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Thermodynamic Properties of Vanadium

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Abstract The thermodynamic properties of vanadium have been evaluated to 3700 K. Selected values include an enthalpy of sublimation of 515 ± 2 kJ/mol at 298.15 K and a boiling point at one atmosphere pressure of 3694 K.

Keywords gas · liquid · solid · thermodynamic properties · vanadium

1 Introduction

This work is one of a series on thermodynamic properties of the elements to appear in the *Journal of Phase Equilibria and Diffusion*. The articles are expected to be especially useful to those who are updating databases for phase diagram prediction and for other applications as well. Each article in the series will list the properties of a single element, including Ag,[1] Au,[2] Be,[3] Cr, Cu,[4] Hf,[5] Mo, Nb, Ta, Ti, V and W. References are given for papers which have already been published. In addition, the series will also include two summary papers on selected values of the melting points and boiling points of the elements and on the enthalpies and entropies of fusion and transition of the elements.

Previous comprehensive reviews on vanadium were by Hultgren et al.,[6] Smith[7] Gurvich et al.[8] JANAF[9] and Desai[10] and reviews on the solid only by Maglić.[11] A further review is justified by including the high temperature enthalpy measurements of Lin and Frohberg.[12]

A superconducting transition temperature (T_C) of 5.435 K as determined by Leupold et al.[13] was accepted because of the high purity of the material used. After correction to the ITS-90 temperature scale the melting point determined by Rudy and Windisch[14] at 2201 ± 6 K was also accepted since this was confirmed by more recent values of 2200 K as determined by Hiernaut et al.[15] and 2199 K as determined by Pottlacher et al.[16]

Wherever possible values have been corrected to the currently accepted atomic weight of 50.9415 ± 0.0001[17] and to the ITS-90 temperature scale using correction factors of Douglas,[18] Rusby,[19] Rusby et al.,[20] and Weir and Goldberg.[21]

It was suggested by Westlake[22] that numerous anomalies found in the measurements of physical properties of vanadium between 180 K and 250 K were due to the precipitation of impurity hydrogen as vanadium hydride. Subsequently, Westlake et al.[23] dehydrogenated samples at 1073 K in high vacuum and found that electrical resistivity and elastic constants measurements no longer showed evidence of such anomalies. However, based on dilatometric measurements on high purity materials containing low hydrogen levels, Bollinger et al.[24] suggested that all of the Group 5 metals did in fact show evidence of a structural distortion below 300 K which was martensitic in character and lead to a structure which was not cubic. They further suggested that the vacuum used in the heat treatment process to remove hydrogen was not high enough to prevent a small amount of oxidation which led to the introduction of interstitial impurities which were enough to completely suppress the martensitic transformation, and this was the reason for the removal of the anomalies and not the removal of hydrogen as suggested by Westlake.[22] However, in spite of this speculation, it is noted that Jung et al.[25] had carried out electrical resistivity measurements

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on samples containing less than 1 wt ppm hydrogen and less than a total of 100 at ppm of oxygen + carbon + nitrogen and found no evidence of anomalies between 6 K and 300 K. Further, Smirnov and Finkel,[26] Schmitz-Pranghe and Dünner[27] and Henry et al.[28] all confirmed that the structure remained as body-centred cubic below 120 K. Even an apparent transition to a tetragonal structure at 230 K observed by Finkel' et al.[29] was shown by Westlake et al.[23] to be due to a mis-interpretation and the correct interpretation indicated that the structure remained in the body-centred cubic form. In view of these findings, it is assumed that until the measurements of Bollinger et al.[24] are independently verified and that the supposed new low temperature structure is fully characterised then the structure is considered to be body-centred cubic over the whole temperature range (Fig. 1, 2, 3).

2 Solid Phase

2.1 Superconducting State: Range 0 to 5.435 K

In the description of the electronic structure of transition metals in terms of two electronic conduction bands, if the scattering of electrons between the two bands is sufficiently weak, then both may separately undergo a transition into the superconducting state with the resultant formation of two energy gaps, which is a Type II superconductor. Anomalies which appeared to confirm this behaviour were observed for vanadium in the specific heat measurements of Shen[30] and Radebaugh and Keesom[31] However for niobium, Sellers et al.[32] showed that the anomalies were due to hydrogen contamination and that with hydrogen removed niobium behaved as a typical Type I superconductor. Therefore, it is considered that vanadium would behave similarly and the anomalies found in the measurements of Shen[30] and Radebaugh and Keesom[31] were ignored. Therefore, below $T_c/T = 2$ the remaining specific heat values from these two sets of measurements were averaged and then fitted to the Bardeen-Cooper-Schrieffer equation and a lattice term after correcting to the selected values given in the Normal State review of $\gamma = 9.67$ mJ/(mol K^2), and $T_c = 5.435$ K and a lattice contribution equal to the selected value of $\theta_D = 397.2$ K. The full representation of the specific heat (Cs) below 2.718 K (T_c/2) as then given by Eq 1:

$$\begin{aligned} C_s(\text{mJ/mol K}) &= C_{es} + A\ T^3 \\ &= 7.227\,\gamma\ T_C\exp(-1.343T_c/T) \\ &\quad + 0.03102\ T^3 \end{aligned} \qquad \text{(Eq 1)}$$

Above a temperature of $T_c/T = 2$, it is a requirement that the entropies of both the superconducting state and the normal state are equal at T_c. At T_c, a value of $C_s = 135.9$ mJ/(mol K) is estimated from the graphical representation of Leupold et al.[13] and this value was combined with the value of 26.52 mJ/(mol K) at 2.718 K obtained from Eq 1 and an intermediate value of 69.944 mJ/(mol K) at the mid-point temperature of 4.076 K obtained by iteration so that at T_c the entropy values of the superconducting state and the normal state are equal. This gives Eq 2 for C_s over the range 2.718 K to T_c:

$$\begin{aligned} C_s(\text{mJ/mol K}) &= C_{es} + A\ T^3 = 9.3258 - 10.1786T \\ &\quad + 5.9883T^2 + 0.03102T^3 \end{aligned} \qquad \text{(Eq 2)}$$

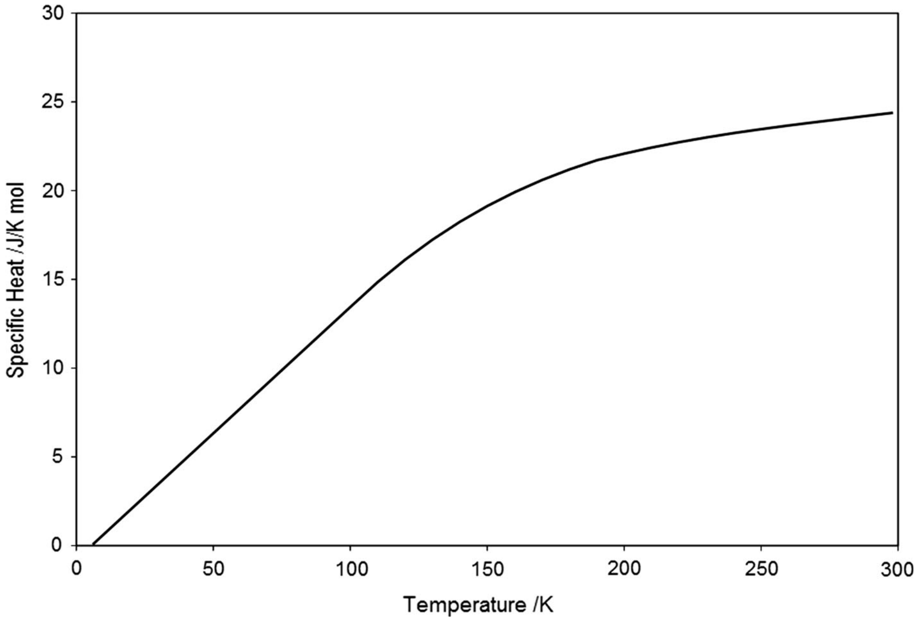


Fig. 1 Low temperature specific heat of solid vanadium, from 6 K to 298.15 K, taken from Table 17

Fig. 2 Specific heat of vanadium for $300 < T < 3700$ K, taken from Table 18

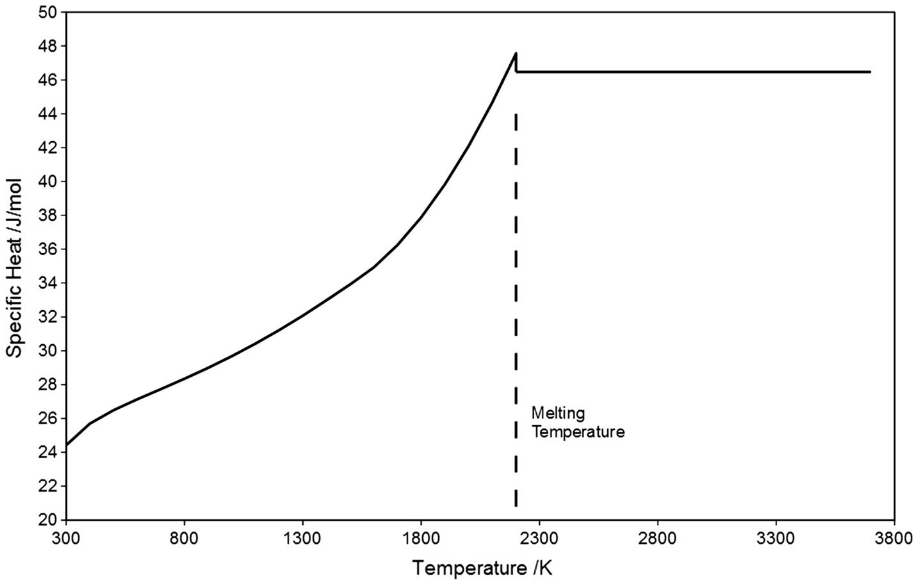
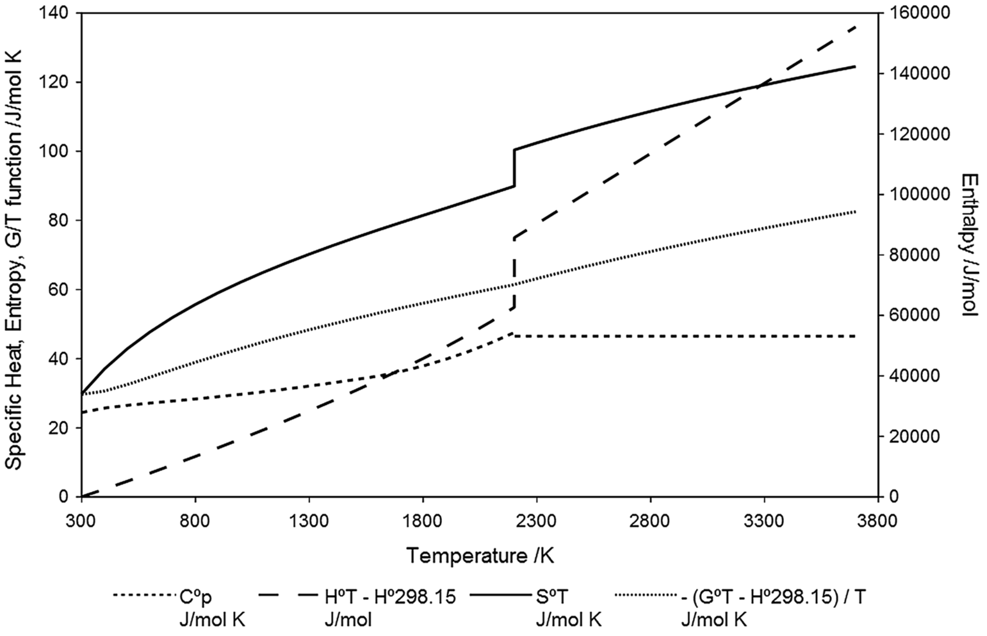


Fig. 3 High temperature thermodynamic properties of vanadium for $300 < T < 3700$ K, taken from Table 18



Derived thermodynamic values based on Eq 1 and 2 are given in Table 16 whilst differences from the selected values of other measurements in this region are given in Table 10.

2.2 Normal State: 0 to 298.15 K

Low temperature specific heat for vanadium in the normal state is given in terms of the modified Debye equation: $C_p = D/T^2 + \gamma T + A T^3$ where D is the nuclear quadrupole coefficient, γ is the electronic coefficient and A is the lattice contribution, which is usually represented in terms of a limited Debye temperature, θ_D, which can be determined by the equation $\theta_D^3 = (12/5)\,\pi\,4\,R/A = 1943.770/A$ where R is the Gas Constant and A is given in units of J (mol K^4). Desai[10] listed a large number of determinations of the values of γ and θ_D but only those where the values of θ_D approach the values determined from elastic constants values of 399.3 K determined by Alers[33] and 403 K determined by Bolef et al.[34] are considered, which consists of the measurements of Shen[30] (<4.2 K), Radebaugh and Keesom[31] (0.4-5.1 K) and Leupold et al.[13] (2-20 K) with values given in Table 1. Because of the very high purity of the samples used, the values of Leupold et al. were selected for γ and θ_D and the values of Shen for D. It is noted that the inclusion of D has little effect on the values of Leupold et al. above 2.5 K.

Table 1 Low temperature normal state specific heat constants

Authors	References	D, mJ K/mol	γ, mJ/mol K^2	θ_D, K
Shen	30	0.041	9.64	400
Radebaugh and Keesom	31	…	9.82	382
Leupold et al.	13	…	9.67	397.2
	Selected	0.041	9.67	397.2

The values selected in Table 1 apply up to 7.47 K at which temperature Leupold et al.[13] showed an abrupt change in the slope of the specific heat values, which was due to the presence of a Kohn anomaly in the phonon density of states. The further measurements of Leupold et al. were selected above this temperature and up to the experimental limit at 20 K.

From 55 to 190 K the specific heat values of Anderson[35] (54.2-296.5 K) were selected since these gave the best correlation with the values of Leupold et al.[13] when interpolating in the range 20 to 55 K. However above 190 K the specific heat values of Takahashi et al.[36] (82-991 K) were selected in order to give continuity with selected high temperature values. Representative equations for the range 20-298.15 K are given in Table 6.

Normal state thermodynamic values below the superconducting temperature are also given in Table 16 and above this temperature in Table 17. The deviations of other normal range specific heat values are given in Table 11 except for the measurements of Chernoplekov et al.[37] (1.5-40 K) which were shown only in the form of a small graph.

2.3 Solid: Range 298.15-2201 K

In the overlap region the smoothed drop calorimetry enthalpy measurements of Berezin and Chekhovskoi[38] (1345-2173 K) and Lin and Frohberg[12] (1809-2176 K in the solid region) initially agree at 1800 K but close to the experimental limit the deviation increases to 2.0%, which is considered to be a poor agreement for consideration in the evaluation. Therefore selected values are based on the closely agreeing smoothed specific heat values of Takahashi et al.[36] (82-991 K) and Cezairliyan et al.[39] (1500-2100 K) which give an exact fit if the specific heat is represented by two equations with a crossover temperature of 1478 K:

$$298.15 \text{ to } 1478\ \mathrm{K}\, C^{\circ}_{p}(\mathrm{J/mol\,K}) = 26.3612 + 3.35842 \times 10^{-4}T + 3.19617 \times 10^{-6}T^{2} - 209,380/T^{2} \quad (\text{Eq } 1)$$

$$1478 \text{ to } 2201\ \mathrm{K}{:}\, C^{\circ}_{p}(\mathrm{J/mol\,K}) = 56.3414 - 3.83985 \times 10^{-2}T + 1.56354 \times 10^{-5}T^{2} \quad (\text{Eq } 2)$$

Based on the original experimental values, Eq 3 has an overall accuracy of 0.3% and Eq 4 0.9%. Derived enthalpy and entropy equations are given in Table 7.

Compared to the solid enthalpy equations given in Table 7 the smoothed enthalpy values of Berezin and Chekhovskoi[38] are initially 2.1% low then converge to the selected values being only 0.3% high close to the melting point whilst the smoothed values of Lin and Frohberg[12] trend from 0.8% low to 1.7% low.

Derived values are given in Table 18 whilst deviations of high temperature solid specific heat values are given in Table 12 and deviations of solid enthalpy values in Table 13 except for the specific heat values of Bendick and Pepperhoff[40] (350-1700 K) which were shown only in the form of a small graph and were not included. All values were compared without correction for possible temperature scale effects.

2.4 A Comparison of Selected Values at 298.15 K

The comparison is given in Table 2. The selected enthalpy and entropy values of Desai[10] and in the present review are similar since they are based on the same data sources.

3 Liquid Phase

After correction to the selected melting point, the enthalpy of fusion determined by Berezin and Chekhovskoi[38] corrected to 23013 ± 516 J/mol, and the value determined by Lin and Frohberg[12] corrected to 23033 ± 618 J/mol, were averaged to 23023 ± 400 J/mol, which is selected and fixes the liquid enthalpy at the melting point as $H^{\circ}_{T} - H^{\circ}_{298.15} = 85,738$ J/mol.

Liquid enthalpy values of Berezin et al.[41] (2084-2325 K) and Lin and Frohberg[12] (2140-2632 K) were re-evaluated leading to liquid specific heat values of 46.225 ± 1.41 J/(mol K) and 46.717 ± 0.58 J/(mol K) respectively and averaging to 47.471 ± 0.71 J/(mol K). In combination with the enthalpy value at the melting point the enthalpy of the liquid can then be represented by the selected equation:

$$H^{\circ}_{T} - H^{\circ}_{298.15}(\mathrm{J/mol}) = 46.4710\,T - 16544.35 \quad (\text{Eq } 5)$$

The selected specific heat is in satisfactorily agreement with the later drop calorimetric value of Schaefers et al.[42] (2016-2403 K) as given in Table 3. Thermodynamic properties derived from Eq 5 are also given in Table 18 and deviations of liquid enthalpy values from the selected values are given in Table 14.

Table 2 Selected values for the solid at 298.15 K

Authors	References	C°_p, J/mol K	$H^\circ_{298.15\ K} - H^\circ_0$, J/mol	$S^\circ_{298.15\ K}$, J/mol K
Hultgren et al.	6	24.89	4640	28.91
Smith	7	24.35	4507	30.89
Gurvich et al.	8	24.48	4580	28.67
JANAF (Chase)	9	24.90	4640	28.94
Desai	10	24.61	4707	29.71
This work	…	24.39	4678	29.64

Table 3 Enthalpy of fusion and liquid specific heat values for vanadium

Authors	References	Method	ΔH s, l, kJ/mol	C°_p, J/mol K	Notes
Seydel et al.	43	RPH	27.5	…	
Gathers et al.	44	RPH	21.9	…	(a)
Pottlacher et al.	16	RPH	20.7	49.1	
Treverton and Margrave	45	DC	…	48.75 ± 1.51	
Berezin et al.	46	DC	23.06 ± 0.73	47.37	
Berezin et al.	41	DC	…	46.20 ± 2.93	
Berezin and Chekhovskoi	38	DC	23.04 ± 0.31	…	
Lin and Frohberg	12	DC	23.04 ± 0.16	46.72 ± 0.58	
Schaefers et al.	42	DC	…	46.68 ± 1.94	(b)
Paradis et al.	47	NEL	26.5	48.3	(c)
		Selected	23.023 ± 0.400	46.47 ± 0.71	

DC Drop calorimetry, *NEL* Non-contact electrostatic levitation, *RPH* Rapid pulse heating

(a) The specific heat trends from 61.4 J/(mol K) at the melting point to 60.7 J/(mol K) at 2560 K to 79.2 J/(mol K) at 4500 K

(b) The specific heat value was calculated from the given data

(c) Average of specific heat trending 47.8 J/(mol K) to 48.9 J/(mol K) over the temperature range

Table 4 Enthalpies of sublimation at 298.15 K

Authors	References	Method	Temperature, Range K	$\Delta H^\circ_{298.15\ K}$ (II), kJ/mol	$\Delta H^\circ_{298.15\ K}$ (III), kJ/mol	Notes
Storms et al.	52	MS	1445-1945	530 ± 2	…	(a)
Moore et al.	53	MS	1600	501 ± 10	…	
Edwards et al.	54	L	1666-1882	508 ± 4	513.9 ± 0.2	
Saxer	55	KE	1771-1880	480 ± 3	514.8 ± 0.6	
Farber and Srivastava	56	KEMS	1900-2155 (s)	508 ± 6	516.1 ± 0.3	
			2198-2412 (l)	491 ± 22	516.2 ± 0.7	
				Selected	515 ± 2	

$\Delta H^\circ_{298.15\ K}$ (II) and $\Delta H^\circ_{298.15\ K}$ (III) are the Second Law and Third Law enthalpies of sublimation at 298.15 K

(a) Average of three separate runs

KE Knudsen effusion, *KEMS* Knudsen effusion mass spectrometry, *L* Langmuir method, *MS* Mass spectrometry

Table 5 Vapour pressure equations

Phase	Range K	A	B	C	D	E
Solid	1150-2201	31.61839	−1.95511	−62851.17	1.28884×10^{-3}	-2.21193×10^{-7}
Liquid	2201-3700	33.73539	−1.92352	−62674.51	-3.78153×10^{-4}	3.24227×10^{-8}

Table 6 Specific heat equations of the solid below 298.15 K

20 to 55 K:

$$C^{\circ}_{P}(\mathrm{J/mol\,K}) = 1.03412\times10^{-2}\mathrm{T} + 7.06949\times10^{-4}\mathrm{T}^2 + 1.51135\times10^{-5}\mathrm{T}^3 - 0.109743$$

55 to 190 K:

$$C^{\circ}_{P}(\mathrm{J/mol\,K}) = 0.344644\mathrm{T} - 1.20959\times10^{-3}\mathrm{T}^2 + 1.50653\times10^{-6}T^3 - 10.4350$$

190 to 298.15 K:

$$C^{\circ}_{P}(\mathrm{J/mol\,K}) = 0.180167\mathrm{T} - 5.89908\times10^{-4}\mathrm{T}^2 + 7.06059\times10^{-7}\mathrm{T}^3 - 29002.35/\mathrm{T}^2 + 4.72523$$

Table 7 High temperature representative equations

Solid: 298.15 to 2201 K

298.15 to 1478 K

$$C^{\circ}_{P}(\mathrm{J/mol\,K}) = 26.3612 + 3.35842\times10^{-4}\mathrm{T} + 3.19617\times10^{-6}\mathrm{T}^2 - 209380/\mathrm{T}^2$$

$$\mathrm{H^{\circ}_T - H^{\circ}_{298.15K}}(\mathrm{J/mol}) = 26.3612\mathrm{T} + 1.67921\times10^{-4}\mathrm{T}^2 + 1.06539\times10^{-6}\mathrm{T}^3 + 209380/\mathrm{T} - 8605.02$$

$$\mathrm{S^{\circ}_T}(\mathrm{J/mol\,K}) = 26.3612\ln(T) + 3.35842\times10^{-4}\mathrm{T} + 1.898085\times10^{-6}\mathrm{T}^2 + 104690/\mathrm{T}^2 - 121.9715$$

1478 to 2201 K

$$C^{\circ}_{p}(\mathrm{J/mol\,K}) = 56.3414 - 3.83985\times10^{-2}\mathrm{T} + 1.56354\times10^{-5}\mathrm{T}^2$$

$$\mathrm{H^{\circ}_T - H^{\circ}_{298.15\,K}}(\mathrm{J/mol}) = 56.3414\mathrm{T} - 1.919925\times10^{-2}\mathrm{T}^2 + 5.21180\times10^{-6}\mathrm{T}^3 - 23854.2$$

$$\mathrm{S^{\circ}_T}(\mathrm{J/mol\,K}) = 56.3414\ln(\mathrm{T}) - 3.83985\times10^{-2}\mathrm{T} + 7.81770\times10^{-6}\mathrm{T}^2 - 297.0697$$

Liquid: 2201 to 3700 K

$$C^{\circ}_{p}(\mathrm{J/mol\,K}) = 46.4710$$

$$\mathrm{H^{\circ}_T - H^{\circ}_{298.15\,K}}(\mathrm{J/mol}) = 46.4710\mathrm{T} - 16544.35$$

$$\mathrm{S^{\circ}_T}(\mathrm{J/mol\,K}) = 46.4710\ln(\mathrm{T}) - 257.2833$$

Table 8 Free energy equations above 298.15 K

Solid: 298.15 to 2201 K

298.15 to 1478 K

$$\mathrm{G^{\circ}_T - H^{\circ}_{298.15\,\mathit{K}}}(\mathrm{J/mol}) = 148.3327T - 1.67921\times10^{-4}\mathrm{T}^2 - 5.32695\times10^{-7}\mathrm{T}^3 + 104690/\mathrm{T} - 26.3612\mathrm{T}\ \ln(\mathrm{T}) - 8605.02$$

1478 to 2201 K

$$\mathrm{G^{\circ}_T - H^{\circ}_{298.15K}}(\mathrm{J/mol}) = 353.4111\mathrm{T} + 1.911925\times10^{-2}\mathrm{T}^2 - 2.60590\times10^{-6}\mathrm{T}^3 - 56.3414\mathrm{T}\ln(\mathrm{T}) - 23854.2$$

Liquid: 2201 to 3700 K

$$\mathrm{G^{\circ}}_{T} - \mathrm{H^{\circ}_{298.15K}}(\mathrm{J/mol}) = 303.7543\mathrm{T} - 46.4710\mathrm{T}\ \ln(\mathrm{T}) - 16544.35$$

Table 9 Transition values involved with the free energy equations

Transition	Temperature, K	ΔH° s, l, J/mol	ΔS° s, l, J/mol K
Fusion	2201	23023.00	10.4607

4 Gas Phase

4.1 Thermodynamic Properties of the Gas Phase

Selected values are based on the 544 energy levels selected by Thorne et al.[48] The thermodynamic properties were calculated using the method of Kolsky et al.[49] and the 2014 Fundamental Constants (Mohr et al.[50,51]). Derived thermodynamic values are given in Table 18.

4.2 Enthalpy of Sublimation

Because of a general lack of detail as to what temperature scales were used and problems associated with the exact measurement of temperature then no attempt was made to correct vapor pressure measurements to ITS-90 from what would have been contemporary scales. Values are summarised in Table 4 where the selected value of 515 ± 2 kJ/mol is an average of the last four Third Law determinations.

Table 10 Deviations of superconducting specific heat values

Authors	References	Temperature range, K	% Deviations from the selected values
Corak et al.	57	1.2-5.4	Run 1: Trends from initial 14.4 low to 14.4 high at 3.8 K to 7.2 high at 4.8 K; Run 2: Trends from initial 14.2 low to 13.0 high at 3.6 K to 12.0 high at 4.9 K: Run 3: Trends from initial 12.2 low to 13.8 high at 3.9 K to 7.0 high at 4.8 K; Run 4: Trends from initial 12.4 low to 13.4 high at 3.6 K to 11.2 high at 5.0 K
Radebaugh and Keesom	31	0.6-5.8	Run 1: Trends from average 21.1 high below 0.95 K to 3.9 low at 1.8 K to 5.7 high at 3.6 K to average 3.8 high above 4.3 K; Run 2: Trends from initially 255 high at 0.6 K to then converge with the selected value at 1.3 K

Table 11 Deviations of low temperature normal state specific heat values

Authors	References	Temperature range, K	% Deviations from the selected values
Corak et al.	57	1.1-5.4	Smoothed values show trend 4.3 low to 1.4 high
Radebaugh and Keesom	31	0.4-5.1	Smoothed values show trend 4.8 low to 2.5 high
Clusius et al.	58	11-274	Trend from average 31.9 low below 25 K to 0.8 high above 250 K
Bieganski and Stalinski	59	25-340	Trends from initially 57.0 low to 1.0 high at 90 K to 0.2 low at 130 K to 3.6 high at 340 K
Anderson	35	54-297	Generally scatter 1.0 low to 1.4 high except for the value at 166 K which is 7.8 low. Smoothed values excluding the value at 166 K are the representative values between 55 and 190 K but above this temperature trend to 1.3 high 297 K
Takahashi et al.	36	82-991	Smoothed values trend from initially 10.1 high to converge to the selected values at 190 K and are then the representative values above this temperature

Table 12 Deviations of high temperature solid specific heat values

Authors	References	Temperature range, K	% Deviations from the selected values
Boggs et al.	60	1089-1589	3.3 high at 1089 K and 3.8 low at 1589 K
Kohlhaas et al.	61	320-1800	Shows scatter but the general trend is from initially 0.6 low to 2.2 high at 1150 K to 5.8 low at 1800 K
Filippov and Yurchak	62,63	1000-1900	Trends from average 6.7 high at 1300 K and below to 1.2 low at 1900 K
Peletskii et al.	64	1400-1700	Trends 6.1 low to 8.9 low
Chekhovskoi and Kalinkina	65	307-892	Shows marked scatter between 2.3 low and 1.4 low. Smoothed values show trend 1.3 low to 2.3 low
Neimark et al.	66	293-1173	Trends from initially 4.8 high to 0.5 high at 573 K to 21.6 high at 1173 K
Kulish and Filippov	67	300-1100	Scatters from 4.4 low to 4.4 high
Stanimirović et al.	68	350-1900	Trends from initially 4.0 high to 2.7 low at 1450 K to 2.3 low at 1650 K to 3.7 low at 1900 K
Beakley	69	311-1255	Initially 2.9 low then shows marked trends 1.0 high at 366 K to 4.5 high at 478 K to 1.2 high at 644 K to 16.0 high at 1089 K to 10.4 high at 1255 K
Knezek	70	811-1089	Initially 1.3 high then trends to 0.8 high at 866 K then to 1.9 high at 1089 K

Table 13 Deviations of enthalpy values in the solid range

Authors	References	Temperature range K	% Deviations from the selected values
Jaeger and Veenstra	71	565-1828	Trends from an average of 1.4 high below 800 K to 4.5 high at 1828 K
Fieldhouse and Lang	72	479-1894	Initially 10.0 high at 479 K then scatters 0.2 low to 6.6 high
Goluvtin and Kozlovskaya	73	489-1486	Marked scatter from 4.9 high to 13.9 high
Gathers et al.	44	1500-2190	Values in solid range. Trends from initially 3.1 low to average 1.8 low at 2000 K and above
Berezin and Chekhovskoi	38	1345-2173	Scatters from 2.8 low to 1.0 high. Smoothed values show trend from initially 2.1 low to 0.3 high
Lin and Frohberg	12	1809-2176	Values in solid range. Scatter 2.4 low to 0.8 high. Smoothed values trend from initially 0.8 low to 1.7 low

Table 14 Deviations of enthalpy values in the liquid range

Authors	References	Temperature range K	% Deviations from the selected values
Gathers et al.	44	2190-4500	Trends from initially 2.6 low to 22.2 high
Pottlacher et al.	16	2199-2900	Trends from initially 3.9 low to 1.2 low
Treverton and Margrave	45	2205-2638	Scatters from 4.0 low to 0.9 low. Smoothed values trend 3.3 low to 1.8 low
Berezin et al.	41,46	2084-2325	Scatters from 0.4 low to 0.8 high. Smoothed values average 0.2 high
Lin and Frohberg	12	2140-2632	Scatters from 1.8 low to 0.2 high. Smoothed values trend from 1.3 low to 0.9 low
Schaefers et al.	42	2016-2403	Scatters from 1.8 low to 0.2 high. Smoothed values trend 1.4 low to 1.1 low

Table 15 Deviations of selected solid specific heat values in the high temperature region

Authors	References	Temperature range, K	% Deviations from the selected values
Hultgren et al.	6	298-2175	Trends from initially 2.1 high to 1.1 high at 700 K to 9.2 high at 1700 K to 1.4 high at 2175 K
Smith	7	298-2183	Trends from initially 0.2 low to 3.5 high at 1700 K to 4.2 low at 2183 K
Gurvich et al.	8	298-2220	Trends from initially 0.4 high to 0.3 low at 500 K to 1.6 high at 1600 K to 9.1 low at 2220 K
JANAF (Chase)	9	298-2190	Trends from initially 2.1 high to 1.1 high at 700 K to 2.6 high at 1500 K to 6.6 low at 2190 K
Desai	10	298-2202	Trends from initially 0.9 high and then agrees with the selected values between 600 and 1100 K and then trends to 1.6 high at 1600 K and to 0.8 low at 2202 K
Maglić	11	300-2100	Trends from initially 2.6 high to 1.4 low at 1400 K then trends to agree with the selected values at 1700 K and above

5 Vapor Pressure

The vapor pressure equations as given in Table 5 was evaluated for the solid from free energy functions for the solid and the gas at 50 K intervals from 1150 K to 2200 K and the melting point and for the liquid at the melting point and at 50 K intervals from 2250 to 3700 K and were fitted to the following equation:

$$\ln(p,\ \mathrm{bar}) = \mathrm{A} + \mathrm{B}\ \ln(\mathrm{T}) + \mathrm{C}/\mathrm{T} + \mathrm{D}\ \mathrm{T} + \mathrm{E}\ \mathrm{T}^2$$

6 Comments on Previous Reviews of the Thermodynamic Properties

Other reviews are considered by comparing selected solid specific values in the high temperature region. As shown in Table 15 older reviews such as those of Hultgren et al.,[6] Smith,[7] Gurvich et al.[8] and JANAF (Chase[9]) tended to show maximum high deviations in the region of 1500-1700 K and then tended to show a marked deviation low in the region of the melting point. More recent reviews

Table 16 A comparison of thermodynamic properties below the superconducting temperature

T, K	Superconducting state			Normal state		
	C°_s, mJ/mol K	$H^\circ_T - H^\circ_0$ mJ/mol	S°_T, mJ/mol K	C°_n, mJ/mol K	$H^\circ_T - H^\circ_0$, mJ/mol	S°_T, mJ/(mol K)
0.5	0.0041	0.00048	0.0013	5.003	1.209	4.836
1.0	0.288	0.0355	0.0411	9.742	4.843	9.680
1.5	3.031	0.701	0.545	14.63	10.92	14.54
2.0	10.12	3.808	2.283	19.60	19.46	19.42
2.5	20.98	11.46	5.652	24.67	30.52	24.34
3.0	33.52	25.07	10.58	29.85	44.14	29.29
3.5	48.39	45.42	16.82	35.18	60.39	34.29
4.0	66.41	73.98	24.43	40.67	79.35	39.34
4.5	87.61	112.4	33.44	46.34	101.1	44.46
5.0	112.0	162.1	43.91	52.23	125.7	49.64
5.435	135.9	216.0	54.22	57.54	149.6	54.22

Table 17 Low temperature thermodynamic properties

Temperature, K	C°_p, J/mol K	$H^\circ_T - H^\circ_0$, J/mol	S°_T, J/mol K	$-(G^\circ_T - H^\circ_0)$, J/mol	$-(G^\circ_T - H^\circ_0)/T$, J/mol K
6	0.0647	0.250	0.0603	0.112	0.0185
10	0.131	0.631	0.107	0.443	0.0443
15	0.272	1.608	0.185	1.104	0.0736
20	0.501	3.495	0.292	2.340	0.117
25	0.827	6.778	0.437	4.145	0.166
30	1.245	11.92	0.623	6.778	0.226
40	2.402	29.77	1.129	15.38	0.385
50	4.064	61.64	1.833	30.02	0.601
60	6.215	112.9	2.761	52.80	0.880
70	8.280	185.5	3.876	85.86	1.227
80	10.166	277.9	5.107	130.7	1.834
90	11.884	388.2	6.405	188.2	2.091
100	13.440	515.0	7.739	258.9	2.589
110	14.845	656.5	9.087	343.1	3.119
120	16.107	811.4	10.434	440.7	3.672
130	17.236	978.2	11.769	551.7	4.244
140	18.241	1156	13.084	676.0	4.828
150	19.130	1343	14.373	813.3	5.422
160	19.913	1538	15.633	963.3	6.021
170	20.599	1741	16.862	1126	6.623
180	21.196	1950	18.056	1300	7.225
190	21.714	2164	19.217	1487	7.826
200	22.086	2383	20.340	1685	8.423
210	22.427	2606	21.426	1893	9.017
220	22.729	2832	22.476	2113	9.605
230	23.000	3060	23.492	2343	10.187
240	23.244	3292	24.477	2583	10.762
250	23.466	3525	25.430	2832	11.329
260	23.672	3761	26.354	3091	11.890
270	23.866	3999	27.251	3359	12.442
280	24.053	4238	28.123	3636	12.987
290	24.238	4480	28.970	3922	13.527
298.15	24.390	4678	29.644	4161	13.955

Table 18 High temperature thermodynamic properties

Temperature, K	C°_p, J/(mol K)	$H^\circ_T - H^\circ_{298.15}$, J/mol	S°_T, J/(mol K)	$-(G^\circ_T - H^\circ_{298.15})/T$, J/(mol K)
298.15	24.390	0	29.644	29.644
300	24.423	45.2	29.795	29.644
400	25.698	2558	37.015	30.620
500	26.491	5169	42.839	32.500
600	27.132	7851	47.727	34.641
700	27.735	10,595	51.955	36.819
800	28.348	13,399	55.698	38.950
900	28.994	16,265	59.074	41.001
1000	29.684	19,199	62.164	42.965
1100	30.425	22,204	65.027	44.842
1200	31.221	25,286	67.708	46.637
1300	32.075	28,450	70.241	48.356
1400	32.989	31,703	72.651	50.006
1500	33.923	35,049	74.959	51.593
1600	34.930	38,489	77.179	53.123
1700	36.250	42,046	79.335	54.602
1800	37.883	45,750	81.452	56.035
1900	39.828	49,633	83.551	57.428
2000	42.086	53,726	85.650	58.787
2100	44.657	58,061	87.764	60.116
2200	47.540	62,668	89.907	61.421
2201	47.570	62,715	89.928	61.434
2201	46.471	85,738	100.389	61.434
2300	46.471	90,339	102.433	63.155
2400	46.471	94,986	104.411	64.833
2500	46.471	99,633	106.308	66.455
2600	46.471	104,280	108.131	68.023
2700	46.471	108,927	109.884	69.541
2800	46.471	113,574	111.574	71.012
2900	46.471	118,222	113.205	72.439
3000	46.471	122,869	114.781	73.824
3100	46.471	127,516	116.304	75.170
3200	46.471	132,163	117.780	76.479
3300	46.471	136,810	119.210	77.752
3400	46.471	141,457	120.597	78.992
3500	46.471	146,104	121.944	80.200
3600	46.471	150,751	123.253	81.378
3700	46.471	155,398	124.527	82.527

such as those of Desai[10] and Maglić[11] tended to show better agreement with the presently selected values.

7 Summary of Representative Equations

Low temperature specific heat equations are given in Table 6 and high temperature representative equations are given in Table 7, free energy equations are given in Table 8 and transition values involved with the free energy equations in Table 9.

8 Deviations from the Selected Values

Deviations of superconducting specific heat values are given in Table 10 and low temperature normal state specific heat in Table 11. Deviations of high temperature

Table 19 Thermodynamic properties of the gas phase

Temperature K	C°_p, J/(mol K)	$H^\circ_T - H^\circ_{298.15}$, J/mol	S°_T, J/(mol K)	$-(G^\circ_T - H^\circ_{298.15})/T$, J/(mol K)
298.15	26.012	0	182.300	182.300
300	25.979	48.1	182.461	182.300
400	24.647	2571	189.729	183.301
500	24.196	5007	195.167	185.152
600	24.283	7423	199.580	187.200
700	24.582	9871	202.345	189.244
800	24.890	12,345	206.648	191.217
900	25.117	14,846	209.594	193.098
1000	25.237	17,365	212.247	194.883
1100	25.262	19,890	214.654	196.572
1200	25.213	22,415	216.851	198.172
1300	25.117	24,931	218.866	199.687
1400	24.995	27,437	220.722	201.194
1500	24.864	29,920	222.443	202.489
1600	24.740	32,410	224.043	203.787
1700	24.631	34,879	225.540	205.023
1800	24.546	37,337	226.945	206.202
1900	24.488	39,789	228.270	207.329
2000	24.462	42,236	229.526	208.408
2100	24.471	44,682	230.719	209.442
2200	24.514	47,131	231.858	210.435
2201	24.515	47,156	231.870	210.445
2300	24.597	49,586	232.950	211.390
2400	24.711	52,051	233.999	212.311
2500	24.865	54,530	235.011	213.199
2600	25.056	57,026	235.989	214.057
2700	25.284	59,542	236.939	214.887
2800	25.547	62,084	237.863	215.691
2900	25.844	64,653	238.765	216.491
3000	26.174	67,253	239.647	217.229
3100	26.536	69,889	240.511	217.966
3200	26.928	72,562	241.359	218.684
3300	27.347	75,275	242.194	219.384
3400	27.792	78,032	243.017	220.067
3500	28.260	80,834	243.829	220.734
3600	28.749	83,685	244.632	221.387
3700	29.256	86,585	245.427	222.026

$H^\circ_{298.15} - H^\circ_0 = 7907.0$ J/mol

specific heat in Table 12 and enthalpy values in the solid and liquid ranges in Tables 13 and 14 respectively. Deviations of other selected specific heat values are given in Table 15.

9 Thermodynamic Tables

Low temperature thermodynamic properties of the solid are given in Tables 16 and 17 and of the high temperature thermodynamic properties of the condensed phases in

Table 20 Vapor pressure

T, K	p, bar	ΔG_T, J/mol	ΔH_T, J/mol	p, bar	T, K
298.15	5.62×10^{-83}	469,486	515,000	10^{-15}	1174
300	2.90×10^{-82}	468,303	515,004	10^{-14}	1228
400	5.30×10^{-60}	453,928	515,013	10^{-13}	1287
500	1.49×10^{-46}	438,674	514,838	10^{-12}	1352
600	1.36×10^{-37}	423,465	514,577	10^{-11}	1424
700	3.41×10^{-31}	408,303	514,276	10^{-10}	1504
800	2.13×10^{-26}	393,186	513,946	10^{-9}	1595
900	1.14×10^{-22}	378,113	513,581	10^{-8}	1696
1000	1.08×10^{-19}	363,082	513,166	10^{-7}	1812
1100	2.96×10^{-17}	348,097	512,686	10^{-6}	1946
1200	3.15×10^{-15}	333,158	512,129	10^{-5}	2102
1300	1.63×10^{-13}	318,269	511,481	10^{-4}	2290
1400	4.77×10^{-12}	303,434	510,734	10^{-3}	2524
1500	8.88×10^{-11}	288,656	509,881	10^{-2}	2816
1600	1.14×10^{-9}	273,938	508,921	10^{-1}	3191
1700	1.08×10^{-8}	259,285	507,883	1	3690.53
1800	7.93×10^{-8}	244,699	506,587	NBP	3693.87
1900	4.70×10^{-7}	230,188	505,156		
2000	2.32×10^{-6}	215,758	503,510		
2100	9.78×10^{-6}	201,415	501,662		
2200	3.60×10^{-5}	187,169	499,463		
2201	3.64×10^{-5}	187,027	499,440		
2201	3.64×10^{-5}	187,027	476,413		
2300	1.11×10^{-4}	174,059	474,243		
2400	3.12×10^{-4}	161,054	472,061		
2500	8.03×10^{-4}	148,140	469,893		
2600	1.91×10^{-3}	135,312	467,741		
2700	4.25×10^{-3}	122,567	465,611		
2800	8.91×10^{-3}	109,900	463,505		
2900	1.77×10^{-2}	97,308	461,427		
3000	3.34×10^{-2}	84,787	459,381		
3100	6.04×10^{-2}	72,334	457,369		
3200	0.105	59,944	455,395		
3300	0.176	47,616	453,461		
3400	0.286	35,346	451,571		
3500	0.452	23,131	449,726		
3600	0.693	10,968	447,929		
3690.53	1.000	0	446,347		
3700	1.038	−1,145	446,182		

NBP Normal boiling point at 1 atmosphere pressure (1.01325 bar)

Enthalpy of sublimation at 0 K: ΔH°_0 511,771 J/mol

Table 18. Thermodynamic properties of the gas are given in Table 19 whilst the vapor pressure summary is given in Table 20.

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