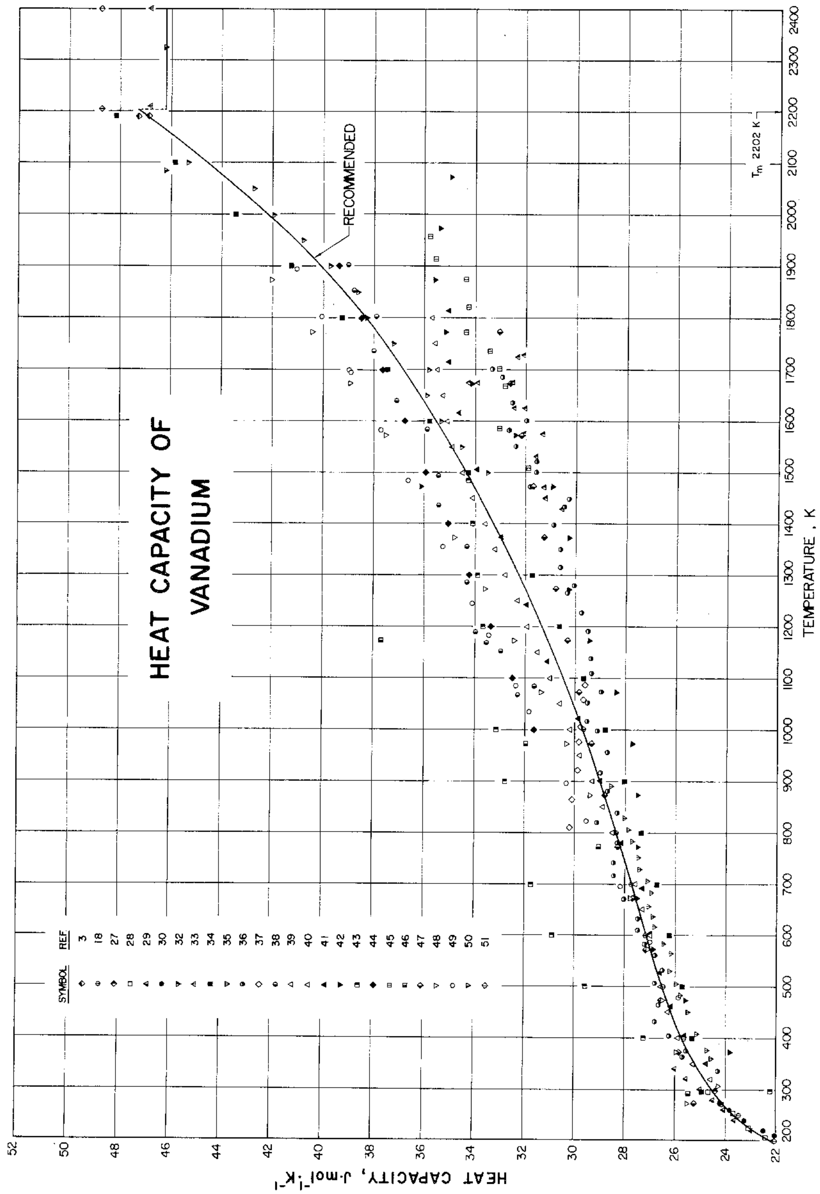

Fig. 3. Heat capacity of vanadium.

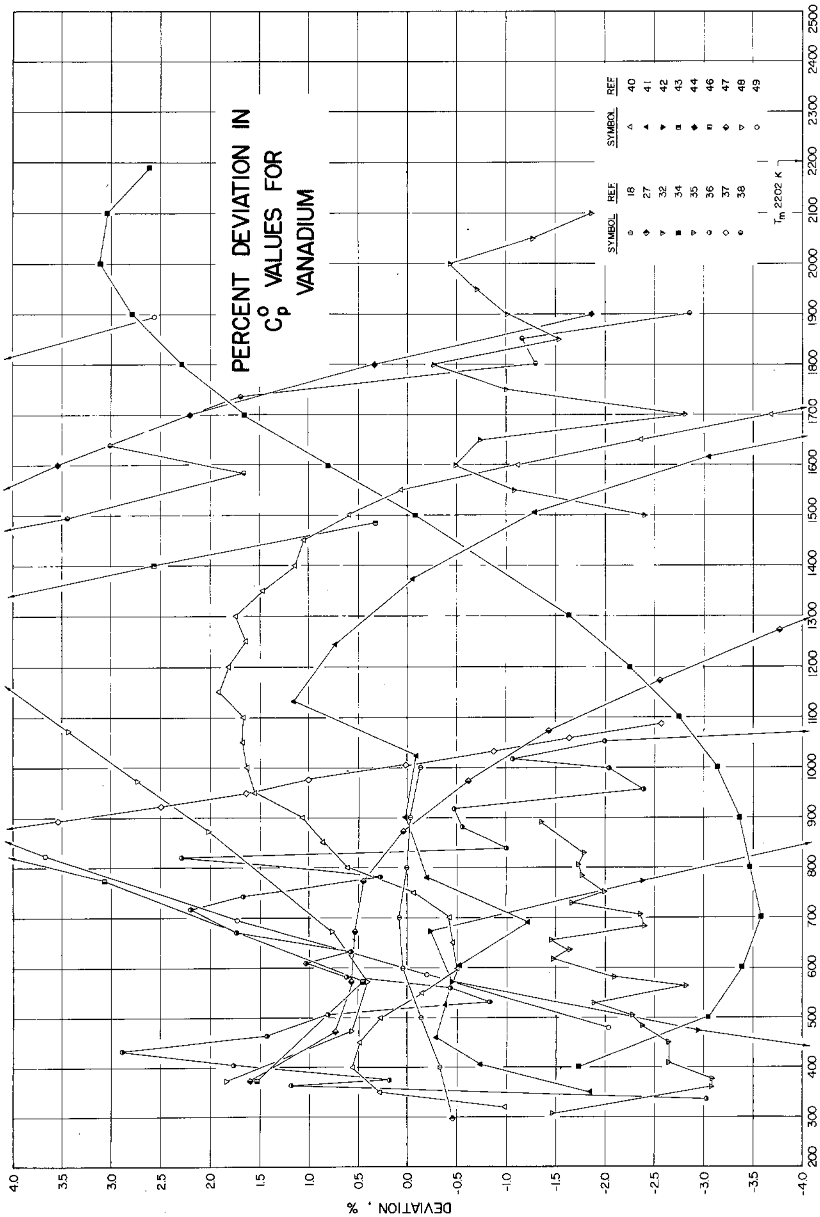

Fig. 4. Percentage deviation in C_p^0 values for vanadium.

Table IV. Percentage Deviation in Heat Capacity for Vanadium

Source	Deviation (%)
Bendick and Pepperhoff [36]	±3 (<1100 K)
	Up to −10 (>1100 K)
Knezek [37]	±3 (>920 K)
	6 (<920 K)
Arutyunov et al. [38]	±3 (>1500 K)
	5–8 (<1500 K)
Peletskii et al. [39]	Up to −14
Kohlhaas et al. [40]	±1 (<900 K)
	Up to 2 (900–1600 K)
	Up to −7 (>1600 K)
Braun et al. [41]	Up to −2 (<1500 K)
	Up to −6 (>1500 K)
Beakley [42]	Up to −22
Filippov [44]	Up to 6
Filippov et al. [45]	Up to −14
Neimark et al. [46]	Up to 19
Smith [52]	±1 (<1200 K)
	±2 (>1200 K)

2.3. High-Temperature Heat Capacity (Solid)

There have been numerous measurements of the heat capacity of vanadium. The recommended C_p^0 values are based on the data of Takahashi et al. [18] (±0.5%), Cezairliyan et al. [32] (±2.5%), and Chekhovskoi and Kalinkina [35] (−3%). A comparison of other C_p^0 measurements with the recommended values is shown in Table IV. A comparison of enthalpy measurements with the recommended enthalpy values $(y = H^0(T) - H^0(298.15\ \text{K})/(T - 298.15)$ is shown in Table V.

Table V. Percentage Deviation in Enthalpy for Vanadium

Source	Deviation (%)
Berezin and Chekhovskoi [34]	Up to −3 (<1800 K)
	±1 (>1800 K)
Golutvin and Kozlovskaya [43]	Up to 13
Jaeger and Veenstra [47]	Up to 4 (<1173 K)
	Up to −3 (>1173 K)
Jaeger and Veenstra [48]	Up to 4
Fieldhouse and Lang [49]	Up to 6

Table VI. Recommended High-Temperature Thermodynamic Properties of Vanadium[a]

	Condensed phase				Gas phase $V(g)$			
T (K)	C_p^0 ($J \cdot mol^{-1} \cdot K^{-1}$)	$H^0 - H^0(Tr)$ ($J \cdot mol^{-1}$)	S^0 ($J \cdot mol^{-1} \cdot K^{-1}$)	$-[G^0 - H^0(Tr)]/T$ ($J \cdot mol^{-1} \cdot K^{-1}$)	C_p^0 ($J \cdot mol^{-1} \cdot K^{-1}$)	$H^0 - H^0(Tr)$ ($J \cdot mol^{-1}$)	S^0 ($J \cdot mol^{-1} \cdot K^{-1}$)	$-[G^0 - H^0(Tr)]/T$ ($J \cdot mol^{-1} \cdot K^{-1}$)
298.15	24.612	0	0.000	29.708	26.012	0	0.000	182.189
300	24.641	46	0.152	29.708	25.978	48	0.161	182.189
400	25.783	2573	7.416	30.691	24.647	2571	7.429	183.190
500	26.517	5189	13.251	32.580	24.196	5007	12.867	185.042
600	27.144	7873	18.143	34.729	24.283	7428	17.281	187.090
700	27.736	10617	22.371	36.912	24.582	9871	21.046	189.133
800	28.343	13421	26.114	39.046	24.890	12345	24.349	191.107
900	28.990	16287	29.489	41.101	25.116	14846	27.294	192.988
1000	29.686	19221	32.579	43.067	25.237	17365	29.948	194.772
1100	30.454	22227	35.444	44.946	25.262	19890	32.355	196.462
1200	31.311	25315	38.130	46.743	25.214	22415	34.552	198.062
1300	32.234	28491	40.673	48.464	25.117	24931	36.566	199.577
1400	33.230	31764	43.097	50.117	24.994	27437	38.423	201.014
1500	34.326	35141	45.427	51.708	24.864	29930	40.143	202.379
1600	35.502	38632	47.679	53.243	24.739	32410	41.744	203.677
1700	36.828	42247	49.871	54.728	24.630	34878	43.240	204.913
1800	38.304	46002	52.017	56.168	24.545	37337	44.646	206.092
1900	40.063	49916	54.133	57.569	24.487	39788	45.971	207.219
2000	42.167	54027	56.241	58.935	24.460	42235	47.226	208.297
2100	44.581	58362	58.355	60.272	24.467	44681	48.420	209.332

2200	47.184	62949	60.488	61.583	24.510	47130	49.559	210.325
2202(s)	47.238	63043	60.531	61.609	24.511	47179	49.581	210.344
2202(l)	46.200	84043	70.068	61.609	24.511	47179	49.581	210.344
2300	46.200	88571	72.080	63.279	24.588	49584	50.650	211.280
2400	46.200	93191	74.047	64.925	24.702	52049	51.698	212.200
2500	46.200	97811	75.933	66.516	24.853	54526	52.710	213.088
2600	46.200	102431	77.745	68.056	25.039	57020	53.688	213.946
2700	46.200	107051	79.488	69.548	25.261	59535	54.637	214.776
2800	46.200	111671	81.168	70.994	25.517	62074	55.560	215.580
2900	46.200	116291	82.790	72.397	25.806	64640	56.461	216.360
3000	46.200	120911	84.356	73.760	26.126	67236	57.341	217.118
3100	46.200	125531	85.871	75.085	26.476	69866	58.203	217.855
3200	46.200	130151	87.337	76.373	26.853	72532	59.050	218.572
3300	46.200	134771	88.759	77.628	27.256	75237	59.882	219.272
3400	46.200	139391	90.138	78.849	27.682	77984	60.702	219.954
3500	46.200	144011	91.478	80.040	28.128	80774	61.511	220.621
3600	46.200	148631	92.779	81.201	28.593	83610	62.310	221.273
3682	46.200	152419	93.819	82.131	28.986	85971	62.956	221.795
3700	46.200	153251	94.045	82.334	29.072	86494	63.100	221.912
3800	46.200	157871	95.276	83.439	29.565	89425	63.881	222.537

[a] Enthalpy reference temperature = Tr = 298.15 K. $T_{fus} = 2202$ K; $\Delta_{fus}H^0 = 21{,}000 \pm 2500$ J · mol^{-1}; $\Delta_{fus}S^0 = 9.537 \pm 1.2$ J · mol^{-1} · K^{-1}.

Table VII. Values for Enthalpy of Fusion and Heat Capacity of Liquid Vanadium

Source	$\Delta_{fus}H^0$ (J·mol^{-1})	C_p^0 (J·mol^{-1}·K^{-1})
Margrave [4]		46.861
		47.279
Gathers et al. [5]	21,905	
Margrave [33]	18,180	46.8
Berezin and Chekhovskoi [34]	23,037	
Berezin et al. [50]		46.191
Treverton and Margrave [51]	17,305	48.744
Smith [52]	21,500	47.43

The recommended C_p^0 values along with the experimental data are listed in Table VI and shown in Fig. 3. For the convenience of readers, a systematic plot of the percentage deviation (up to $\pm 4\%$) in C_p^0 values from various measurements is shown in Fig. 4.

2.4. High-Temperature Heat Capacity (Liquid)

The recommended values for the enthalpy of melting, $\Delta_{fus}H^0 = 21{,}000 \pm 2500\ \text{J} \cdot \text{mol}^{-1}$ and $C^0_{p(l)} = 46.200 \pm 2.0\ \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$, are based on the data from the reported values given in Table VII.

2.5. Ideal Gas Properties

Thermodynamic quantities for $V(g)$ reported in Table VI are calculated from $C_p^0(g)$ and $S^0(298.15\ \text{K})(g)$ values reported by Chase [54].

Table VIII. Values for Enthalpy of Sublimation of Vanadium at 298.15 K

Source	$\Delta_{sub}H^0$ (kJ · mol^{-1})
Saxer [55], 1771–1880 K, Knudsen method	514.53 ± 1.02
Edwards et al. [56], 1666–1882 K, Knudsen method	513.69 ± 0.61
Moore et al. [57], 1600 K, mass spectrometer–Knudsen method	501.21
Farber and Srivastava [58], 1900–2412 K, mass spectrometer–Knudsen method	515.82 ± 1.26
Recommended value	$514.20\ (\pm 1.00)$

Table IX. Recommended Vapor Pressure of Vanadium, $V_{(s,l)} = V_{(g)}$ [a,b]

T (K)	p (atm)	ΔG^0 ($\mathrm{J\cdot mol^{-1}}$)	ΔH^0 ($\mathrm{J\cdot mol^{-1}}$)
298.15	7.57×10^{-83}	468,738	514,200
300	2.72×10^{-82}	468,456	514,200
400	6.58×10^{-60}	453,200	514,198
500	1.76×10^{-46}	437,969	514,018
600	1.56×10^{-37}	422,783	513,755
700	3.81×10^{-31}	407,645	513,454
800	2.34×10^{-26}	392,551	513,124
900	1.23×10^{-22}	377,502	512,759
1000	1.16×10^{-19}	362,495	512,344
1200	3.32×10^{-15}	332,617	511,300
1400	4.98×10^{-12}	302,944	509,873
1600	1.18×10^{-9}	273,506	507,978
1800	8.12×10^{-8}	244,337	505,535
2000	2.36×10^{-6}	215,476	502,408
2100	9.91×10^{-6}	201,174	500,519
2202(s)	3.73×10^{-5}	186,686	498,336
2202(l)	3.73×10^{-5}	186,686	477,336
2300	1.13×10^{-4}	173,798	475,213
2400	3.17×10^{-4}	160,740	473,058
2500	8.18×10^{-4}	147,770	470,915
2600	1.95×10^{-3}	134,886	468,789
2700	4.35×10^{-3}	122,084	466,684
2800	9.12×10^{-3}	109,359	464,603
2900	1.81×10^{-2}	96,707	462,549
3000	3.43×10^{-2}	84,126	460,525
3100	6.21×10^{-2}	71,613	498,535
3200	0.108	59,163	456,581
3300	0.182	46,775	454,666
3400	0.296	34,443	452,793
3500	0.467	22,167	450,963
3600	0.717	9,941	449,179
3682	1.000	0	447,752
3700	1.076	−2,239	447,443
3800	1.576	−14,372	445,754

p (atm)	T (K)
10^{-10}	1503
10^{-9}	1593
10^{-8}	1695
10^{-7}	1811
10^{-6}	1945
10^{-5}	2101
10^{-4}	2289
10^{-3}	2522
10^{-2}	2813
10^{-1}	3185
1	3682

$\Delta_{vap}S^0(3682\,\mathrm{K}) = 121.606 \pm 0.27$ ($\mathrm{J\cdot mol^{-1}\cdot K^{-1}}$)

$\Delta_{sub}H^0(0\,\mathrm{K}) = 511.00 \pm 1.00$ ($\mathrm{kJ\cdot mol^{-1}}$)

[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).

2.6. Vapor Pressure Data

Application of the third-law test to the vapor pressure measurements gave the enthalpies of sublimation at 298.15 K listed in Table VIII.

The values for ΔG^0, P, and ΔH^0 reported in Table IX are calculated using $\Delta_{sub}H^0(298.15\text{ K})$ and the Gibbs values for $V(s, l)$ and $V(g)$ from Table VI.

Most of the measurements for the thermodynamic properties have been carried out on the International Practical Temperature Scale of 1948 or 1958 (IPTS-48 or IPTS-58). It is worth noting that the effect of conversion of these properties to IPTS-68 is small and well within the uncertainty of these values.

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